CAROLINE KOZAK

WATER QUALITY ASSESSMENT AND ITS EFFECTS ON DIFFUSE POLLUTION CONSIDERING A NEW WATER QUALITY AND QUANTITY APPROACH

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Thesis submitted as partial requirement for the Degree of Master at the Graduate Program on Water Resources and Environmental Engineering, Technology Sector, Federal University of Paraná.

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“It's the time you spent on your rose that makes your rose so important...People have forgotten this truth, but you mustn't forget it. You become responsible forever for what you've tamed. You're responsible for your rose.”

The Little Prince
Antoine de Saint-Exupéry

To my families,
without you I could not get here.

Abstract

Diffuse pollution process, as point source pollution, can cause water quality degradation in water bodies. Diffuse pollution sources are extensive and difficult to quantify and, receive strong influence from rainfall events When rainfall happens, the runoff causes superficial area washing-off, promoting pollutant mass contribution into the river. The rainfall events are difficult to predict, therefore inducing an interesting monitoring problem associated to sampling collection for assessment of the contribution of pollutant mass pollutant in rivers. Accordingly, an alternative is the requirement of an automatic sampler, which ensures samples collected during rainfall events, through an intelligent interface, according to variation of water levels, following rising and falling hydrograph. The objective of this study is to use the SBN intelligent interface, connected to an automatic sampler (ISCO), to assess water quality and diffuse pollution effects at Barigui River, in a monitoring site called BA01 located in Almirante Tamandaré. The intelligent sampler was installed to an pluviometric station in Almirante Tamandaré, connected to a datalloger information system. The programming for sample collect was performed for each five centimeters variation in water level, either rising (+ 5 cm) or falling (- 5cm) hydrograph. After sampling and end of the rainfall event, samples were collected and delivered to laboratory to analytical procedures of distinct water quality parameters. The results shows that water quality parameters had a similar behavior to each specific hydrograph. The mass pollution contribution into the river reveals the concentration increasing during hydrograph peak. Event mean concentrations (EMC) analyses showed a trend in some parameters (specially turbidity and solids series). The trend consist in better describing the first-flush increasing concentration during the event, and after, the dilution due assimilation pollutant by the river. Interestingly, distinct events characteristics, as transported volume and maximum flow, impose bigger pollutant contribution. In general, SBN works as expected, performed sampling following hydrograph. It was observed that occurs mass pollutant contribution due diffuse sources at Barigui River, on site BA01 in Almirante Tamandaré. However, all the analytical work demanded to quantify this information is significant for each event analyzed.. In terms of water resources management planning and management, this research highlights the need for more in depth analysis of the potential impacts for all instruments established by the Brazilian legislation. More researches about diffuse pollution process are necessary to provide reasonable data, especially the integration to the use in mathematical models calibration of water quality simulation in rivers.

Key-words: Non-point sources; Monitoring system; SBN; Intelligent automatic sampler; Barigui River

Resumo

Os processos de poluição difusa, assim como as fontes de poluição pontual, podem causar degradação da qualidade da água nos rios. As fontes difusas são abrangentes e de difícil quantificação além de receberem grande influência dos eventos de chuva. Quando a chuva acontece, o escoamento causa lavagem da área superficial, promovendo contribuição de massa poluidora para dentro do rio. Os eventos de chuva são de difícil previsão, induzindo portanto a um interessante problema de monitoramento, que está associado a coleta de amostra para a avaliação da contribuição da massa poluidora dos rios. Portanto, uma alternativa é o uso de amostrador automático, o qual garante que as amostram sejam coletadas durante o evento de chuva, funcionando através de uma interface inteligente, de acordo com as variações da coluna água e seguindo a ascendência e descendência do hidrograma. O objetivo deste estudo é usar a interface inteligente SBN acoplado a um amostrador automático comercial (ISCO) para avaliar a qualidade da água e os efeitos da poluição difusa no Rio Barigui, no ponto de monitoramento denominado BA01, localizado em Almirante Tamandaré/PR. O amostrador inteligente foi instalado junto a uma estação pluviométrica em Almirante Tamandaré, conectado a um sistema de informações *datalloger*. A amostragem foi programada para cada 5 (cinco) centímetros de variação na coluna d'água, tanto na subida (+ 5 cm) quando na descida (-5 cm) do hidrograma. Após amostragem e o final do evento de chuva, as amostras foram coletadas e levadas para o laboratório para os devidos procedimentos analíticos dos distintos parâmetros de qualidade da água investigados. Os resultados mostram que os parâmetros de qualidade da água tiverem comportamento similar para cada hidrograma específico. A contribuição da massa poluidora para o rio revelou que as concentrações aumentam durante o pico do hidrograma. A análise do evento médio de concentração (EMC) mostrou certa tendência para alguns parâmetros (especificamente turbidez e série de sólidos). A tendência consiste em uma melhor descrição do fenômeno de first-flush, causando aumento da concentração durante o evento, e posteriormente, a diluição devido a assimilação do poluente pelo rio. Curiosamente, diferentes características do evento, como volume de água transportado e vazão máxima, impuseram maiores contribuição de poluição. De forma geral, SBN trabalhou como o esperado, realizando a coleta das amostras seguindo o previsto pelo hidrograma. Foi observado que ocorreu contribuição de massa poluidora devido a fontes difusas no Rio Barigui, no ponto BA01 em Almirante Tamandaré. Entretanto, todo trabalho analítico demandado para quantificar todas as informações para cada evento analisado neste trabalho é significativo. Em termos de gestão de recursos hídricos, planejamento e gerenciamento, esta pesquisa ressalta a necessidade de maiores analises dos potenciais impactos para em todos os instrumentos de gestão estabelecidos pela legislação Brasileira. Mais pesquisas sobre os processos de poluição difusa são necessário para fornecer razoável quantidade de dados, especificamente na integração do uso na calibração de modelos matemáticos de simulação da qualidade da água em rios.

Palavras-chave: Fontes não pontuais; Sistema de monitoramento; SBN; Amostrador automático inteligente; Rio Barigui.

Summary

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Abbreviations

DO – Dissolved Oxygen

COD – Chemical Oxygen Demand

BOD – Biochemical Oxygen Demand

TN – Total Nitrogen

TP – Total Phosphorus

TS – Total Solids

FTS – Fixed Total Solids

VTS – Volatile Total Solids

SS – Suspended Solids

FSS – Fixed Suspended Solids

VSS – Volatile Suspended Solids

OM – Organic Matter

DOC – Dissolved Organic Carbon

AS – Ambient Sample

RS – Refrigerated Sample

AAS – Ambient Acidified Sample

RAS – Refrigerated Acidified Sample

LABEAM – Francisco Borsari Neto Environment Engineering Laboratory

Chapter 1

Introduction

> “I’ve learned everyone wants to live on top of the mountain,
> but all the happiness and growth occurs while you are climbing it”.
> **— William Shakespeare**

Water is a natural resource, a public domain resource with economic value (Brasil, 1997), which is fundamental to maintenance of life, by all means is it all intrinsic values and forms. The Earth has about 1.36 x 10^8 cubic meters of water, where 97% is water from the seas, 2.2% is glaciers and only 0.8% is fresh water. From this small part, only 3% are superficial water (Von Sperling, 2005).

Rivers systems, through hydrological processes, are the main source for a variety of distinct uses, as we known, for the need for domestic, industrial and irrigation purposes (Singh et al., 2005), are faily well understood. In such a context, the rivers usually form, through a set of water bodies, a drainage network, that always converge to a same point, called drainage point (Tucci, 1997), but that highlights the effects of the watershed nature. Most importantly, it is in a watershed area that human activities are developed (Porto and Porto, 2008) and produce the most significant water quality transformations.

From 20th century the population growth was remarkably fast, inducing the competition for natural resources, mainly water and soil (Tucci, 2008). The different land use, human occupation and water resources availability, in fact, cause different environmental impacts. The search for life maintenance, water and food supply induces the water quality degradation and biodiversity destruction, both in urban and rural watershed.

According to Coelho (2013),the physical and chemical effects of urbanization in superficial water resources are the most studied impact due urban expansion. Considering population growth, the urban environmental makes an important difference in biogeochemical cycles, as carbon, nitrogen and phosphorus cycles, which included steps in atmospheric, aquatic and terrestrial environment. Braga (2013) highlights that Brazilian water bodies, especially, in urban areas require further attention, due to impacts consequences and water quality degradation.

At the same time to the population growth and water quality degradation, policies are required and come true in the sense of establishing the basis for water resources planning and management. In Brazil, the Federal Law n° 9.433 of January 1997 establishes the National Water Resource Politics focusing on sustainability concepts based upon water use. The main idea is to provide several objectives and action guidelines to ensure water quality and quantities for the sustainable water management.

The law established the main instruments for these purposes which are: water resource plans; water bodies classification according their uses; payment for the use water resources; legal granting for the of water resources uses; and the information system about water resources. These instruments are independent each other and if used together they can provide a several database for the monitoring and must be strategically thought and implemented integrated.

Pollution is water quality degradation due direct and indirect activities that damage population well being, health, from social and economic activities, inducing strong impacts on biota and environment, introducing matter or energy in disagreement with established environmental standards (Brasil, 1981). Obviously, point sources pollution is more visible and, theoretically, easier to control than non-point sources. However, non-point pollution is as important as punctual sources, due several variables that conduct transport process and uncertainties. Based upon these variables and uncertainties, studies about diffuse pollution are not easy and extremely interesting, singular and curious (Kozak et al., 2015).

According to Kozak et al. (2015), to control diffuse pollution it is important to ensure and/or improve water quality in rivers. However, it is an arduous task due to wide temporal and spatial range of the rainfalls. Rain is the main phenomenon that induces diffuse pollution process (Lee et al., 2010). Monitoring rainfall events is necessary for specific operational questions, as a quali-quantitative monitoring (Braga, 2013). Braga (2013) highlights the need to overcome sampling limitations during rainfall events.

The literature provides some interesting results that establish this connection through automatic sampling. However, the great majority of the international experience known, presents wider variety water quality parameters analysis and results through correlation of physical high frequency parameters (Li et al., 2008; Moraetis et al., 2010; Métadier and Bertrand-Krajewski, 2012; Chittoor Viswanathan et al., 2015; Darwiche-Criado et al., 2015).

Therefore, research is necessary to investigate appropriate conditions of sampling coupled to analytical procedures in laboratory. The result of this association can be a effective and efficient management tool to monitoring water bodies.

1.1. Significance of this research

The law defines instruments to promote sustainable water resources planning and management. Therefore technical information system and background are significantly important, considering the goal of sustainable water resources planning and management thorough a solid and real integrated information system. It can be assumed that in order to establish the water classification of rivers, it is more a planning strategy that a command-control that, requiresd consistency quali-quantitative monitoring. Additionally, for management purposes, there is need to look for the future and to find new monitoring strategies. The technique of establishing scenarios is fundamental to make the right questions and to define the real problems and to find the most appropriate solutions.

In this study, the scenario is a river that receives the contribution of diffuse sources pollution. In order to achieve a better understanding of its behavior, the solution is to monitor this river to evaluate how the diffuse pollution affects the ecosystem observing the water quality behavior in a specified monitoring point. Main philosophical questions can be proposed: Is this easy? Which is the representativeness considering aquatic ecosystem? Which is the sampler frequency to provide real information? How the sampling will be done? Which parameters are needed to be monitored? Those questions has been focus of intense research, but with very few results that link the water quality representativeness based upon the behavior of distinct water quality parameters.

Pollution from diffuse sources is driven by meteorological events, as precipitation (Novotny, 2002) and main mechanism processes related to the characteristics of the land use. However the challenge of monitoring these processes is related to: rainfall randomness and the potential dynamic characteristics within the watershed. During rainfall events under saturated soil conditions is when the significant mass transport occurs into the water body. According to Braga (2013), it is required to integrate carefully water quantity and quality during rainfall events, in order to better evaluate the consequent impacts. In such a context, automatic sampling is necessary to properly integrate water quantity and quality.

The research strategy in this research has focus on: a) to measuring the effective concentration distribution during the normal (without rainfall) and precipitations events; b) to evaluate the precipitation effects over water quality conditions of the water body; c) establishing which parameters are relevant and what are the feasibility operational conditions of the sampler.

1.2. Objectives

The effects of diffuse pollution can be assessed by distinct traditional manners both to explore quantification methods. In this research, the questions associated to the impact of rainfall event and automatic sampling are addressed, just to ensure analysis of dynamic external effects (land use and rainfall intensity) and the relevance of automatic sampler to establish a distinct opportunity for understanding distinct water quality parameters.

In order to achieve it, the following specific goals are entitled:

(i) To produce pollutographs based on parameters of water quality;
(ii) To assess potential impacts of water quality dynamics from precipitation events;
(iii) To assess event mean concentration (EMC) of main rainfall events
(iv) To test water quality parameters in order to verify intelligent automatic sampler limitations;

1.3. Methodological Approach

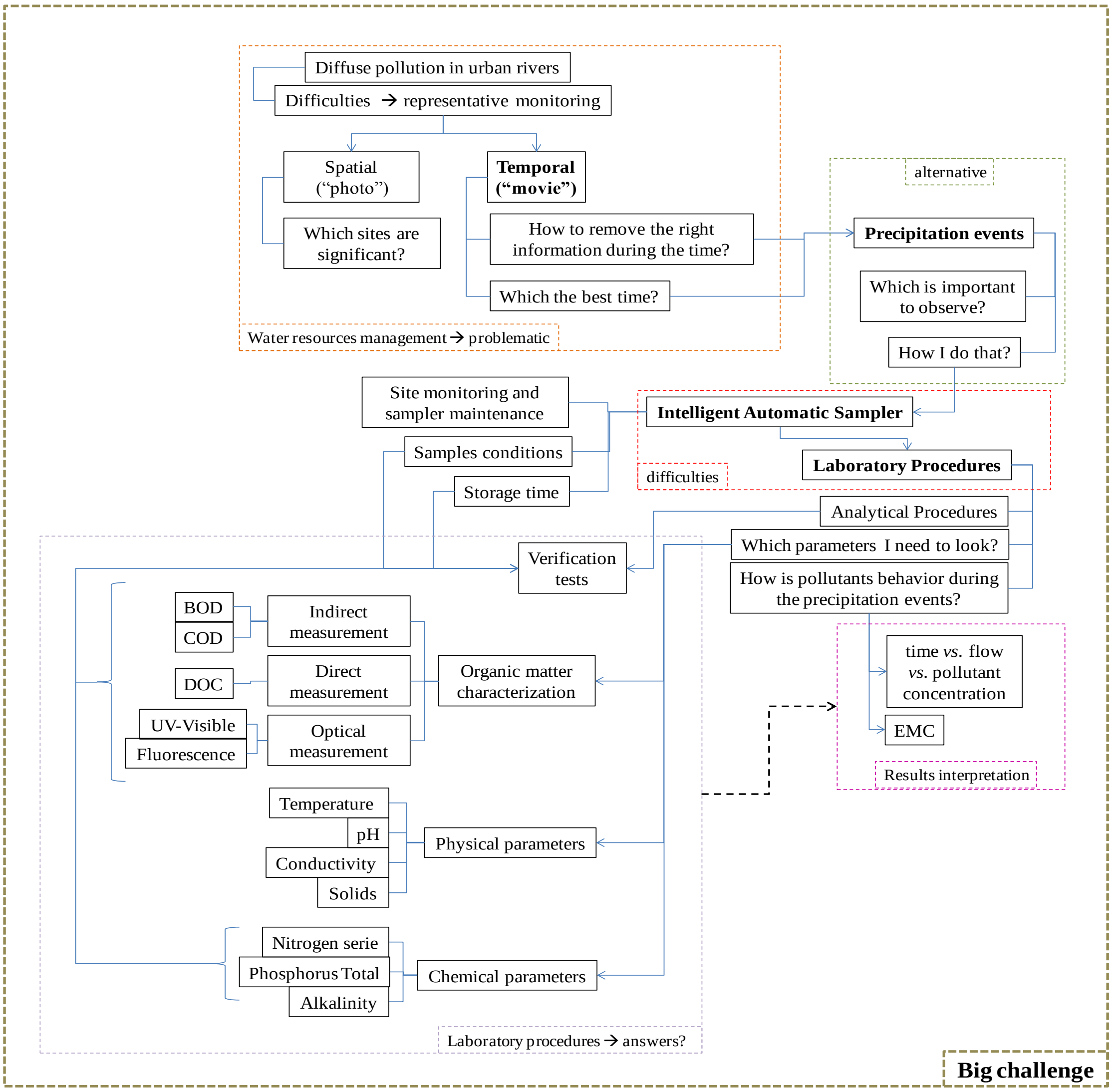
The challenge of consolidating the methods to address the main goals of this research is summarized in Figure 1, as follows, through 5 interconnected branches, that summarizes the “Big Challenge” associated to diffuse pollution:

i) Water resources management problems: How is the behavior of diffuse pollution? How to quantify it to address water quality degradation? How to evaluate uncertainties related to spatial and temporal distribution of main variables that produces water quality degradation
ii) Is there any alternative strategy to quantify the diffuse pollution contribution in a water body: What is the right alternative to quantify it? What is the best time to observe this?
iii) To understand the difficulties involving this methodology: the use of automatic samplers to proceed sampling during rainfall event which can represent diffuse

pollution contribution, following by the analytical procedures to be realized in the laboratory.

iv) Laboratory procedures: What is the best form to represent water quality parameters? How these parameters are observed? Chemical, physical and organic matter characterization are relevant? Automatic sampler can provide the right and the best information? Analytical procedures are enough?

v) Results interpretation: After all analyses, how should the results be the interpreted? What is the best form to describe these values? What is the best form to evaluate these values? What mean all these information? What are the answers?



BOD – biochemical oxygen demand; COD – chemical oxygen demand; DOC – dissolved organic carbon; EMC – event mean concentration

Figure 1 - Schematic representation of thesis

1.4. Thesis Organization

The dissertation is divided in 6 main chapters, as presented in Figure 2. **Chapter 1** presents thesis introduction, highlighting main concepts about water quality and quantity integration, objectives and methodological approach. **Chapter 2** summarizes theoretical background based on three essential pillars: land use and soil occupation, automatic samplers and water quality parameters. Additionally, comments on strategies to quantify water quality parameters during rainfall events are presented. **Chapter 3** presents the study area and the analytical procedures performed in laboratory, and description of intelligent automatic sampler (SBN) used in this research. **Chapter 4** shows the results of the water quality behavior during rainfall events, presented as pollutographs and Event Mean Concentration (EMC) curves. **Chapter 5** shows some reflections about the analytical water quality requirement and criteria for using data from automatic sampling strategies. Finally, **chapter 6** presents final considerations, and chapters 7 and 8 presents reference and data appendix, respectively.

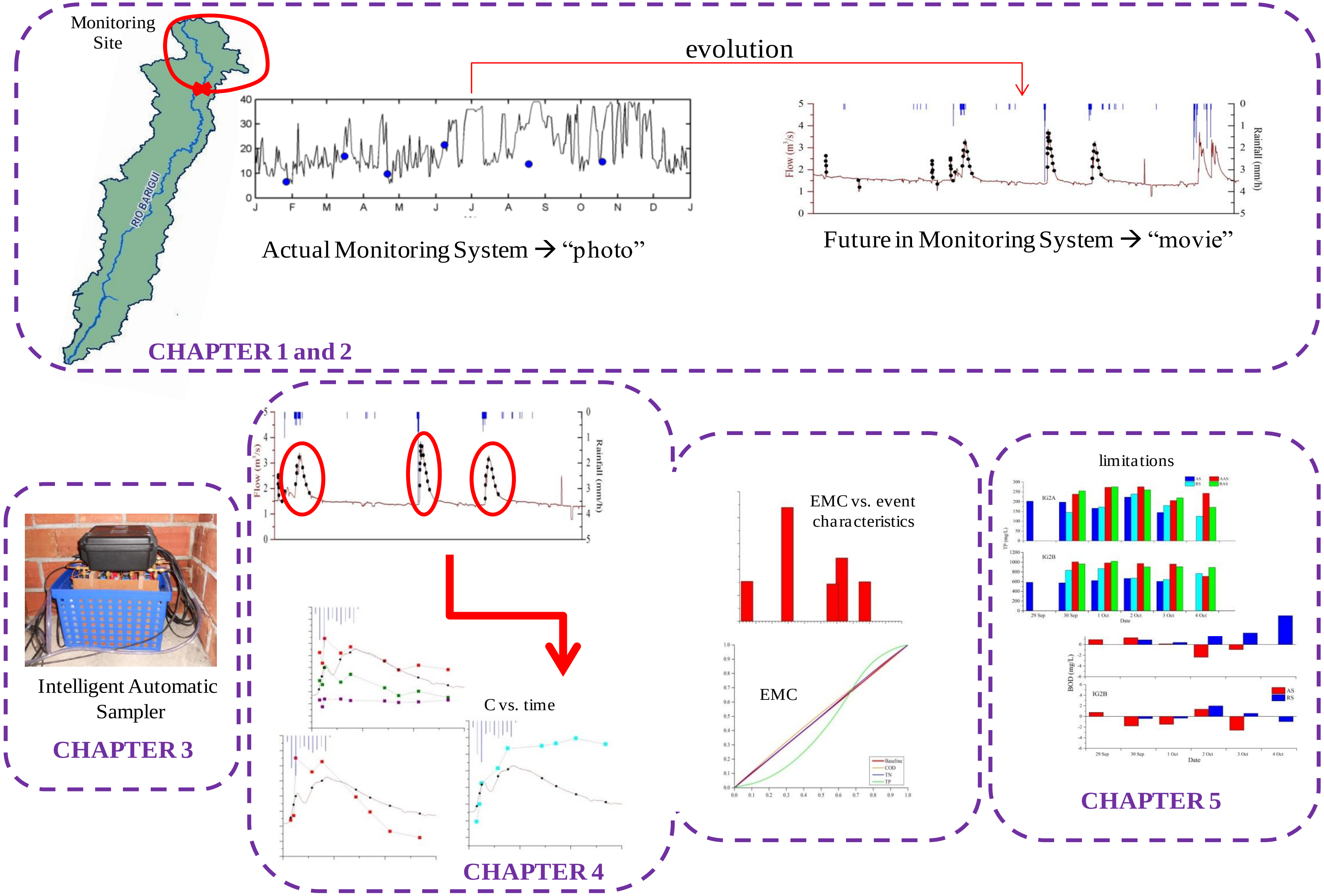


Figure 2 - Thesis Organization

Chapter 2

Diffusion Pollution and Theoretical Background

> “The problem is not the problem.
> The problem is your attitude about the problem.”
> **— Captain Jack Sparrow**

2.1. Introduction

This chapter presents literature review considering three main aspects: i) land use and soil occupation, an important factor that contributes to diffuse pollution characterization and compounds; ii) automatic samplers, a key equipment to sampler water during rainfall events (inducing mechanism of transport); and iii) water quality parameters that are a second key to understand aquatic process into the river. The connection of these aspects guide this thesis bases. To interpret results some quantifying strategies were investigated in order to answers to the questions formulated.

2.2. Land use and soil occupation

Watershed, or drainage basin, is an area where the water converges to a channel or a set of channels and is composed of water bodies, slopes and drainage network (Tucci, 1997; Novotny, 2002). Watershed is formed by topographical unevenness that guide the water from the higher area to the lower area by gravity force. Several small water bodies forms a mainly water body, following rivers hierarchically (Pereira and Scroccaro, 2010). Novotny (2002) states that "a large watershed contains a number of small watersheds that are defined by the stream-order; streams are classified numerically from first-order headwater to higher-order downstream section". A second-order river has at least one first-order tributary, as well as a third-order river has one or more second-order tributaries.

The origin of the water is hydrological cycle that has several surface and subsurface pathways (Novotny, 2002). According to Barrella et al. (2001), after the precipitation, a portion of water flows on the surface (which forms the rivers and streams) and other portion infiltrates into the soil (which forms springs and supply groundwater). Besides hydrological cycle, some relationships among precipitation and watershed soil are important, and are called pathways. Figure 3 shows a schematic watershed hydrology and pathways representation.

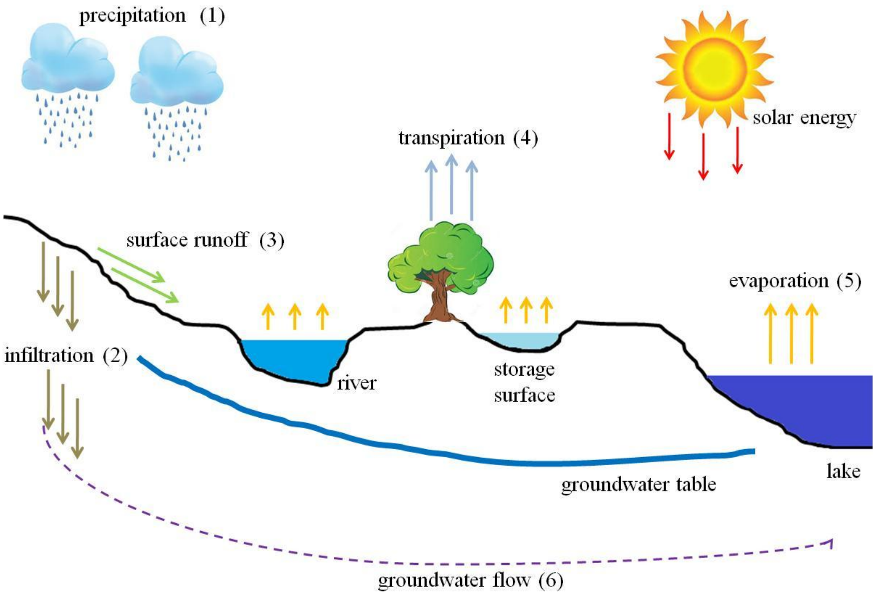


Figure 3 – Representation of watershed hydrology and pathways

Source: adapted from Águas Paraná (2015)

Precipitation is the more important hydrological cycle component, and is formed by water vapor condensation in atmospheric until saturation point. Water falls into surface, and infiltration starts: water enters from surface or surface storage to into the soil due gravity and capillary forces. This step is a function of surface soil and subsoil permeability, vegetation cover, soil moisture and others parameters.

Infiltration depends of soil type, and process continues until all pores are filled with water. Hence, rate infiltration is reduced to a level of saturation permeability, starting surface runoff. The surface runoff is a residual of precipitation after loses by infiltration, vegetation interception, transpiration and evaporation. The surface runoff causes the highest transport of pollution (mainly in impermeable surface) into the river. Transpiration and evaporation can happen simultaneously and depends on solar energy rates. At final step, water evaporates and returns to atmosphere until start the cycle again (Novotny, 2002; Von Sperling, 2005; Braga et al., 2005). Groundwater flow is a part of runoff that contributes from spring and wells (Novotny, 2002). Watershed runoff depends on the rainfall, temperature, topology, soil, geology, land use and cover watershed (Lalika et al., 2015).

Soil is basically formed by disaggregated rocks which mix with organic matter in decomposition and contain, in different proportions, water, air and microorganisms. Granulometry or texture is basic soil classification, which divides mineral soil components in proportions of sand, silt and clay (Braga et al., 2005).

Sand are particles with diameter between 0,05 and 2 mm basically formed by quartz mineral. Due the larger pores, sand particles cannot retain water against gravity force, therefore water is drained into the soil and air intake occurs. Sandy soil is well aerated, released, infertile, and prone to drought. Silt are particles diameter less than 0,05 mm but greater than 0,002 mm, and can be composed by weatherable minerals. Silt pores are smaller than sand pores. Silt retains water and allows less drainage rate. Due to low stickiness and plasticity, soils compound by silt and fine sand are highly susceptible to wind and water erosion. Silty soils are easily carried by runoff. Clay particles are smaller than 0,002 mm which means larger superficial area causing high absorption of water and other substances. Clay particles have colloids behavior i.e. not deposit easily when suspended. Clay pores are tiny and irregular, occurring slow water and air dynamic, however retain lots of water (Brady and Weil, 2010). According to Braga et al. (2005), rarely a soil is composed by only one of the fractions, but for a combinations of that in different proportions.

Soil is formed by a combination between climate, ecosystem nature, materials origin, relief and time, i.e. weathering. Soil formation stage is classified by time and called horizons, divided into five layers (Figure 4), causing implications on hydrological cycle and water resources system. Horizon O is a surface with decaying organic debris and little soil. Horizon A is a profile with approximately one meter of thick, considerable leaching and great densities of roots, soil organisms and organics. Horizon B is a profile under horizon A, and is where most leached salt, clay and chemicals may deposit; there is not much organic matter and few plant roots (except for large plant and trees). Horizon C is the soil evolved by weathering, found under the horizon B. Horizon D are consolidated rocks (Novotny, 2002). According to Novotny (2002) horizon A is the layer where most adsorption and biochemical degradation of pollutants takes place, having an important effect to diffuse pollution studies. Furthermore microbial processes (pollutants, nitrogen and phosphorus decomposition) are confined primarily into horizon A.

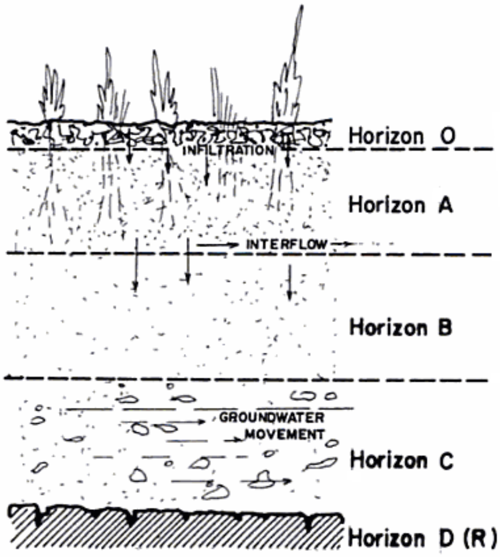


Figure 4 - Soil profile

(Source: Novotny, 2002)

Normally, water composition should be a composition of natural compounds occurred by natural process. However this composition is modified by human activities. Water quality parameters express water composition in terms of quality and quantity of measures compounds. Pollution is caused by humans and their actions and can be from different sources and causes (Novotny, 2002).

The pollution can be from two types: point and non-point sources. Point source is when pollution is discharged in a concentrated form into the water body. Examples are domestic and industrial wastewater and drainage system (Von Sperling, 2005). Non-point source (or diffuse source) is generally caused by rainfall carrying over and through soil and ground cover (USEPA, 1984). Examples of non-point sources are agricultural sources, pollutant loadings caused mining activities, silvicultural activities (USEPA, 1984), atmospheric deposition, water and sediment chemical, irrigation (Novotny, 2002), pollutant loadings caused by runoff from urban lands, erosion particles, (USEPA, 1984; Novotny, 2002).

Non-point sources contribution to water quality pollution depends of different volumes occurred during storms events, sewage or point combination, and concentrations during different flow regimes (USEPA, 1984). Corroborate to USEPA (1984), Novotny (2002) affirms that pollutants loads from diffuse sources into the water body are transported either over surface or through subsurface paths (Figure 5).

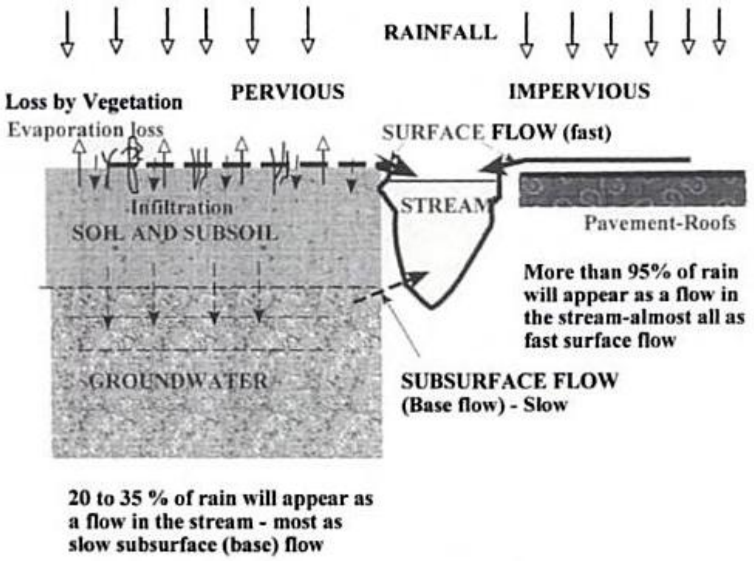


Figure 5 - Surface and subsurface pathways of diffuse pollutants

(Source: Novotny, 2002)

Soil characteristics and land use and occupation influences water dynamics, quality and quantity (Prodanoff, 2005). Bu et al (2014) affirms that land use patterns affects water quality through changing hydrological and chemical runoff processes. Anthropogenic actions development into watershed on land use changes could influence in degree and type of pollution (Porto and Porto, 2008; Bu et al., 2014). It is a cause-effect relationship (Pereira and Scroccaro, 2010). Therefore, determined proportions of certain land use types in watershed can help to predict water quality (Bu et al., 2014). Several studies showed the relationship between land use/land cover with water quality, some indicating differences during dry and rainy seasons, summarized in Table 1.

According to Table 1, it was identified that water quality varies with land use and seasons. Urban areas had more influence in water quality degradation due increase population and economic development (Li et al., 2008), which contributes with impervious areas, wastewater, and industrial wastes. Punctual sources increase the amount of phosphorus, decrease pH, had low values of dissolved oxygen that block nitrogen cycle, and for consequence, the nitrogen was accumulated into the river (Li et al., 2008; Bu et al., 2014; Yu et al., 2016). Yu et al. (2016) says during dry seasons impervious area contributes to surface runoff rates carrying the amount of pollution accumulated, mainly soil particles. At the same time, agricultural land had strong relationship with water quality degradation due fertilizers and transport of suspended particulate matter (Bu et al., 2014; Yu et al., 2016).

In Bu et al. (2014) study, agricultural land is worst in rainy seasons due runoff increase and soil erosion, transporting many pollutants into the river. In the other hand, Yu et al. (2016) says that agricultural land is worst in dry seasons because without rain is necessary irrigation. Water returns to water body by surface and surface pathways intensifying fertilizer carry and water quality degradation. Vegetation land had positives influences in water quality. In Li et al., (2008) study found a decrease in the concentration of nitrate-nitrogen, total dissolved solids and electrical conductivity in vegetated area. Complementary, Bu et al., (2014) found the positive relationship between vegetative areas with pH and dissolved oxygen.

Water quality is influenced by all types of land uses (Yu et al., 2016). Therefore, the effects of land use intensification on water quality depend on some factors. These factors are different due hydrology, landscape and dominant hydrological pathways, land use intensity, connectivity of those paths, and biogeochemical reactions during transport (Smith et al., 2013). Several studies can help to determine how types of land use/land cover can controlling water quality, and how the seasonal and spatial patterns of water quality reflects on sources and polluted areas, which is very important for water quality conservation (Li et al., 2008).Similarly, Park et al., (2009) claims the quantity and quality of runoff also are affected by geophysical conditions, as well as

Table 1 - Summary for relationship between land use/land cover and water quality

WATERSHED		ANNUAL PRECIPITATION	LAND USE								SOME RESULTS	REFERENCE
Name (Location) - Size	**Characteristics**		**Water Body**	**Urban**	**Forest**	**Agriculture**	**Wetland**	**Barren**	**Pasture**	**Soil Composition**		
Wei River (Gansu Province, China) - 619.123 km²	Large amount of industry and high percentage of sealed surface	-	~ 2%	~ 4%	~ 21%	~ 47%	-	~ 1%	~ 31%	-	Dry stations associated type and land use had more influence into water quality than rainy stations	Yu et al. (2016)
Jing River (Gansu Province, China) – 454.605,5 km²	Oil extractions		-	~ 1%	~ 9%	~ 51%	-	-	~ 40%			
Beiluo River (Gansu Province, China) – 269.243 km²			-	~ 1%	~ 24%	~ 27%	-	~ 1%	~ 48%			
Pangani River Basin (Tanzania) - 43.650 km²	Have several sub-catchments of widely different characteristics Dominance forest and semiarid grassland	650 – 2500 mm per year (its depends of topography characteristics)	Pangani River is the main river	4.5 million people;	e.g.: mangrove, African coastal, afromontane and riverine forest	-	Nyumba ya Mungu 9320 km²	-	-	-	Land use (and other factors) affects the water level and reduced water flow Unsustainable land use practices had negative effects in natural ecosystems	Lalika et al. (2015)
Jialing River Watershed (China) - 156.141km²	Climate: sub-tropical monsoon with an average temperature of 16-18 ˚C Economic development: agriculture	1098 mm that occurs between May to September(70-90%)	0,48%	0,03%	12,03%	38,91%	-	0,64%	47,91%	purple, brown, yellow-brown soil	On simulated scenarios where ↓ cropland ↑ forestland pollution by N and P will decline In other words the water quality improve	Wu et al. (2012)
Lee catchment (Otago, New Zealand) – 6830 ha	Land cover has modified to improve pasture	492 mm	-	-	Native and exotic scrub; Tussock grassland	Utilized to pasture	-	-	Sheep and deer farming	-	Pasture land use was significantly related to TN and TP in different catchments scales, as well as, can be better or worse to large or small streams.	Buck et al. (2004)
Tuakitoto catchment (Otago, New Zealand) – 6450 ha	Land use is dominated by sheep and cattle farming with several dairy farms	631 mm	-	-	Little regenerating native forest area	-	-	-	-	-		
Barbours catchment (Otago, New Zealand) – 320 ha	Land use is tussock grassland Water quality is high	492 mm	-	-	-	-	-	-	-	-		

Continued table 1

Scotts Creek (south-western Victoria, Australia) – 361 km^2	Temperate climate: cool winters and warm summers The major land use is agriculture and native vegetation reserves	915 mm	-	-	-	-	-	-	91%	Surface textures: clay loams to sands Subsoils texture: clay content from heavy clays to light clays	Nutrient exports is function of land use, farm management, pratices, climate soil type, and hydrology Dairy farming is directly related to poor water quality	Smith et al. (2013)
Kennedys Creek (south-western Victoria, Australia) – 268 km^2		891 mm	-	-	-	-	-	-	64%			
Pirron Yallock Creek (south-western Victoria, Australia) – 166km ^{2}		810 mm	-	-	-	-	-	-	81%			
Hun River (Qingyuan County, China) – 2332 km^2 and Suzi River (Xinbin County, China) – 2087km ^{2}	Continental monsoon climate and four distinct seasons	826.8 mm that occurs between June to August (50–60%)	3,6	2,25	76,63	1.70 (paddy field) 15.81 (dry farmland)	-	-	-	brown soil; dark brown soil; turfy soil; paddy soil; albic soil; boggy soil	Agricultural land plays a dominant role in the deterioration of water quality within the river basin Forest cover better water quality Dry farmland is likely to generate pollution	Ye et al. (2014)
The TaiziRiver(Northeast China) – 13.202 km^2	Warm temperate monsoon climate zone,	778.1 mm	~ 1%(a)	~ 4%	~ 60%	~ 35%	-	-	-	-	Dry and rainy stations associated type and land use had different influences into water quality	Bu et al. (2014)
Institut National de la Recherche Agronomique (INRA – Rennes, France) – 2250 m^2	Temperate climatic mean annual temperature - 12.5 °C	750 mm which occurs between September to March(70%)	-	-	-	-	-	-	-	71 % silt 15% clay 14% sand	↑DOC without intense rainfall: due watershed characteristics and land-uses, which lead water quality degradation	Delpla et al. (2011)
Han River (China) – 159.10^3 km^2	Climate sub-tropic monsoon	700 – 1800 mm which occurs between May to October (80%)	-	~1%	~80%	~14%	-	~ 5%	-	-	Types of land use had different influence in water quality	Li et al. (2008)

impervious, slope, type of soil, rain intensity and duration, and quantity of previous dry days.

Precipitation drives process that generates diffuse pollution, consequently, pollutant loads are difficult to measure due randomness and unpredictability of this event (Novotny, 2002). Rainfall events have the potential to export pollutants into receiving waters due the runoff volume produced (Delpla et al., 2011). Pollution rate is generally greater at the beginning of rainfall, and decreases over the time (Kim et al., 2004). Initial surface washing is called "first flush" phenomenon (Kim et al., 2004; Braga, 2013). First flush analysis can be conducted by observing the relationship between the cumulative mass curve and the cumulative runoff volume curve as Ballo et al. (2009) studied. In Delpla et al. (2011) study soluble organic carbon had the maximum rate during the first flush on the rainfall event and decreased continuously afterwards. But sometimes concentrations decline by an increasing runoff rate as a storms progresses (Kim et al., 2004), fact verified for Chittoor Viswanathan et al. (2015). They found high variation of nitrate during the rainfall event followed by reduction in nitrate concentration due dilution effect.

In this sense and according to Braga (2013), it is required an integrated quantity and quality analysis especially during the rainfall event which is when most pollutant concentration are carried into a water body.

2.3. Samplers

Sampling is the action of selecting a portion of material (water, air or soil) that represent part of the environment. But the main difficulty is to collect a representative, accurate, and integrative sample (Madrid and Zayas, 2007; Chapin, 2015). Some factors are important to ensure samples have the best environmental representative, such as: sampling site, sample containers (e.g.: glass or polyethylene bottles), preservation (e.g.: protection from external agents, addition of preservatives and storage at low temperature), sample-preparation (e.g.: filtering) and sampling (Madrid and Zayas, 2007).

The most common method used to collect water sample is manual sampling, also known as “grab”, “spot”, “passive” or “bottle” sampling (Madrid and Zayas, 2007; Facchi et al., 2007; Chapin, 2015). This sampling method is performed filling a bottle under water surface, in a single point usually at the mid-point of the channel cross section (Facchi et al., 2007). This is the cheapest and easy way to perform a sampling collection (Facchi et al., 2007), but information sampling correspond to a unique space and time selected (Madrid and Zayas, 2007), in order words, this represent a "picture" of water quality condition.

Thus, an interesting way to overcome problems with grab sampling and increase picture representativeness of water quality over the time is using automatic samplers (Facchi et al., 2007; Madrid and Zayas, 2007; Chapin, 2015).Collection can be in two forms: time-interval sampling (samples are collected by regular time intervals) or flow-interval sampling (samples are collected in response to discharge changes) (Harmel et al., 2003; Facchi et al., 2007; Madrid and Zayas, 2007).

According to Harmel et al., (2003), time-interval sampling is simple, reliable, easy and clock failures are rare, but a proper programming is necessary. The advantage of flow-interval sampling is frequency sampling during high flows (Harmel et al., 2003), providing a better discretization of pollutant concentration behavior over hydrograph (Braga, 2013). The disadvantages of these samplers systems are cost and maintenance (Madrid and Zayas, 2007; Braga, 2013; Chapin, 2015).

In addition, for understanding biochemical and geochemical water process, frequency of water quality and quantity monitoring should be high (Moraetis et al., 2010). Terrado et al., (2010) states that automatic sampling networks can measure continuously physical and chemical parameters in specific locations at high temporal frequency. At the same time, Moraetis et al. (2010) complements that wireless use in monitoring stations can provide information with high performance computing environmental in real-time. For Chapin (2015) high frequency monitoring help to measure water quality parameters (e.g.: stream flow and conductivity) more easily, demonstrating changes that occur on timescale ranging from seconds to years.

Moreover, many sensors have been developed for sampling sites and can provide easy, rapid, on-situ or in-situ measurements of water quality parameters (Madrid and Zayas, 2007). Chittoor Viswanathan et al. (2015) used high frequency monitoring with in-situ loggers to quantify electrical conductivity, temperature, pH, pressure and dissolved oxygen. For Delpla et al., (2011) study was used a data logger continuously monitoring data, and after, were transmitted via cellular modem. On telemetric gauging station of Moraetis et al. (2010) five sensors and independent level logger collected data at 5 minutes intervals and measured pH, nitrate, water temperature, dissolved oxygen and river stage.

According to Novotny (2002) many of the problems associated with water quality degradation is due to diffuse pollution. But, measurements and sampling water sample that represent the influence of this source of pollution are complex, even more if engaging quali-quantitative aspects (Braga, 2013). Yet according to Braga (2013), rainfall randomness imposes technique and logistic difficulties: a rainfall event can occurs any moment and having longer or shorter duration, not necessarily predictable.

There are many equipments that can be adapted to measure rainfall event and quantify diffuse pollution (Braga, 2013). Commercial automatic samplers are: ISCO samplers (ISCO, Inc., Lincoln, Nebr.), American Sigma, Inc. (Loveland, Colorado), Global Water Instrumentation (Gold River, California), Intermountain Environmental (Logan, Utah), Hach, Sirco, and many others (Harmel et al., 2003; Chapin, 2015). This equipment is located out of water and use a pump to fill bottles with water sample. The command to collect is started to pre-determinate trigger (Chapin, 2015) and depends for each research. For exemple, in Braga (2013) study the trigger was a minimun varation of the water column level.

OsmoSamplers were developed for Jannasch et al. (2004) and consist in a osmotic pump with a semi-permeable membrane separating two chambers by salinity difference; pump sampling continuously across a long micro-bore (0.5 – 1.2 mm) with a flow rate 1 a 500 µL/hour; volume samples are 0.5 – 1 mL with proper cooling. OsmoSampler equipment is innovator and can collect continuous small-volume water samples for monitoring aqueous environments for up to several years. After that Gkritzalis-Papadopoulos et al., (2012) and Chapin (2015) made their OsmoSamplers version: the first adapted the OsmoSampler to sampling water surface, so then added a solenoid pump that injected 50 µL of rhodamine (due to temperature variations) and 60 µm filter to prevent input suspended materials; the second author added a micro-pumps that inject acid preservative and were configured to change sampling in response a rainfall event (e.g.: daily sampling then hourly sampling during an event). This equipments cost around 2000 USD (American dollar). Table 2 summarizes some automatic samplers studied.

Table 2 - Summary of automatic samplers used in water quality monitoring

Automatic Sampler	Compounds	Flow rate	Type of Sample	Samples details	Preservation	Observations	Reference
OsmoSampler	Osmotic pump: semi-permeable membrane separating two chambers; Continuously pumping a long micro-bore sample tube (0,5 to 1,2 mm)	1 - 500 µL/hour	Seawater sample	Vial with 0,5 to 1 mL of sample	Refrigerated	Samples are separated by difference of salinity	Jannasch et al. (2004)
OsmoSampler addapted	Osmotic pump which continuously draws fluid into a long small-bore (1 mm inner diameter) teflon tube; Solenoid pump: inject 50 µL of rhodamine due temperature; 60 µm filter to prevent suspended materials	~ 1mL/day	Water surface	30 samples	-	Adaptation for collected water surface	Gkritzalis-Papadopoulos et al. (2012)
MiniSipper (OsmoSampler expanded)	micro-pumps that inject acid preservative; filtering system: 10 µm polyethylene solvent filter	1 - 500 µL/hour	Water surface	250 samples with 5 mL	Acid	Adaptation for collected water samples in acid mine drainage	Chapin (2015)
EPIC 1011	portable automatic sampler (Bulher-Montec, UK)	-	Water surface	-	Cold box during the transportation and them kept 4°C until analyses	40% formaldehyde solution was added in bottles before the sampling to inhibit all biological transformations	Facchi et al. (2007)
ANEMONE-11 (Advanced Natural Environmental MONitoring Equipment)	1 pump unit; 4 valve units equipped with 32 electromagnetic valves; 4 sets of 32 water-sampling cylinders; One control unit.	One piezoelectric pump has a fluid volume flow rate of 10 mL/min; four pumps in parallel create a pumping volume flow rate of 40 mL/min.	Seawater sample	128 water samples with 40 mL	After collection	Before deployment, all sampling cylinders should be filled with distilled water to prevent damage due to water pressure.	Okamura et al. (2014)
SBN	Control unit; Bottles to store the samples; Pumping station; Flux distributor system.	-	Water surface	24 sample bottles with 1 liter	No	10 days of independence with 7Ah battery; low fabrications cost	Braga (2013)

Continued Table 2

ISCO®	Autosampler (ISCO 3700)	Flow meter (ISCO 4230)	Water surface	Volume of 0.6 or 1.2 L in 24 bottles	Stored at 4 °C until analysis immediately after collection.	On Site measurements: Neotek Ponsell to measure pH, and Hach Lange for conductivity	Delpla et al. (2011)
ISCO®	Auto Sampler (ISCO 6712) collecting smaple at 1 minute intervals	-	Water surface	-	Just in laboratory	Set manually to take samples at 1 min intervals when runoff from rainstorms began to flow and at 1 h intervals after flow rates stabilized.	Gao et al. (2014)
No information	pH, nitrate, water temperature, DO, and river stage → multi parameter Troll9500 Air temperature, humidity and precipitation → meteorological stations	-	Water surface	-	-	Continuous telemetric monitoring network (5 min) : water level logger (miniTroll-model: Professional by In Situ Inc.) and 2 meteorological stations Telemetric data → 5 minutes intervals	Moraetis et al. (2010)
Auto sampler →24-hour sampling	Five stations of water quality monitoring	-	Water surface	-	-	High frequency monitoring of electrical conductivity (EC), temperature, pH, pressure and DO (at 15 min intervals) was carried out using insitu loggers.	Chittor Viswanathan et al. (2015)
Automatic water sampler → EcoTech Umwelt-Meβsysteme GmbH	YSI 6920 (YSI Incorporated) → water stream level and turbidity continuously	Sampling varied from 3 min to 15 hours during storms events.	Water surface	8 bottles with 2 liter each	Just in laboratory	The probe was programmed to activate the automatic water sampler when the water level varied more than 10 cm on both rising and falling stages of storm events.	Ramos et al. (2015)
Automatic sampler	Parshall flume plus water-level recorder (TruTrack WT-R500 and 1000, Christchurch, New Zealand).	Collection performed every 0.5 h, sometimes every 1 or 2 h during the falling limb of the hydrograph	Water surface	-	Just in laboratory	Automatic sampler was activated automatically when the water table increased.	Zhang et al. (2008)

Braga (2013) developed an automatic sampler from an adaptation of ISCO® (Teledyne ISCO), called SBN. The concern in Braga (2013), study was exactly know about diffuse pollution process and its effects into a water body, mainly during the rainfall events (which is the main physical mechanism inductor transport process (Lee et al., 2010). SBN works by flow-interval sampling just measuring rainfall event contribution into a water body, called intelligent sampling. SBN is composed by a microprocessor control unit, 24 bottles to store the samples (1 liter each), pumping station and flux distributor system (more details are presented in section 3.2 Automatic Sampler). Comparison between intelligent sampling and temporized sampling are shown in Figure 6.

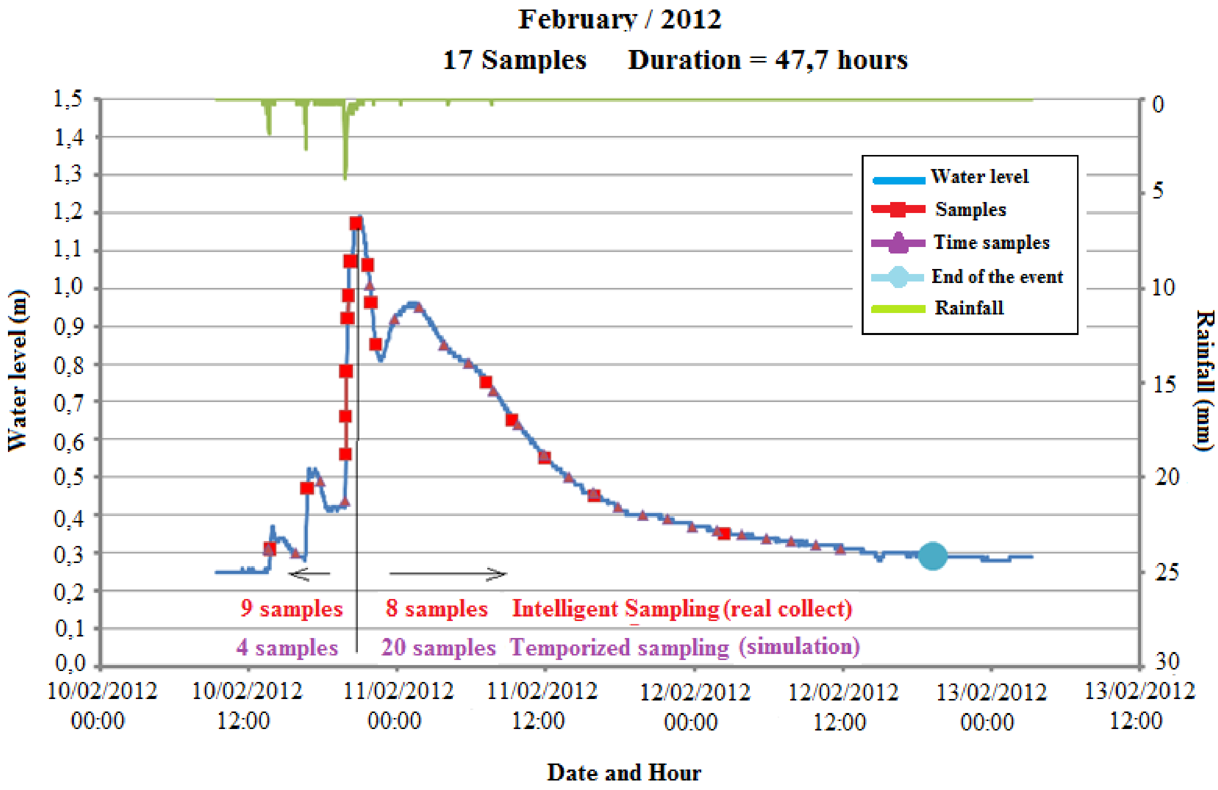


Figure 6 - Intelligent sampling vs. temporized sampling

Source: adapted from Braga (2013)

Braga (2013) states that if automatic sampler was programmed to sampling for each hour, a short rainfall event would benefit with a major sampling resolution, but if it happens a long rainfall event this would be sub-sampled. Larger time intervals helps to minimize the problem, but not solve them. Fixed level triggering for event beginning do not work either, background river levels vary with the variation of the interval since the end of the previous event. However, with intelligent sampling, equipment can detect the event begging by rising the short term variation on the river level), collecting more representative samples in terms of diffuse pollution (Figure 7).

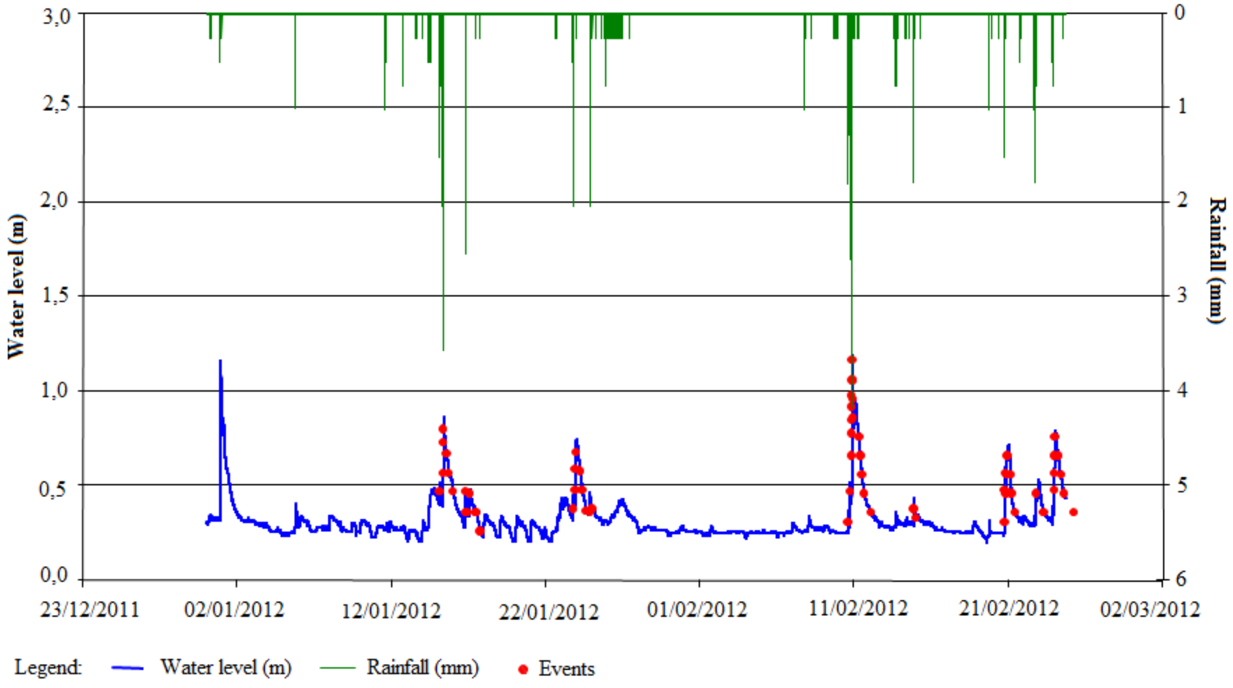


Figure 7 - Hydrograph and sampling for Braga (2013) study between January and February 2012

Source: Braga (2013)

Lastly, Braga (2013) highlights that SBN has been shown to adequately perform the routine proposed for the intelligent sampling. But some difficulties are still challenging, as: (i) limited number of samples, (ii) samples preservations, and (iii) water quality parameters really significant in diffuse pollution studies.

2.4. Water Quality

Water quality can be represented through several parameters which provide information about physical, chemical and biological water body characteristics. Physical parameters correspond to color, taste and odor, turbidity, temperature and solids series. Chemical parameters are pH, alkalinity, acidity, nitrogen, phosphorus, oxygen dissolved, organic matter (TOC, BOD and COD) and others. Lastly, biological parameters are associated to indicators microorganism, bacteria and algae (Von Sperling, 2005).

In aquatic ecosystem, organic compounds are naturally present as food chain portion and nutrients cycles process. These compounds can be found in dissolved or particulate form, in sediment and aquatic biota (Fernandes et al., 2014). Excess of organic matter and nutrients can produce changes in water quality, as depletion in oxygen dissolved concentration, pH, alkalinity and luminosity characteristics (Westerhoff e Anning, 2000). According to Knapik (2014), oxygen depletion is caused by organic matter decomposition; additionally, eutrophication process originates an excess of organic matter. Thus, oxygen depletion and eutrophication represents consumption and production cycles, and also can represent a single problem (Figure 8) (Knapik, 2014).

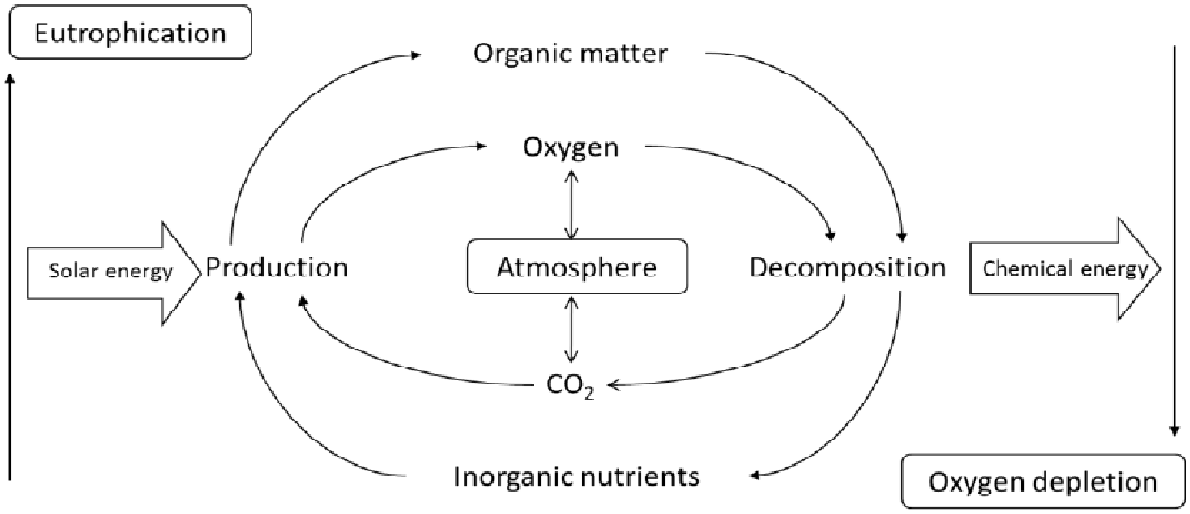


Figure 8 - Production and consumption natural cycle

Source: Adapted from Chapra (1997)

In rivers, pollution control is related to an ecologic balanced environment, considering priority uses and environment quality classes required by legislation (CONAMA, 2005). Main water quality parameters are organic compounds and nutrients, also utilized in water quality modeling (Chapra, 1997). Natural elements to life, called nutrients, are incorporated in the form of organic compounds involved in several chemical reactions essential to organism activities.

These can be divided into two groups: i) macronutrients: presents in amounts greater than 0.2 percent in dry weight, as carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), sodium (Na), calcium (Ca), magnesium (Mg) and iron (Fe); ii) micronutrients: present in smaller quantities than 0.2 percent in dry weight, as aluminum (Al), boron (Bo), chrome (Cr), zinc (Zn), molybdenum (Mo), vanadium (V) and cobalt (Co) (Braga et al., 2005). According to authors, is possible distinguish two types of biogeochemical cycles: vital elements cycle (C, N and P) and vital compounds (water).

Next will be presented a synthesis about nitrogen, phosphorus and carbon cycles. Eutrophication and organic matter dynamic will be presented as complement to the three main nutrients in environment, due strong relationship between them.

2.4.1. Nitrogen

Nitrogen is an important molecule constitute of proteins, nucleic acids, vitamin, enzymes and hormones, vital to organisms. This macronutrient is present in atmosphere at about 78 percent (Chapra, 1997; Braga et al., 2005). Nitrogen cycle (Figure 9) is more expansive than carbon cycle, although a few organisms use nitrogen.

Nitrogen cycle is constituted by four important stages: i) N fixation as organic nitrogen by symbiotic organism; ii) ammonification: bacteria mineralize organic molecules constituted of nitrogen producing gas ammonia (NH_3) and ion ammonium (NH_4^+). Ammonia forms are dependent of pH; when pH is higher than 7 occurs decrease of NH_4^+ species and increase the NH_3 species (Von Sperling, 2005).

iii) nitrification: nitrogen ammonium is converted in nitrite (NO_2^-) and nitrate (NO_3^-) by chemical-synthesize bacteria, as *Nitrosomonas* and *Nitrobacter*, respectively for each process. Nitrificationcauses decrease in DO concentration due to bacterial consumes (1). Equation "a" represents nitrogen ammonia to nitrite transformation, and "b" transformation of nitrite to nitrate.

$$NH_4^+ + 1{,}5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \quad (a) \tag{1}$$

$$NO_2^- + 0{,}5O_2 \rightarrow NO_3^- \quad (b)$$

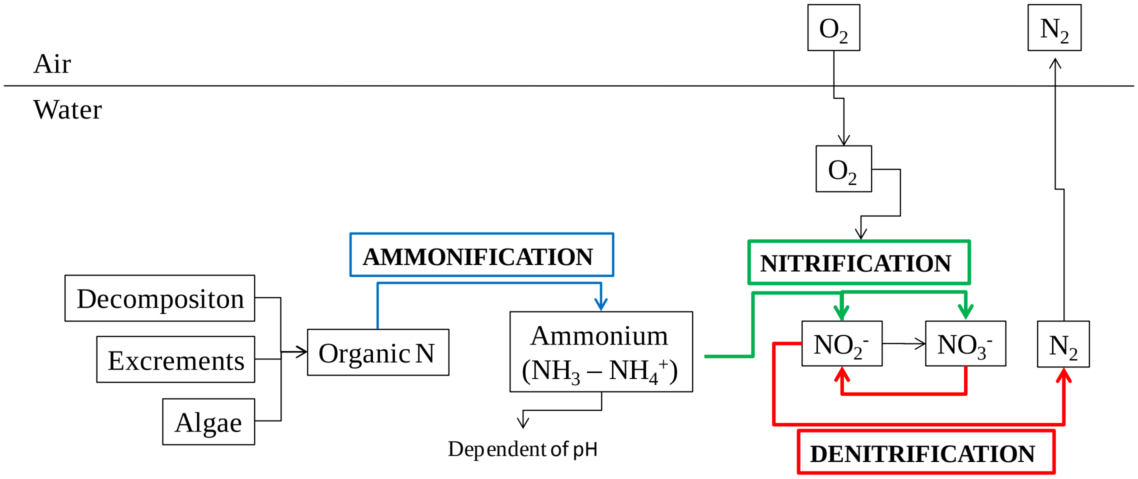


Figure 9 - Nitrogen cycle

Source: adapted from Chapra (1997)

iv) denitrification: nitrate suffers oxygen reduction and transforms in nitrogen gas (N_2) by pseudomonas bacteria; this phenomenon occurs necessarily without present of oxygen (2).

$$NH_4^+ + 2O_2 \rightarrow 2NO_3^- + 2\,H^+ + H_2O + energy \tag{2}$$

Nitrogen can be found naturally in organism proteins and biological compounds, and by anthropogenic source, as residential and industrial wastewater, fertilizer, and animal excrements. Recent pollution in water body can be acknowledged by organic nitrogen present, while remote pollution is acknowledged by nitrate presence (synthesized form) (Von Sperling, 2005).

2.4.2. Phosphorus

Phosphorus is present in genetic material as ribonucleic and deoxyribonucleic acid molecules (RNA and DNA) besides composing bones and teeth (Von Sperling, 2005), been essential to all life (Chapra, 1997). At water quality perspective, phosphorus is important because is present in short supply (Chapra, 1997) and instead carbon and nitrogen reservoir, phosphorus reservoir in the environment is lithosphere (phosphates rocks) (Braga et al. (2005).

Phosphorus passes from lithosphere from hydrosphere by erosion, a very slow physical process. Figure 10 shows phosphorus cycle.

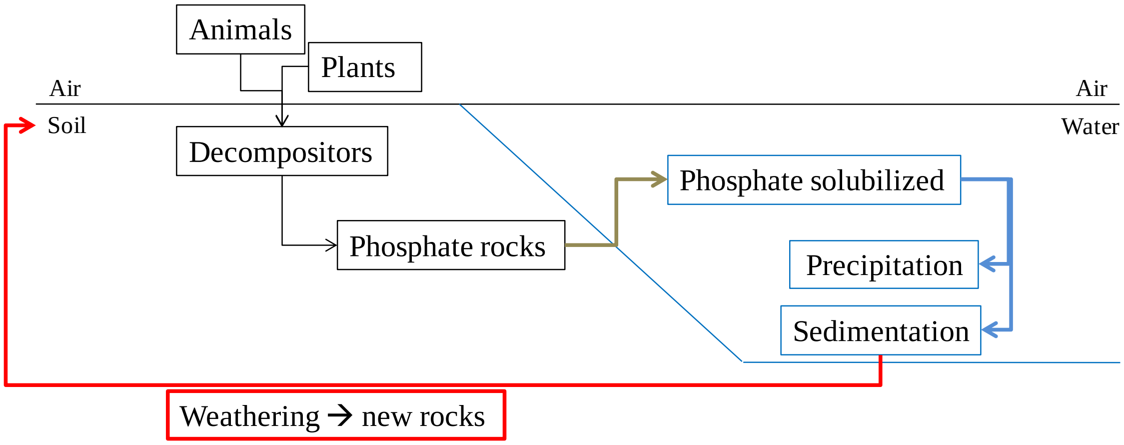


Figure 10 - Phosphorus cycle

Source: Adapted from Chapra (1997)

In water body, phosphorus can be found as soluble reactive phosphorus (also called orthophosphate: PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$), particulate and non-particulate organic P, and particulate and non-particulate inorganic P (e.g.: phosphate minerals and detergents, respectively) (Chapra, 1997). Natural sources of phosphorus are soil compounds dissolution, organic matter decomposition, and organisms cellular composition. Anthropogenic sources are domestic and industrial wastewater, animal excrements, fertilizer, and detergent (Von Sperling, 2005).

The excess of nitrogen and phosphorus in water body can cause eutrophication (Novotny, 2002; Braga et al., 2005; Von Sperling, 2005; Bem, 2009). According to Thomann and Mueller (1987), eutrophication consist in the overgrowth of aquatic plants (phytoplankton and macrophytes) in levels that can interfere water body uses. However, eutrophication is not synonymous of pollution, but pollution can accelerate eutrophication (Novotny, 2002). Rate of eutrophication depends on some factors as solar radiation, geography around water body, incidence of solar radiation into water column, amount input of nutrients, movement, transport, and dispersion in water body (Bem, 2009), but usually this factors are uncontrollable (Novotny, 2002). Furthermore, is important to identify which of several nutrients controls level of plants growth in water body, called limiting nutrient (Chapra, 1997). This rule is determined by nitrogen and phosphorus ratio: an N:P ratio less than 7.2 suggest nitrogen as limiting factor, instead (N:P > 7.2) higher levels imply phosphorus as an limiting (Chapra, 1997).

According to Braga et al. (2005), eutrophication can be classified in: oligotrophic: lower biological productivity and nutrients concentration; eutrophic: excessive vegetal production and higher nutrients concentration; mesotrophic: intermediate characteristics between oligotrophic and eutrophic. Eutrophication consequences are visible in ecosystem and water quality impacts as low dissolved oxygen concentration, decrease of ecological biodiversity, high concentration of dissolved organic compounds (e.g: trihalomethanes), decrease of water column transparence, anaerobic decomposition, and as a consequence, release of gases that change the environmental conditions. However preventive and corrective actions can be used to control eutrophication as: reduction of diffuse and punctual extern charges (e.g.: more efficient wastewater treatment, lower use of fertilizer, urban drainage control) and actions on the process of nutrients circulation and ecosystems (Braga et al., 2005).

2.4.3. Carbon

Carbon cycle is perfect because all carbon is returned to the environment at the same rate which is synthesized, due photosynthesis and respiration reaction (3 and 4).

$$6CO_2 + 6\,H_2O + solarenergy \rightarrow C_6H_{12}O_6 + 6O_2 \tag{3}$$

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 640\frac{Kcal}{mol} \tag{4}$$

Photosynthesis (3) happens only in presence of solar energy. Plants use CO_2 and water vapor to synthesize carbon organic compounds. Two observations must be highlighted: carbon fixation happened in organic form and solar energy is stored as chemical energy by the organic molecules. Respiration (4) is the opposite process. Energy accumulated is released by the molecules break, energy essential to vital activities of the organisms. Through this reaction, carbon passes from inorganic stage to organic stage and then return to inorganic stage, completing their cycle. According to Chapra, (1997), carbon can develop three functions in water quality, as a i) nutrient; ii) biomass (large component of organic compounds); and iii) pollutant (organic carbon decomposition affect oxygen concentration in aquatic ecosystem).

Organic matter (OM) is complex mixture of organic compounds which can be found in all superficial area, underground, and soil. (Filella, 2009; Knapik, 2014). OM can be classified according to their origin into two categories: i) autochthonous: formed in water mass itself throught first productivity, plankton’s excretion and decomposition and aquatic bacteria; ii) allochthonous: formed by bacteria and fungi decomposition of higher plants, been rich in fulvic acid (Filella, 2009), basically is from outside of the system (e.g. atmospheric deposition or soil material transported by runoff (Knapik, 2014). A mixture of allochthonous and autochthnous materials, found in terrestrial source, form OM present in rivers (Pradhan et al., 2014).

According to Filella (2009), OM can be divided in three forms: i) biochemical as carbohydrate, protein and lipid, which constituted about 20 – 40 % of natural OM in ecosystem; ii) physical as dissolved organic matter (DOM) and particulate organic matter (POM); iii) chemical as labile and refractory compounds. Lability is OM capacity to degrade itself during a time interval, as well as, a labile compound is consumed in minutes to days scale, while the refractory compound years to millennium scale (Filella, 2009).

Organic matter dynamic happen due physical, chemical and biological process between air, water and sediment interface. Environmental factors are temperature, solar radiation, flow, biologic community and physical, chemical, and biological process (Knapik, 2014). Figure 11 shows organic matter sources and pathways in aquatic system.

Organic matter is found in every water supply and their quantification is important for, water ecological health, biological growth, treatment cost and efficacy (Bridgeman et al., 2015). There are many methods to characterize organic matter and depends on the type of organic matter you want to quantify (Figure 12).

Procedures called Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are the two indirect measurement and the most used ways to the evaluation of organic matter content in a water body (Knapik, 2014). Also, volatile fraction in series solids (volatile total solids and volatile suspended solids) can predict, as indirect measurement, organic quantity. Another procedure used to assess the organic matter concentration is total organic carbon (TOC), dissolved organic carbon (DOC) (Bridgeman et al. (2015), and particulate organic carbon (POC) (Knapik, 2014). This type of measurement are a direct estimation and according to Bridgeman et al. (2015) TOC is widely used to quantify organic carbon atoms present in water. Another technique that can be applied for organic matter characterization (compounds and origins) is UV-visible and fluorescence spectrophotometry (Knapik, 2014). Fluorescence analysis is a rapid technique that requires small volumes of sample and little sample preparation (Bridgeman et al., 2015). Figure 12 shows methods to quantify organic matter.

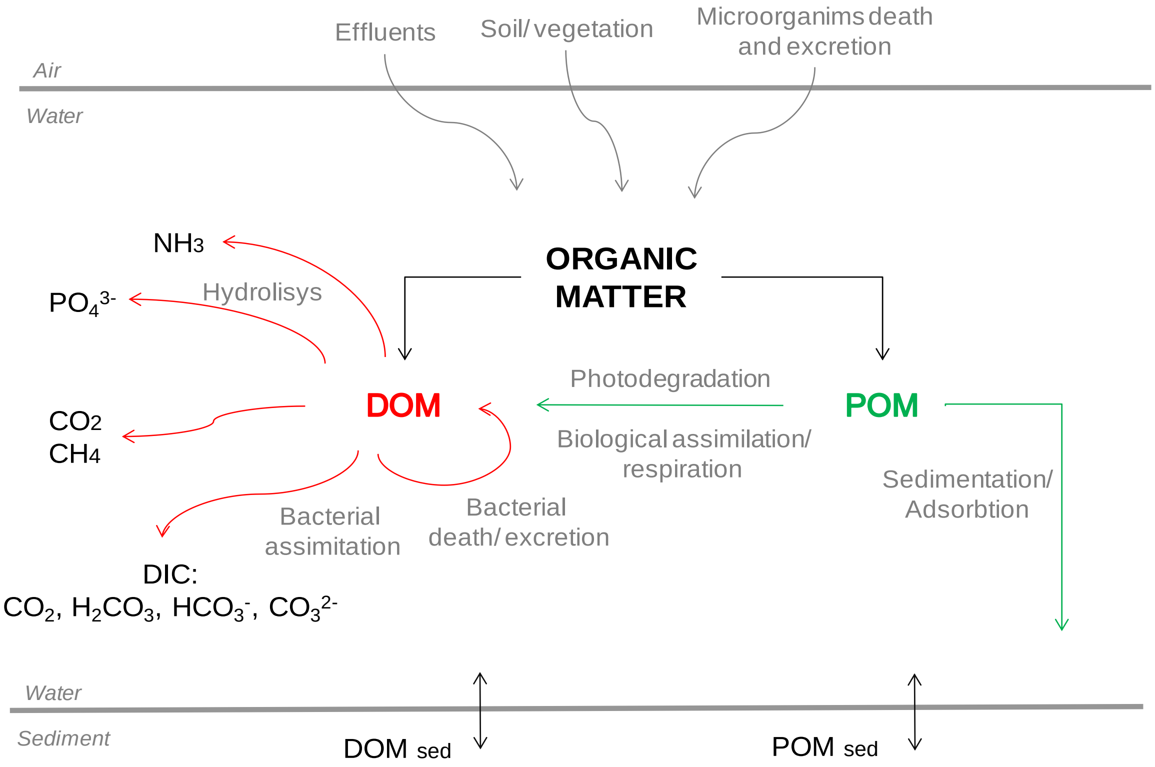


Figure 11 - Organic matter sources and its dynamic between air, water and sediment

(Source: Knapik, 2014).

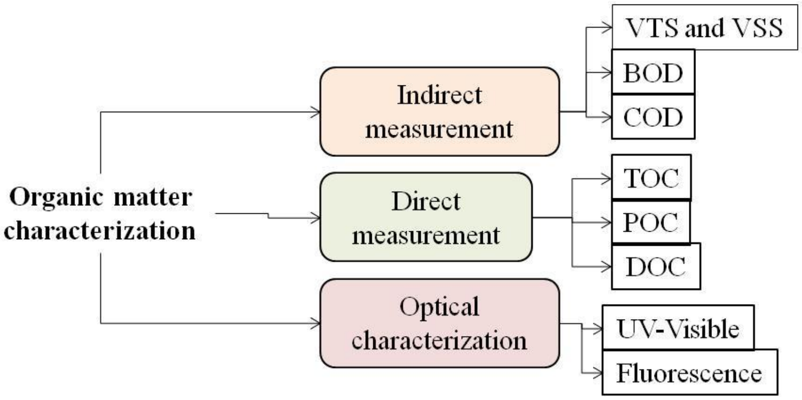


Figure 12 - Different methods to quantify organic matter

Source: Adapted from Knapik (2014)

Despite several methods to quantify organic matter (direct and indirect), all of them are important and essential to water quality characterization and understanding. Each method is dependent of different biochemical process, providing different kind of information about organic matter determination. Therefore, TOC is a direct expression of total organic content, but does not provide the same information of BOD or COD (APHA, 1998). Characterization and quantification of organic matter reflects their origin and history, and thus, this property provides useful information about biogeochemistry (Maie et al., 2014), been important in assessment of water quality**.**

In general, water quality studies considering diffuse pollution into the river to characterize and understand rainfall events. Water quality parameters most found in studies were: nitrogen series (including nitrite, nitrate, ammoniacal nitrogen, dissolved total nitrogen) (Buck et al, 2004; Zhang et al., 2008; Moraetis et al, 2010; Chen et al., 2012; Gao et al., 2014; Yu et al, 2016), phosphorus and derivates (Zhang et al., 2008; Moraetis et al., 2010; Chen et al 2015), DOC and TOC (Kayhanian et al., 2007; Fellman et al., 2009; Moraetis et al., 2010; Delpla et al., 2011), COD (Kim et al., 2007; Moraetis et al., 2010) and solids contents (Kayhanian et al 2007; Kim et al 2007; Li et al 2008).

Table 3 summarizes some water quality parameters, analytical procedure, and samples preservation in studies focused in rainfall events.

Some studies showed parameters measured with multi-parameters probes. Values of pH, DO, electrical conductivity (EC), and total dissolved solids were measured in situ using multi-parameter instrument (YSI 85) in Yu et al (2016). In situ loggers were used in Chittoor Viswanathan et al (2015) study to measure EC, temperature, pH, pressure and DO at 15 minutes intervals. Delpla et al (2011) used Neotek Ponseel probe for pH and Hach Lange probe for conductivity.

Water quality parameters are being investigated by several studies, to find which parameters is the best one, to find which parameters can be enough to represent pollutant transport process along the river. Also, a strategy is necessary to quantify parameters to provide response to the questions. One strategy studied is detailed in the next item.

Table 3 - Summary of water quality parameters most commum performed in studies

Parameters analyzed	Preservation	Analytical procedure	Observations	Reference
pH, TEMP, TUR, NO_3^- ,total ammonium, total alkalinity and bicarbonate conductivity, SS, DO, BOD, TP, coliforms	not mentioned	APHA 1998	not mentioned	Andrade et al. (2007)
pH EC	not mentioned	WTW inoLab pH 720 Conductivity cell TetraCon 325	not mentioned	Changwony et al. (2015)
TN and TC		CNS elemental analyzer		
TOC and DOC	Stored 4°C until analyses immediately after collection	thermal oxidation coupled with infrared detection (Multi N/C 2100 Analytik Jena	For DOC and UV spectra the samples were filtrated through 0.45 µm HAWP nitrocellulose filter papers (Millipore)	Delpla 2011
N-Kjeldhal		mineralization with H2SO4 > distillation by titration		
TUR		nephelometry		
UV spectra		UV-vis spectrometer Perkin Elmer Lambda 35		
EC, TEMP, pH pressure and DO	not mentioned	loggers	not mentioned	Chittoor Viswanathan et al. (2015)
NO_3^-, DOC and isotopes		not mentioned		
NH_3-N, NO_2-N, NO_3-N, PO_4^{3-}, and TP.	polyethylene bottles and stored on ice during transport to the laboratory.	national standard criterion - GB 3838-2002	samples to dissolved nutrients were filtrated in the field through glass fibre filters (Whatman GF/F type, nominal pore size=0.7 mm)	Yu et al 2016
pH, DO, EC and TDS,		YSI 85 - multiparameter instrument		

Continued Table 3

DO conductivity and TEMP	Acid-washed polyethylene bottles and stored on ice during transport to the laboratory	YSI Model 85	Dissolved nutrients were filtered in the field through glass fibre filters (Whatman GF/F type, nominal pore size of 0.7µm)	Buck et al 2004
TUR		Hach 2100A Model		
SS, NH_3-N, NO_2-N, NO_3-N, and dissolved reactive phosphorus		APHA 1998		
TN e TP		Ebina et al 1983		
NO_2-N, NO_3-N, NOx Kjeldahl N and TKN); TP, EC and SS	not mentioned	APHA, 1992; Australian Water Technologies, 1999.	not mentioned	Smith et al 2013
NH_3-N, NO_2-N, NO_3-N, and dissolved total nitrogen	Polyethylene bottles pre-rinsed with river water. Samples were stored in a coll box and delivered to the laboratory. Samples were frozen at -20 Celsius	SEPA 2002	Filtration through 0.45µm nucleopore membranes	Chen et al 2012
DOC	Stored in refrigerator until analyzes	High-temperature combustion using a Shimadzu TOC-V Organic Carbon	Filtered through precombusted, Gelman A/E glass fiber filters (0.7 µm pore size)	Fellman et al 2009

SS – suspended solids; DO – dissolved oxygen; BOD – biochemical oxygen demand; TP – total phophorus.; NO_3^- - nitrate ; EC – electrical conductivity; TC – total carbon; TN – total nitrogen; TOC – total organic carbon; DOC – dissolved organic carbon; TUR – turbidity; TEMP – temperature; TDS – total dissolved solids; PO_4^{3-} - orthophosphate

2.5. Event Mean Concentration – Quantifying strategy

Quantifying of pollutant load from punctual sources in an interval of time is a ratio between flow (L^3T^{-1}) of runoff pollutant and their concentration (ML^{-3}), which is reasonable simple and easy task to be carried out. Knowing this information pollutant load (MT^{-1}) can be determined. In other hand, for diffuse sources has much restriction in measurement due to information lack about source identification (Braga, 2013). According to Madrid and Zayas (2007),hydro-morphological and hydrological conditions associated with diffuse pollution lead to spatiotemporal variations into physical and chemical water characteristics.

After long periods without precipitation pollution is accumulated, and when rainfall of some intensity occurs, significant mobilizations of accumulated pollutants and debris take place. This condition is known as “first-flush effect”, increasing pollutant load (Delpla et al., 2011; Moraetis et al., 2010; Braga, 2013). However opposite effect can occurs too, where pollutant concentration decrease due flow and runoff increase (Braga, 2013; Viswanathan et al., 2015). Impervious areas can help in increase storm-water flow and flash floods (Chittoor Viswanathan et al, 2015).

For real quantifying of pollutant from diffuse sources is necessary to measure flow and concentration (considering temporal dynamic), in order to calculate event mean concentration – EMC (5) (Braga, 2013), since pollutant concentration varies during event (Lee et al., 2010).

EMC is by definition the arithmetic mean of individual sample concentration collected on equal discharge intervals, and when multiplied by the total flow volume represent rainfall event load (Harmel et al., 2003), present in equation 6, where: M is total mass of pollutant during rainfall event (kg); V is runoff volume caused by rainfall event (m^3); c(t) is pollutant concentration along the time (mg/L); q(t) is flow along the time (L/min) and T is runoff total duration (min).

$$\mathrm{EMC} = \frac{\mathrm{M}}{\mathrm{V}} = \frac{\int_0^{\mathrm{T}} \mathrm{c(t).q(t)dt}}{\int_0^{\mathrm{T}} \mathrm{q(t)dt}} = \frac{\sum_{\mathrm{o}}^{\mathrm{T}} \mathrm{c(t).q(t)}}{\sum_{\mathrm{o}}^{\mathrm{T}} \mathrm{q(t)}} \qquad (5)$$

For achieving a good evaluation of load pollution from rainfall event, samples should be collected in appropriate moment and in enough number to be representative. Knowing the instantaneous value for water quality parameters and flow it, is possible to obtain average rainfall event value (Braga, 2013). Loads may not be eventually distributed throughout the event. Some studies try to characterize the first flush event, for example in Kim et al., (2004), Lee et al., (2002) and Lee et al., (2011).

The first step for identification of first flush in Kim et al (2004) study was: if more than 50% of the mass is emitted during first two hours of rainfall event, it is called a first flush. With some additional information (rainfall event were monitored from 0.28 to 15.6 cm; total runoff volume varied from 8 to 1420 m³ among the six sites) EMC was calculated: for total gross pollutants ranged from 2.1 to 259 mg/L and for additional information event, that is a high value due the percentage of impervious area (~100%). Considering impervious area (almost 100%) in Lee et al., (2002) study, happened a strong first flush due the difference between the mass and volume curve.

For Lee et al. (2011), that studied EMC characteristics from rainfall runoff on an urban highway with catchment area about 2500 m² and with residential and commercial surrounding land use. Relationship between EMC and total suspended solid and chemical oxygen demand are good for this situation, where: increasing EMC with runoff until 70-80 m³/event and decrease EMC after 70-80 m³/event; to ensure the relationship two general non-linear equations were created (Lee et al, 2011).

Braga (2013) used information provided by pluviometric station and made analysis about pollutants transport unit and calculated EMC. He investigated differences between physic and chemical parameters transported during a rainfall event (Figure 13). EMC values for TS and total suspended solids were 710 and 484 mg/L respectively. Also according to Braga (2013), for right EMC calculation for any pollutant is necessary a good sampling distribution along the rainfall event.

EMC use is interesting for evaluating the effects of rainfall event, and consequently runoff on receiving waters. However, river respond slowly to rainfall runoff inflows compared to the rate at which pollutant concentrations change during events. Thus, EMC is an important analytical parameter, because represents a flow weighted average concentration computed as the ratio between total pollutant mass and total runoff volume, considering determined event duration. (Lee et al., 2002).

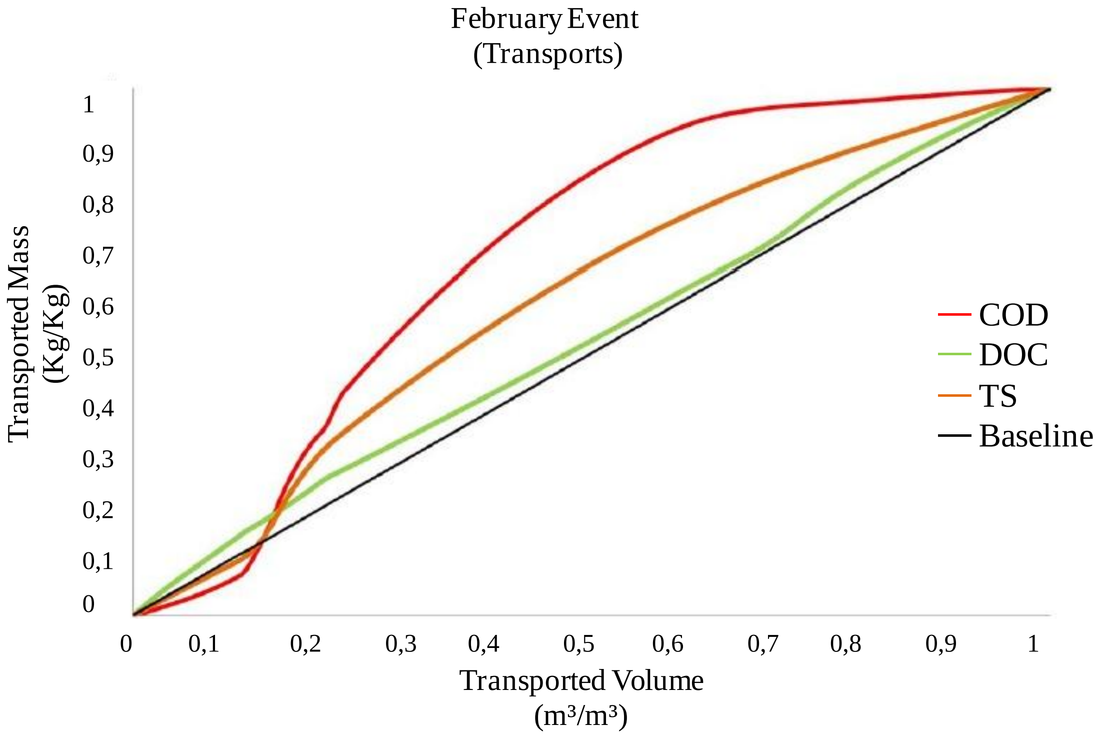


Figure 13 - Comparison between chemical oxygen demand (COD), total solids (TS) and dissolved organic carbon (DOC) transport unit

Source: Braga (2013)

2.5.1. Métadier and Bertrand-Krajewski (2012) approach

Métadier and Bertrand-Krajewski (2012) study proposed a alternative method for EMC curves classification to facilitate the comparison of pollutographs. The method consist to classify curves in three zones (A, B and C) (Figure 14) that are symmetric around the bisector. According Metádier and Bertrand-Krajweski (2012) these curves are established from continuous time series with hundred values or ten values, instead of a limited number of samples collected during rainfall events.

Zone A include events which a fraction of the total event pollutant load is transported in a fraction of the total event volume significantly lower than pollutant load. Zone A classification means pollutant is transported in little water volume causing pollutant concentration, and if curves are frequently observed, means that relatively small storage volumes are sufficiently to intercept a portion of pollutant laod. This concept was used to define first flush phenomenon in Metádier and Bertrand-Krajweski (2012) study.

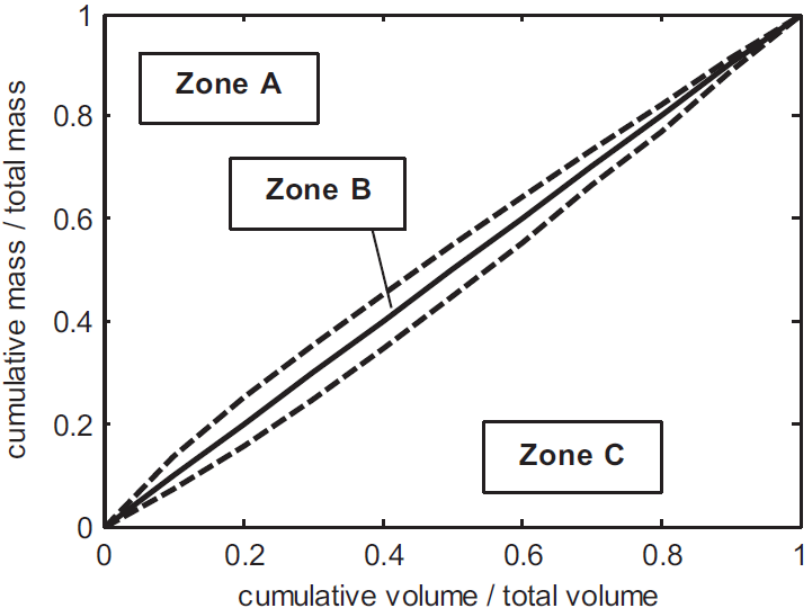


Figure 14 - EMC curves in three zones classification

Source: Metádier and Bertrand-Krajweski, 2012

In zone B, fraction of the total event pollutant load is transported in a fraction of the total event volume relatively similar than pollutant load, so pollutant loads leads to the same fraction of the total volume. Zone C include events which fraction of the total event pollutant load is transported in a fraction of the total event volume significantly bigger than pollutant load. In general, Metadier and Bertrand-Krajweski (2012) affirm that this simple classification allows comparison between events and catchments.

2.5.2. Butturini et al., (2006, 2008) approach

Additionally, another method to classified rainfall event by events characteristics is proposed by Butturini et al. (2006, 2008) as C-Q responses, also called hysteresis. C-Q response is characterized by two semiquantitative descriptors that summarize solute fluctuations during a rainfall episode: ΔC and ΔR. ΔC (%) describes relative changes in solute concentrations (6) and ΔR provide information about the area and rotational pattern of C-Q responses (7).

$$\Delta C = \frac{(C_s - C_b)}{C_{max}} * 100 \tag{6}$$

$$\Delta R = R * A_h * 100 \tag{7}$$

Where: C_s is solute concentration during peak rainfall flow; C_b is solute concentration at base flow; C_{max} is the highest concentration observed during a rainfall; R is rotational pattern of c-q hysteresis; A_h is area of the c-q hysteresis.

ΔC can range between -100 and 100. Negatives values represent hysteresis with negative trend in relation to the discharge (i.e. pollutant dillution), while positive values indicate opposite case (i.e. pollutant concentration). Rotational pattern can be 1 if clockwise rotational pattern is indentified and -1 to anticlockwise rotational pattern. The area of c-q hysteresis is estimate through unity values of discharges and concentrations (Figure 15).

Figure 15 represent ΔC and ΔR descriptor estimation. C* and Q* are concentration and discharges standardized to a unity scale. Grey region is area of C-Q hysteresis (A_h). Arrows indicate rotational direction and open circles (Cb, Cs and Cmax) represent pollutant concentration in base flow, in peak discharge and maximum values observed during rainfall event, respectively.

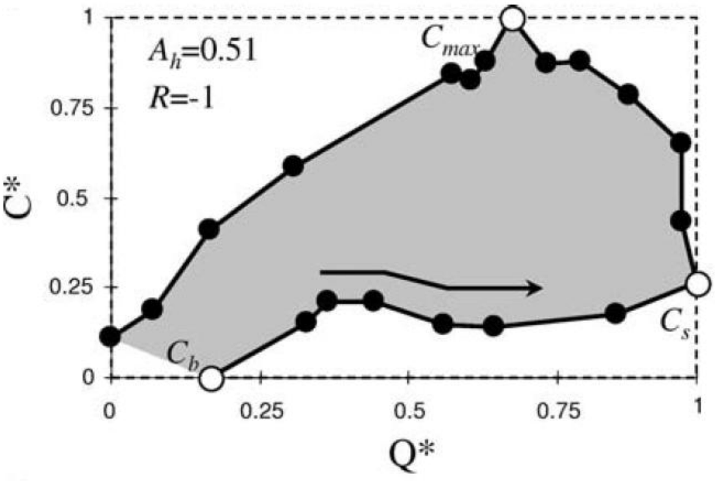


Figure 15 - Schematic example of C-Q hysteresis

Source: Butturini et al (2006)

The combination between ΔC and ΔR synthesizes variability of geometrical properties in two dimensional continuum unity plane. In this plane, nine regions can be identified, where six of them are C-Q hysteresis (ΔR ≠ 0) and three linear C-Q responses (ΔR ~ 0), as can be observed in Figure 16.

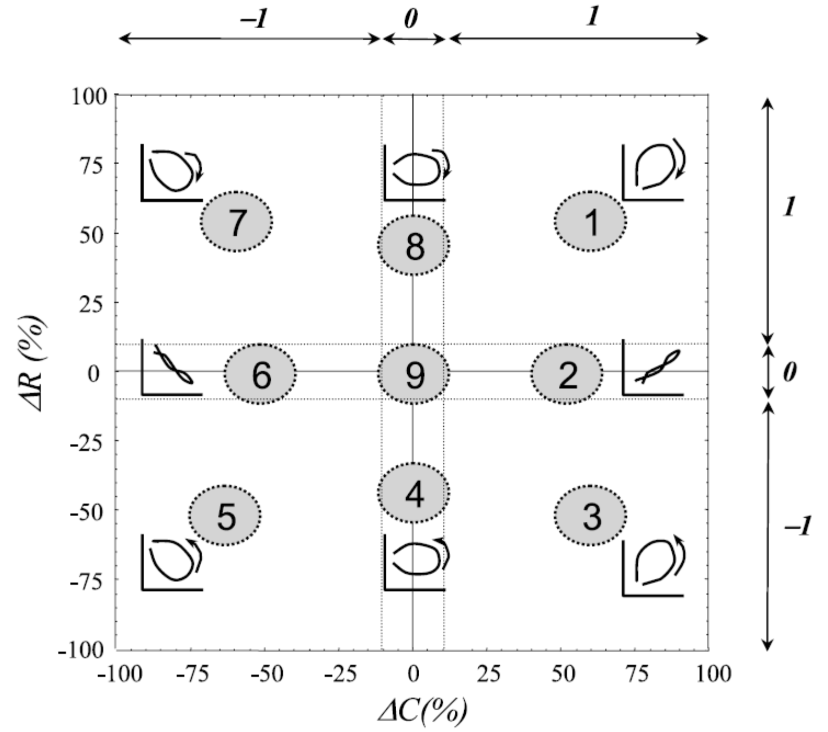


Figure 16 - Schematic representation of unity plane ΔC vs. Δ R

Source: Butturini et al (2008)

Each region identifies a C-Q response type, divided in three qualitative categories (-1, 0 and 1). Classification as "-1" happens as pollutant dilution ($\Delta C < -10\%$) with anticlockwise loop ($\Delta R < -10\%$). Category "0" happens for neutral ($-10\% \leq \Delta C \leq 10\%$) and no loop condition ($-10\% \leq \Delta R \leq 10\%$). Lastly, category "1" indicate pollutant concentration ($\Delta C > 10\%$) and clockwise loop ($\Delta R > 10\%$).

Butturini et al (2006) classified rainfall events using DOC and nitrate parameters. DOC concentrations increased in all rainfall events (presented $\Delta C_{DOC} > 0$), therefore data points were located exclusively in regions 1 and 7; Rotational patterns ranged from anticlockwise and clockwise. For nitrate determination, usually flushed during rainfall events ($\Delta C_{NO3} > 0$) and most of the values were located in region 7 of the plane. Chen et al. (2012) also studied nitrate distribution during rainfall event plus nitrogen ammonia. They found a clockwise pattern trajectory that means nitrate supply was dominated by within-channel mobilization and diluted by increasing discharge. For ammonia, was observed anticlockwise trajectory, indicating a flushing from upstream area and a delay delivery downriver to the outlet of Jiulong River.

Ramos et al. (2015) investigated nitrate losses during rainfall event considering seasons and agriculture land use. Nitrate losses were mostly observed during early spring and autumn, due crop fertilization during sowing. Hysteresis analyzes showed predominately anticlockwise trajectory that indicates the amount of nitrate were transported from distant areas of the catchment studied due nitrate infiltration. Nitrate first infiltrated in the soil only reaching later the water stream through superficial flow. This transport was possible due specific soil characteristics.

In Minella et al. (2011) hysteresis study showed clockwise pattern in seventeen events of nineteen events observed. Additionally, one event show anticlockwise pattern and other "eight format". This tend behavior are controlled by physiographic basin characteristics, small drainage area, hillslope, closely of drainage set and sediment sources, land use, and soil type.

Each method to characterize rainfall events is complementary to other. Chose any of them need be made to find appropriate and representative answers provide by monitoring site and samples performed.

2.6. Summary and Reflections

This chapter reports concepts about diffuse pollution, the mechanism involved and the factors that have influence on this dynamic. The mainly mechanism that contributed to diffuse pollution is precipitation (rainfall events). During rainfall events occurs the mainly pollutant transport. In addition, factors as land use and soil occupation have driven the intensity of diffuse pollution transport and contribution to water quality degradation. Also, were approached water quality parameters, and strategy to quantify them. Method available and proposed are EMC curves analyzes in zones (A, B and C), and hysteresis analyzes.

The study about contribution of rainfall event in transport of diffuse pollution is a challenge facing all variables involved. Some variables are time elapse between field and laboratory, amount of samples to measure, analytical procedure representativeness, data processing and analyses. Considering that, is noticeable the need of more information and improvements into monitoring site and laboratory work to provide a better understanding about the diffuse pollution process.

Chapter 3

Integrating Water Quality and Quantity

> “What we need to understand,
> what we need to see in all these things is the beauty behind,
> because, in essence, all that is very beautiful.”
> **— Cristóvão Fernandes**

3.1. The importance of the case study

This study was developed at Barigui River Watershed, which is a sub-basin located in the central of the Upper Iguaçu Watershed at Paraná State (southern Brazil), shown at Figure 17. The Barigui River starts at Almirante Tamandaré city, located in metropolitan region of Curitiba (RMC), intersecting north to south until arrive at the Iguassu River. The Barigui River Watershed drains an area of approximately 267 km² and includes the Almirante Tamandaré, Curitiba and Araucária cities, besides some ecological parks, as Barigui and Tingui Park (SUDERHSA, 2002). Barigui River has 67 km of extension (Gonçalves, 2008).

This watershed can be divided into three parts: south, median and north. The south portion is the industrial area, occupied at Curitiba city (in left margin) and Araucária city (in right margin). In the median portion there is an intense urban occupation (Curitiba city), with residential, services and commercial activities. The north portion, the most upstream, is predominantly rural land use and some diffuse urban centers, where is located Almirante Tamandaré city and the site of this study. The Figure 18 shows the monitoring site location.

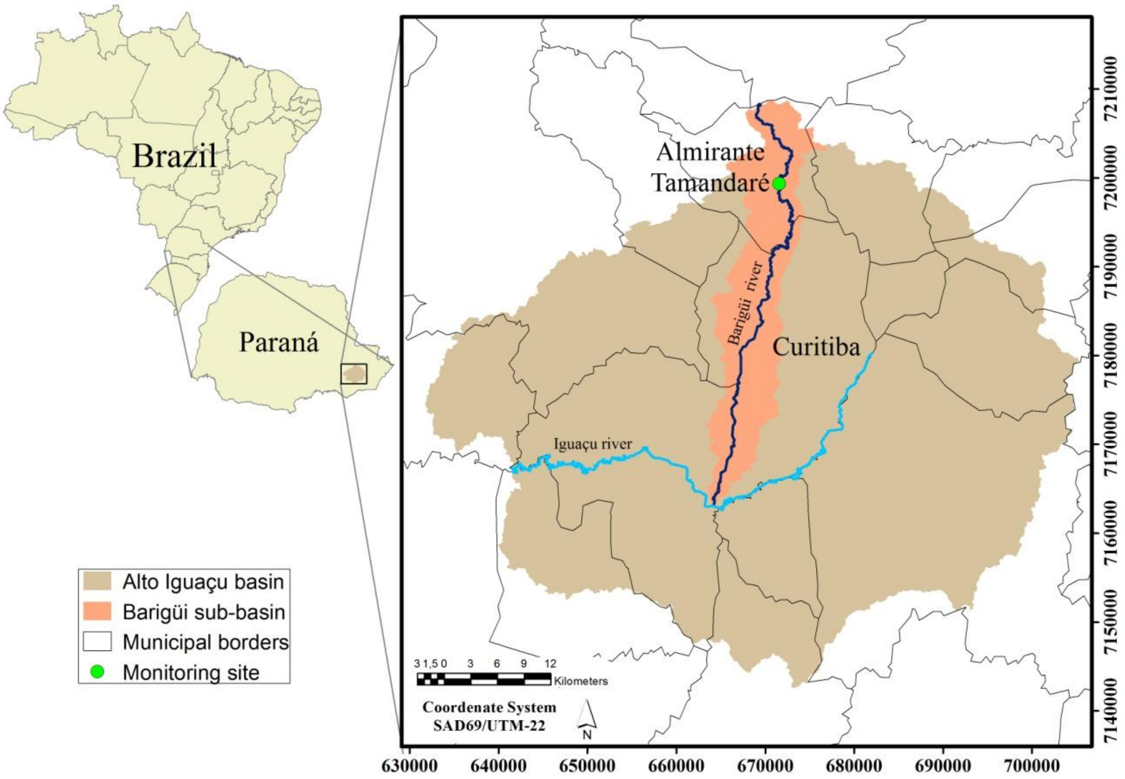


Figure 17 - Location of monitoring site at Barigui River Watershed

(Source: adapted from Dec, 2016)

Figure 18 - Location of monitoring site in Almirante Tamandaré (PR)

This site was chosen by the existence of a monitoring automatic pluviometric station installed in urban area of Almirante Tamandaré city (coordinates 25°18,7720 S; 49° 17,7412 O), called BA01. According to Gonçalves (2008), BA01 is located in the Guabirotuba formation, at First Paraná Plateau, over precambrian rocks; soil type is Cambisol Ca5, strong hillslop and clayey texture. The drainage area in monitoring site is about 60,9 km², from which only 10% are in urban zone (Gonçalves, 2008; Braga, 2013). The land use and soil occupation in BA01 is classified as mixed use, where agricultural activities and other soil uses live together, in properties scale (SUDERHSA, 2007).

Braga (2013) and Gonçalves (2008) shows some features of this area that are relevant to understand the choice of this site as monitoring point, like: proximity to Curitiba; the river is located in limestone land with mining and agricultural activities (~0,11 km² of permanent culture and ~3,48 km² of temporary culture); the degradation level increasing downstream Curitiba; inexistence of registered industries or sanitary landfill;

3.2. Automatic Sampler

For this study it was used an ISCO automatic sampler, commanded by a waterlog H500-XL Logger which was programmed to works as SBN, the intelligent automatic sampler development by Braga (2013) (Figure 19). The SBN is an instrument composed by microprocessor control unit; bottles for samples storage; pumping station, and flux distributor system. Some characteristics make SBN an innovative instrument which can be used easily, as: ability to read the column water level; low energy consumption (10 days of independence with 7Ah battery), capacity for 24 bottles of 1 liter and low fabrications cost. Figure 20 show ISCO under SBN adaptation and SBN schematic representation into the river.

SBN was chosen for ability to interpret water level variation in real time in order to take the best sampling approach for different events, as studied in Braga (2013). Although a fully operational SBN sampler was not available for this work (the equipment is being developed at LME – Eletronic Monitor Laboratory at DHS-UFPR). The operational capacities were set using a fully programmable datalogger, an Isco sampler and a specially built interface that turns the IscoSampler into a slice of the Programmable Logger, as Braga (2013) did.

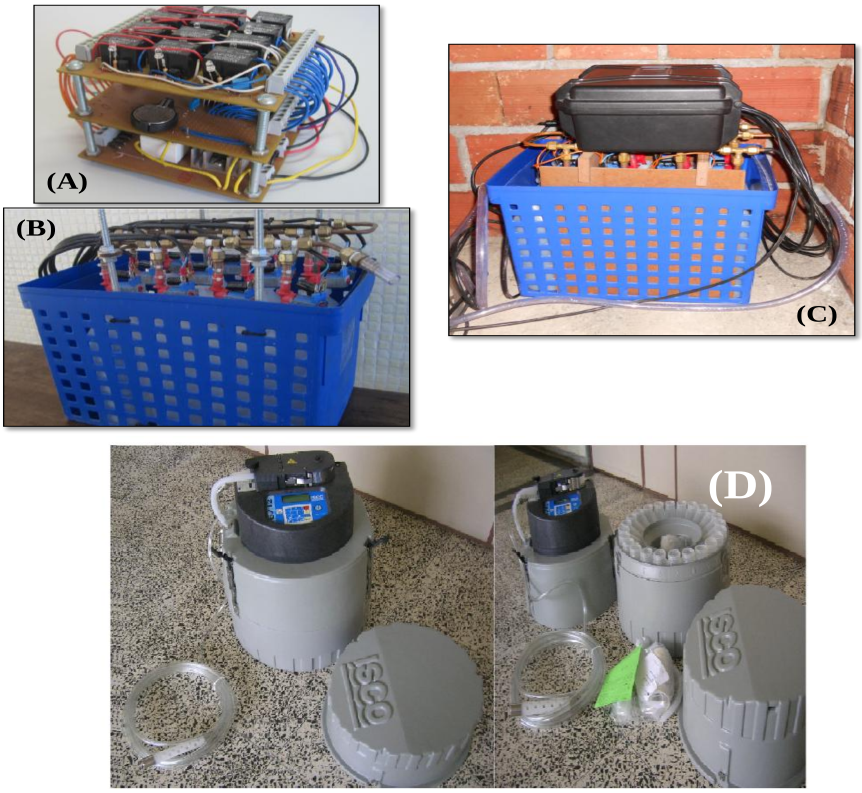


Figure 19 – Intelligent automatic sampler SBN: (a) unity of command; (b) set of sample bottles; (c) SBN installed in monitoring site; (d) automatic sampler ISCO with SBN interface

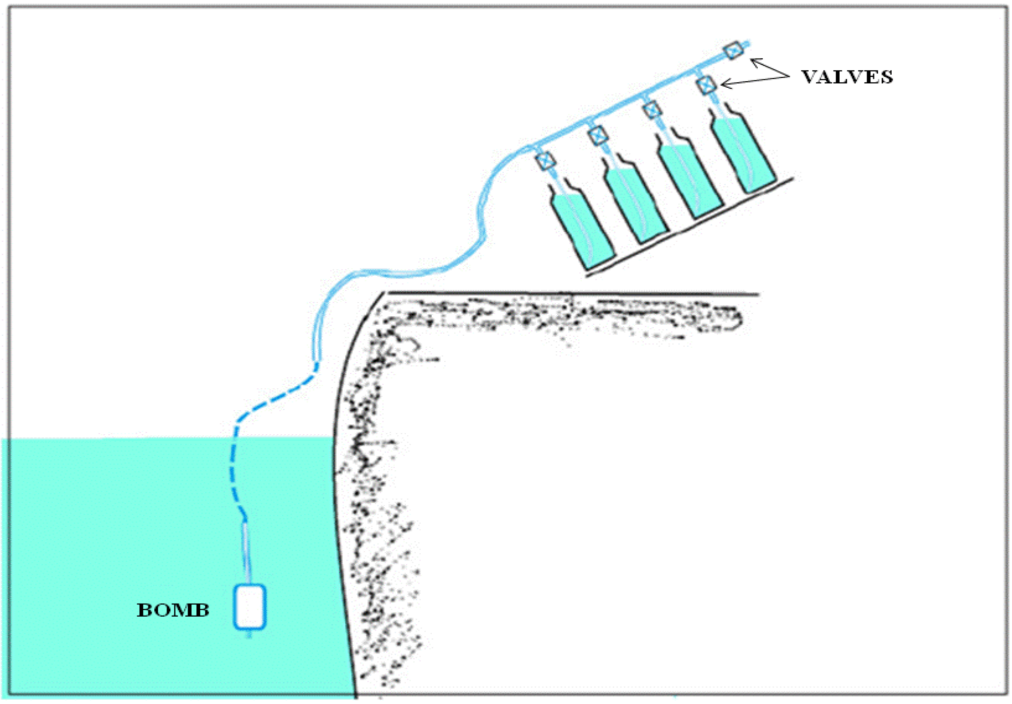


Figure 20 - SBN schematic representation

(Source: Braga, 2013)

For now, when is mention SBN refers to this arrangement in which an intelligent sampling program, developed for SBN instrument, was executed in the datalogger, which commanded the actions of an ISCO Sampler, in order to produce a good collection of diffuse pollution events properly sampled. Figure 21 presents the logical operational scheme of SBN, a program to performed that scheme was developed for waterlog H500-XL Logger, which is logger of Almirante Tamandaré hydrological station. Figure 22 shown SBN installation scheme in Almirante Tamandaré/PR.

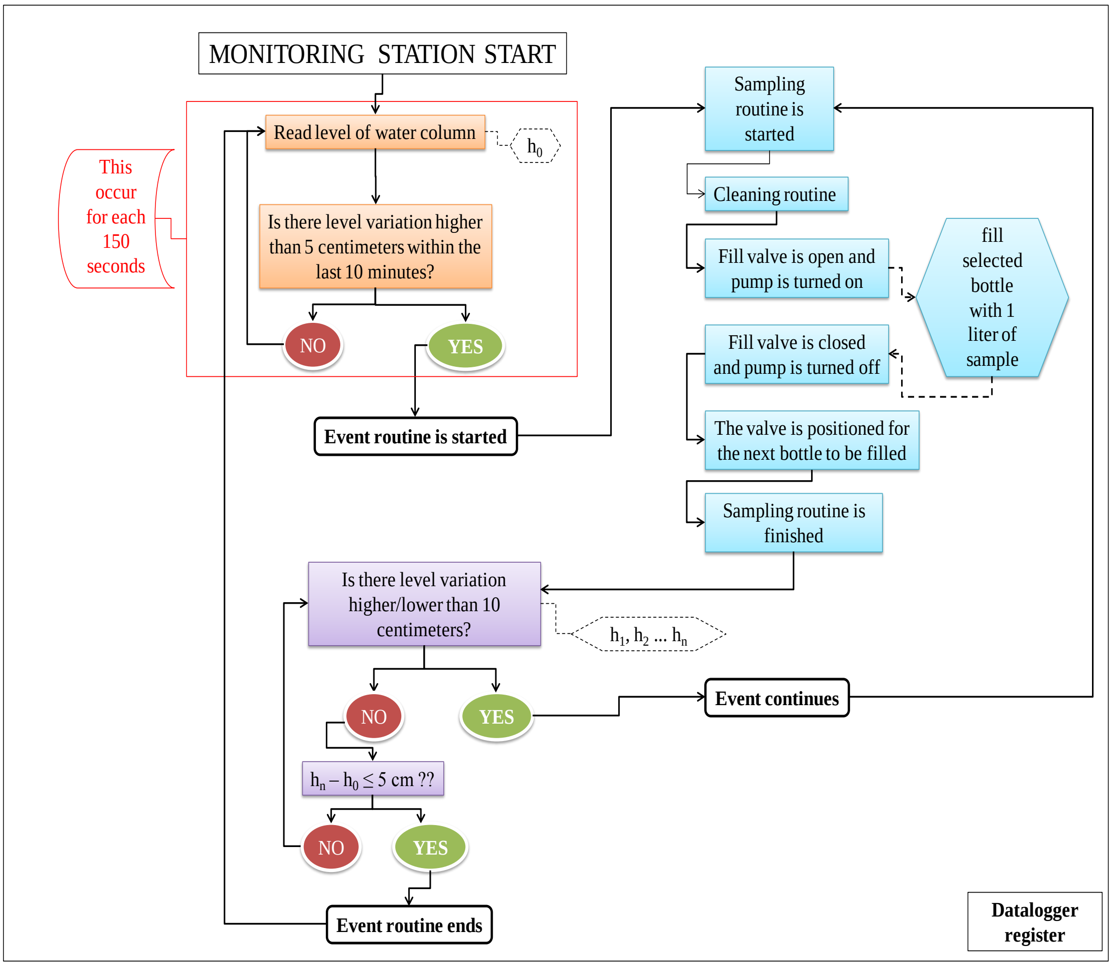


Figure 21 - Operation scheme of SBN

Considering the study of Almirante Tamandaré monitoring site, the initial detection baseline was set at five centimeters (5 cm) variation, happened in a maximum range of 10 minutes (four datalogger readings) (Braga, 2013). A comparison routine starts to analyze the behavior of water levels at the monitoring site. The comparison happens with the new and old readings of the water column. If the difference has more than 5 cm within 10 minutes, the program will be start the pumping routine (elevation detection) and the same will be happen if the difference has less than 10 cm (recession detection). So, for each variation of at least 10 cm in the water level, one bottle was filled with a sample.

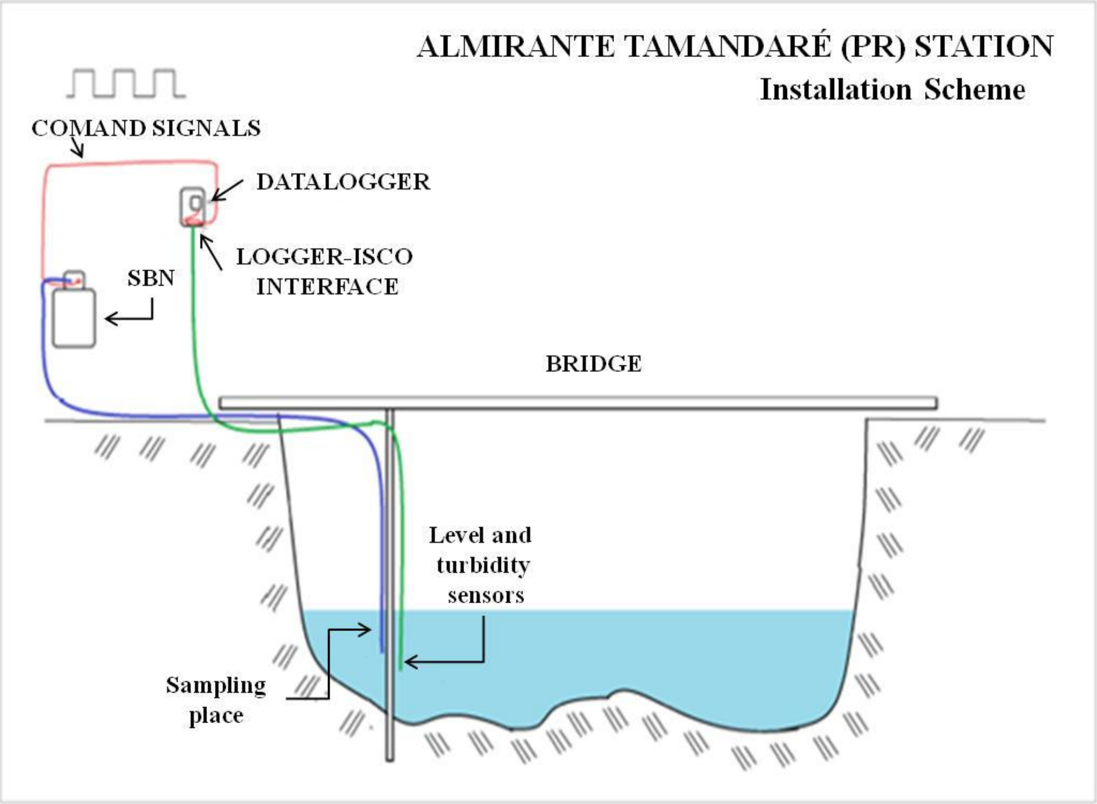


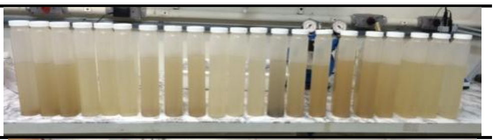
Figure 22 - SBN installation scheme in Almirante Tamandaré/PR

(Source: Braga, 2013)

The samples pumped were stored in polyethylene bottle with capacity for one liter (1 L). It was constantly opened during the pumping and after that. The discharge pump produced pressure for filling the bottles. The water level was read every 150 seconds by the logger, and then commands the pumping routine, if necessary. When the event finishes and if all bottles are filled, the SBN is programmed to stop pumping more samples, but the datalogger continues saving the station information.

This study started on February 19, 2015 and finished on May 11, 2015 registering 7 campaigns with 9 precipitation events identified by SBN. It has to be mentioned, that the first campaign was carried out using the ISCO sampler with a normal temporized sampling, configured to sample each 4 hours until filled all 24 bottles. The others campaigns occurred with SBN by intelligent sampling (according Figure 21). Additionally was performed a manual campaigns on February 19, 2015 that represents baseline river conditions. This campaign occurred collecting manually samples in each hour, during 8 hour. The Table 4 shows the information about the precipitation events registered by the station and studied in this research also the respective photos for each collecting of samplings.

Table 4 - Information about the precipitation events sampling by SBN studied in this thesis

Sampling	Number of bottles sampling	Number of events sampling	Photos
Manual	8	0	
Sbn1[(a)]	24	1	
Sbn2[(b)]	19	2	
Sbn3[(b)]	24	2	
Sbn4[(b)]	11	0	-
Sbn5[(b)]	6	0	-
Sbn6[(b)]	21	2	
Sbn7[(b)]	21	2	

(a) Temporized sampling
(b) Intelligent sampling

For each sample, analytical procedures in laboratory were performed to determine the water quality during the precipitation events, according determined for APHA (1998).

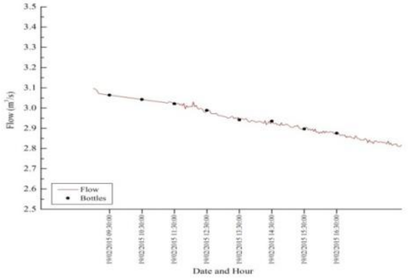
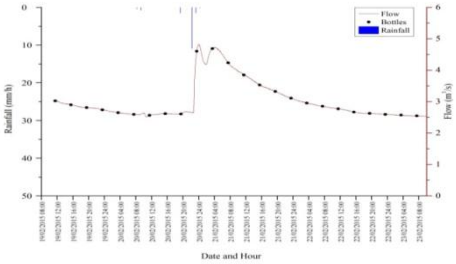
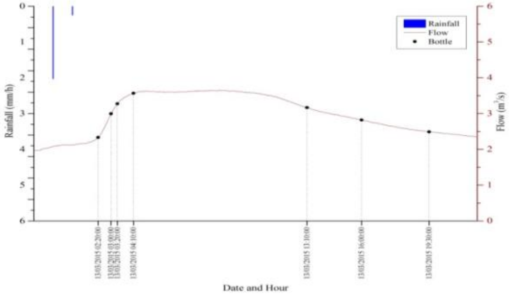
The datalloger registers the water levels (cm). This information was converted to flow using the Barigui River key-curve (6) (Fill et al., 2002)

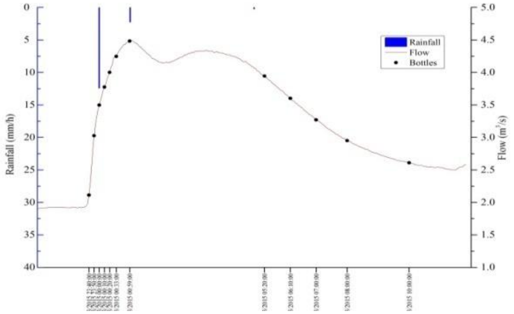
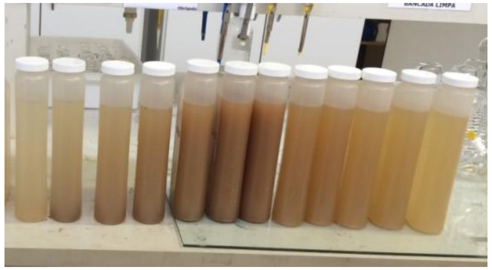
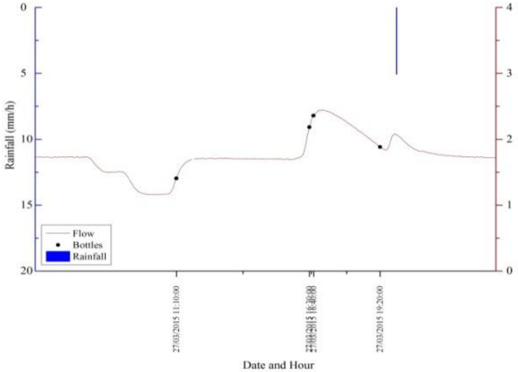
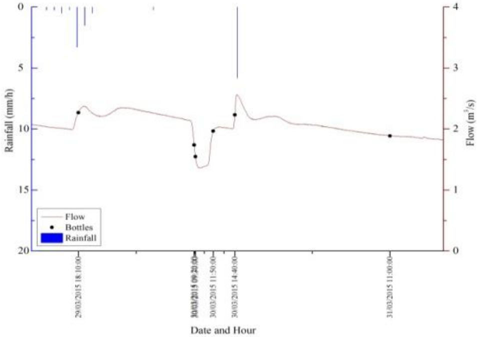
$$\mathbf{Q = 3.1517 * (h + 0.07941)^{1.0907}} \tag{6}$$

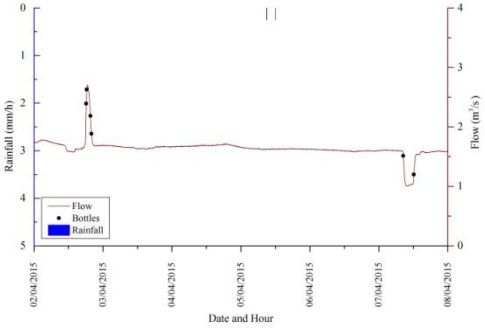
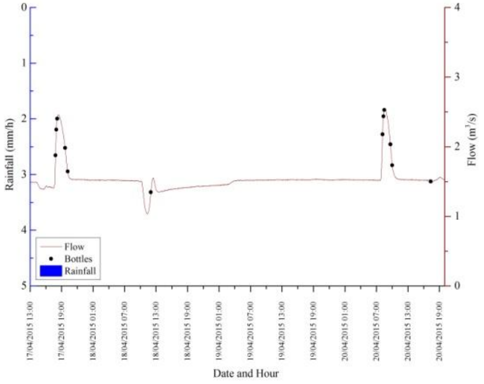
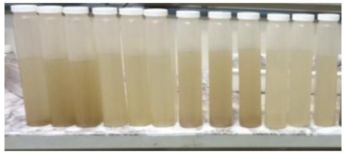
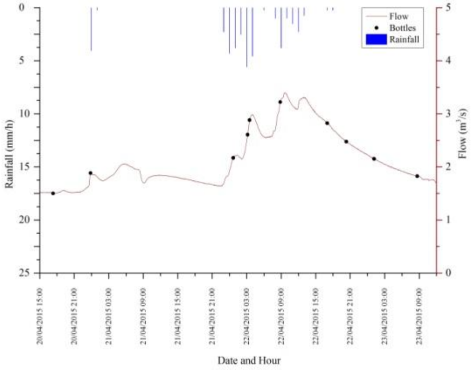
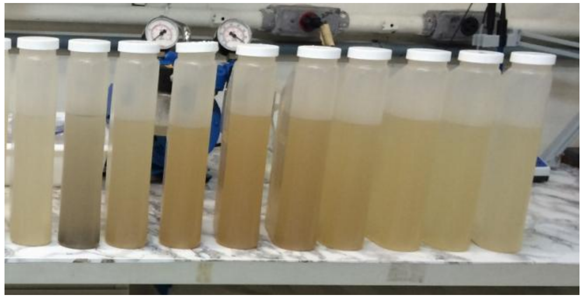
where: Q – flow (m^3 s^{-1}); h – level of water column (m).

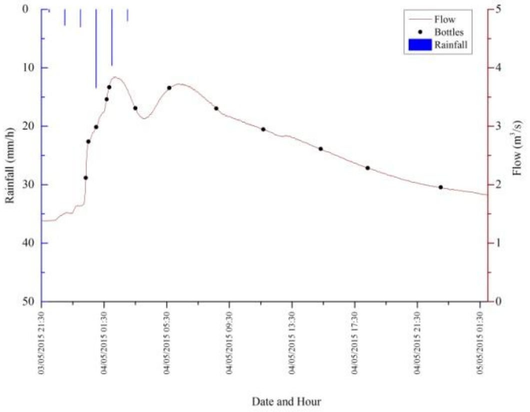
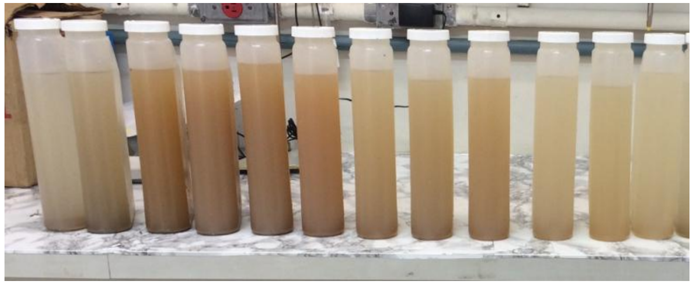
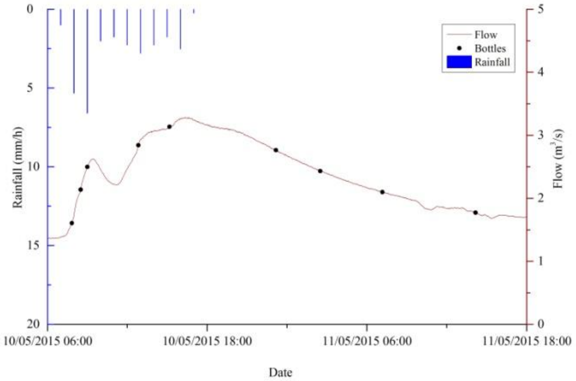
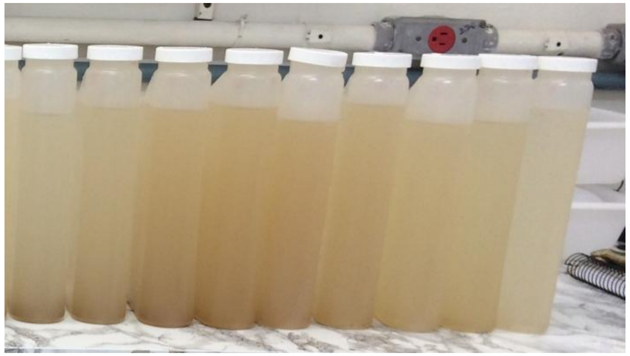
Events were divided in categories: Baseline corresponds to manual sampling. Temporized event consist in sampling according time index. These events did not respond to rain influences. Events collected with equipment operating as intelligent automatic equipment, it responds to rain influences. In other words, when rain happens and origin superficial runoff, this water amount is discharge into the river, causing changes in water column level. Diffuse pollution event are sampled when occurred this significantly changes by rain influence. Special events are sampled with differences in water column level in a river but without rain presence. It can be classified as illegal water sink or water discharge, or these differences can be due rain upstream of monitoring site. Table 5, as follows, summarizes all events in the period, their classifications, the hydrograph and respective photo.

Table 5 - Event performed classified according their characteristics

Campaign	Event	Characteristic	Hydrograph	Picture
Manual	Manual	Baseline		
SBN 1	Test	Temporized		
SBN 2	1	Diffuse Pollution		

SBN 2 + SBN 3	2	Diffuse Pollution		
SBN 4	5	Water Sink / Discharge		* no information
SBN 4	6	Water Sink / Discharge		*no information

SBN 5	7	Water Sink / Discharge		*no information
SBN 6	8	Water Sink / Discharge		
SBN 6	9	Diffuse Pollution		

SBN 7	10	Diffuse Pollution		
SBN 7	11	Diffuse Pollution		

3.3. Water Quality Analysis

After identification of a precipitation event samples were collected in field and transported to Francisco Borsari Neto Environmental Engineering Laboratory (LABEAM) for the analytical procedures. Parameters, such as conductivity (µS/cm), turbidity (NTU), temperature (°C), dissolved oxygen (DO) and pH were determined using in situ analyzes (as shown in Table 6). This measurements were made in laboratory, after sample collection in the field. Parameters analyzed in laboratory were: chemical oxygen demand (COD), total nitrogen (TN), nitrite (N-NO_2^-), nitrate (N-NO_3^-), ammonia nitrogen (N-NH_3), total phosphorus (TP), alkalinity, dissolved organic carbon (DOC), total solids (TS) and their fractions (fixed total solids – FTS and volatile total solids – VTS) and suspended solids (SS) and their fractions (fixed suspended solids – FSS and volatile suspended solids – VSS). Methods to determine water quality parameters are show in Table 7.

Table 6 - Equipment details

Parameters	Equipment	Details
Conductivity	Q795P - Quimis	- Range: entre 0,0 e 19.999 µS - Accuracy: ± 1%
Turbidity	2100Q - Hach	- Range: 0 to 1000 NTU; - Accuracy: ± 2% of readingplus stray light;
Dissolved Oxygen	LDO101 – Hach	- Range: 0.1 to 20.0 mg/L (1 to 200% of saturation); - Accuracy: ± 0.1 mg/L for 0 to 8 mg/L and ± 0.2 mg/L for greater than 8 mg/L.
pH	QX 1500 pH/mV com RS232	- Range: -2.0 to 20 pH/ ± 1800 mV - Accuracy: ± 0,002 pH/ ±0,2 mV or 0,05%
Temperature	Hach	- Range: -10.0 to 110.0; - Accuracy: ± 0.3 ºC (± 0.54 F)

Table 7 - Analytical procedures to determinate the water quality parameters in laboratory

Parameter	Method	Range	Reference
COD*	5220 D: closed reflux, titrimetric method	420 nm: 0 – 90 mgO_2/L 600nm: 100 – 900 mgO_2/L	Adapted from APHA (1998)
TN	4500-N. C: persufalte method follow 4500-NO_3^-. E: cadmium reduction method	< 2.9 mg N/L 0.01 – 1 mg NO_3^- -N/L	APHA (1998)
N-NO_2^-	4500-NO_2^-. B: colorimetric method	10 – 1000 µg NO_2^- -N/L	APHA (1998)
N-NO_3^-	4500-NO_3^-. E: cadmium reduction method	0.01 – 1 mg NO_3^- -N/L	APHA (1998)
N-NH_3	4500 – NH_3 F: phenate method	10 – 2000 µg/L	APHA (1998)
DOC	5310 B: high-temperature combustion method	1 – 50 mg/L	APHA (1998)
TP	acid digestion method 4500-P. E: ascorbic acid method	> 10 µg P/L	Proposed Method APHA (1998)
TS	2540 B: total solids dried at 103º-105ºC	< 200 mg	APHA (1998)
FS and VS	2540 E: fixed and volatile solids ignited at 550ºC	< 200 mg	APHA (1998)
Alkalinity	2320 A: titrimetric method	In the range of 10 – 500 mg/L, it is accepted a standard deviation of 1 mg/L of CaCO3	APHA (1998)

* Method adapted from APHA (1998)

For COD determination was performed an adaptation in analytical procedure from APHA (1998). The adaptation consists to use 2 mL of sample, digestion solution and catalytic solution, in order to minimize residuals to disposal. Other steps are similar to proposed for APHA (1998).

Some difficulties were found during the phosphorus analyses. At the first moment, the procedure used was based on alkalinity digestion followed by ascorbic acid method proposed for APHA (1998). Until third campaign this method show low phosphorus concentration in samples, getting harder to determinate concentration precisely. After some tests, were proposed a hypothesis: the pH values of the samples could becomes determining factor in phosphorus analytical procedure. Due to the characteristic of study area, samples had pH more alkaline, and when submitted to alkaline digestion interferes on phosphorus concentration. Therefore, another type of digestion was proposed to determine this parameter with more precision: acid digestion (procedure details and comments in Appendix 1). Water quality parameters performed in this research are summarized in Table 8.

Table 8 – Parameters performed in thesis

Water Quality Parameters	Events										
	Baseline		Diffuse Pollution Events					Special Events			
	Baseline	Temporized	1	2	9	10	11	5	6	7	8
NB	8	24	7	17	9	12	9	4	3	6	12
Cond	✓	✓	✓	✓	✓	✓	✓	✓	✓	✗	✓
Alka	✗	✗	✓	✓	✓	✓	✓	✓	✓	✗	✓
Temp	✓	✓	✓	✓	✓	✓	✓	✓	✓	✗	✓
pH	✓	✓	✓	✓	✓	✓	✓	✓	✓	✗	✓
DO	✓	✓	✓	✓	✓	✓	✓	✓	✓	✗	✓
DOC	✓	✓	✓	✓	✓	✓	✓	✗	✓	✓	✓
COD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
TN	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
NH_4^+	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
NO_2^-	✓	✓	✓	✓	✓	✓	✓	✗	✗	✓	✓
NO_3^-	✗	✗	✗	✗	✓	✓	✓	✗	✗	✓	✓
TP	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Turb	✓	✓	✓	✓	✓	✓	✓	✓	✓	✗	✓
TS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
FTS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VTS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
SS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
FSS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VSS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

NB - number of bottles; Cond – conductivity (µS/cm); Alka – alkalinity (mg $CaCO_3$/L); Temp – temperature (°C); DO (mg/L); DOC (mg C/L); COD (mg O_2/L); TN (mg N/L); NH_4^+ - nitrogen ammonia (µg/L); NO_2^- - nitrite (µg/L); NO_3^- - nitrate (µg/L); TP (mg P/L); Turb – turbidity (NTU); TS (FTS:VTS) and SS (FSS:VSS) (mg/L).

3.3.1. Detection and Quantification Limits

Detection and quantification limits were performed according to proposed by INMETRO (2010): Accreditation Manual – Guidance to methods validations.

Detection Limit (DL)

Some samples are low levels of analyte (e.g.: traces elements) been important to know less value of analyte concentration that can be detected by the analytical procedure. The probability of detection does not change from zero to one when their threshold is exceeded, and can oscillate in function of the sample type. Besides, is essential to ensure that all procedures steps are included in this determination. The analytical procedure and DL should be submitted it the same unit, according to the proposed method. The index to determine DL was equation 7:

$$DL = \bar{x} + t_{(n-1,1-\propto)}.s \tag{7}$$

Where: DL is the detection limit; $\bar{x}$ is average values of white sample; t is Student distribution (is dependent of sample quantity and degrees of freedom); s is standard deviation of white samples.

Quantify Limit (QL)

QL is calibration standard with smaller concentration. The analyte concentration overall is the average value of standard samples plus five, six or ten standard deviation. The analytical procedure and DL should be submitted it the same unit, according to proposed by method. The index to determinate QL was equation 8.

$$QL = \bar{x} + 10.s \tag{8}$$

Where: QL is the quantify limit; $\bar{x}$ is the average value of standard samples and s is standard deviation of standard samples.

To measure DL and QL values, in this study, were performed: ten zero-standard samples (used to calculated average and standard deviation values), calibration curve, and two know standards with values inside the calibration curve to verify the method and procedure precision and accuracy. For the calculations were considered ten degrees of freedom and 99% of assurance. Value of *t Student* value is 2,821. Analytical procedures used was the same mentioned in Table 7. DL and QL values were calculated for equations Results are show in Table 9.

Table 9 - Detection and Quantification Limits

Water quality parameter	Average (x)	Standard deviation (s)	DL	QL	Standard proposed	Standard found
Nitrite	0,0020	0,0003	0,79	1,63	30 70	29,76 78,48
Nitrate	0,0178	0,0007	6,07	8,51	150 650	162,86 697,09
N-ammonia	0,0289	0,0010	10,04	16,59	150 550	144,98 539,8
TP	0,0056	0,0001	0,20	8,30	35 120	41 119
COD	0,4210	0,0061	0,44	4,35	20 62,5	19,32 60,52

Nitrite (µg/L); Nitrate (µg/L); Nitrogen Ammonia (µg/L); TP (mg/L); COD (mg/L)

The standard deviation calculated indicate samples and method representative, because the low values. DL indicates that below values calculated is impossible quantify concentration in the sample. Thus, QL indicates that below values calculated is possible affirm concentration existence but without quantify the real concentration value. Finally, the standard found had close values according to standard proposed.

3.4. Summary of the Chapter

In this chapter the data from monitoring site is presented, as well as the intelligent automatic sampler used (SBN, Braga, 2013) and the analytical procedures used to determine water quality parameters during the rainfall events. The use of automatic sampler has been an innovation in terms of water quality monitoring, used in several studies (Yu et al 2016; Chen et al 2015; Ramos et al 2015; Etheridge et al 2015; Gao et al 2014; Fellman et al 2009; Li et al 2008; Buck et al 2004).

Some of them use high-frequency monitoring with in situ loggers, as in Chittor Viswanathan et al (2015) measured electrical conductivity, water temperature, pH, pressure and DO at 15 minutes of intervals. Using the same concepts, Moraetis et al (2010) prepared monitoring site with telemetric gauge station sending information about pH, nitrate, temperature, DO, river stage and lever with 5 minutes of interval. Etheridge et al (2015) fuse a portable UV-Vis spectrometer with multi parameter probe to measure salinity, dissolved organic matter, total phosphorus, nitrite (and others) in a interval of 15 minutes. Also, Darwiche-Criado et al. (2015) used a probe to measure nitrate continuously, however they performed sample collection (with automatic samples) to measure nitrate punctually.

Furthermore, some studies were conducted with automatic sampler (automatic or not) followed by analytical procedures in laboratory. Delpla et al (2011) programmed a flow meter (ISCO 4230) to collect samples in auto sampler (ISCO 3700) and samples were stored at 4°C immediately after collections. Gao et al (2014) used a ISCO 6712 to take samples at 1 minute intervals when rainfall events and at 1 hour intervals after flow rates stabilized, and samples also were stored in refrigerator (4°C). Some studies bring similar situations with SBN performance as reported in Chen et al (2015) and Ramos et al (2015).

Chen et al (2015) used ISCO 6712 to sampling a 1 hour interval during rise and fall hydrograph, however they found limitations, reporting in some cases, sampling were started a little late because rain started at night so they missed some early rainfall events. And Ramos et al (2015) use a probe to monitor water stream level and turbidity, and automatic sampler to sampling water during rainfall. Similar to the SBN, a probe was programmed to activate the automatic sampling when the water level varied more than 10 cm on rise and fall hydrograph. After water quality parameters were measure in laboratory.

The use automatic sampler came to improve the water quality monitoring, mainly during rainfall event that out of human control (where and when will happen), but the chemistry in quality parameters is conventional, and never evolves in terms of considering a good and precise information. The chemistry in samples in this study was performed, as conventional way, to obtain general view water quality parameters during rainfall events. Concerns about sample preservation and time elapsed need to be investigated.

Chapter 4

Water Quality Analysis and Diagnosis

"Imagination is more important than knowledge. For knowledge is limited to all we now know and understand, while imagination embraces the entire world, and all there ever will be to know and understand."

— Albert Einstein

This chapter presents the main water quality results of the case study at the monitoring point P1, at Barigui River during events of precipitation sampled by SBN. Considering the amount of information obtained, the strategy here in presented, is based on event explanations with a general view about sampling performed. Each campaign is reported in detail highlighting its main peculiarities, appropriate classification, physical hydrograph correspondent and water quality parameters description.

4.1. General view of the sampling date

Figure 23 and Figure 24 shows the hydrographs that represents sampling performed, divided into two periods: between February-March and April-May. The continuous line is the flow (m^3 s^{-1}) measured from level water column using the flow discharge curve (flow-level curve); the blue line is the rainfall measured by the pluviometric station and the black points are when the SBN identified the water level change and made a sampling.

Events were classified according their characteristics as diffuse pollution event (event 1, 2, 3, 4, 9, 10 and 11) or water sinks and discharge events (campaigns 5, 6, 7 and 8).

In order to establish some reference guidance, it was defined a manual event, that represent the river baseline followed by a temporized event with SBN programmed to operate according to the pre-defined time sampling..

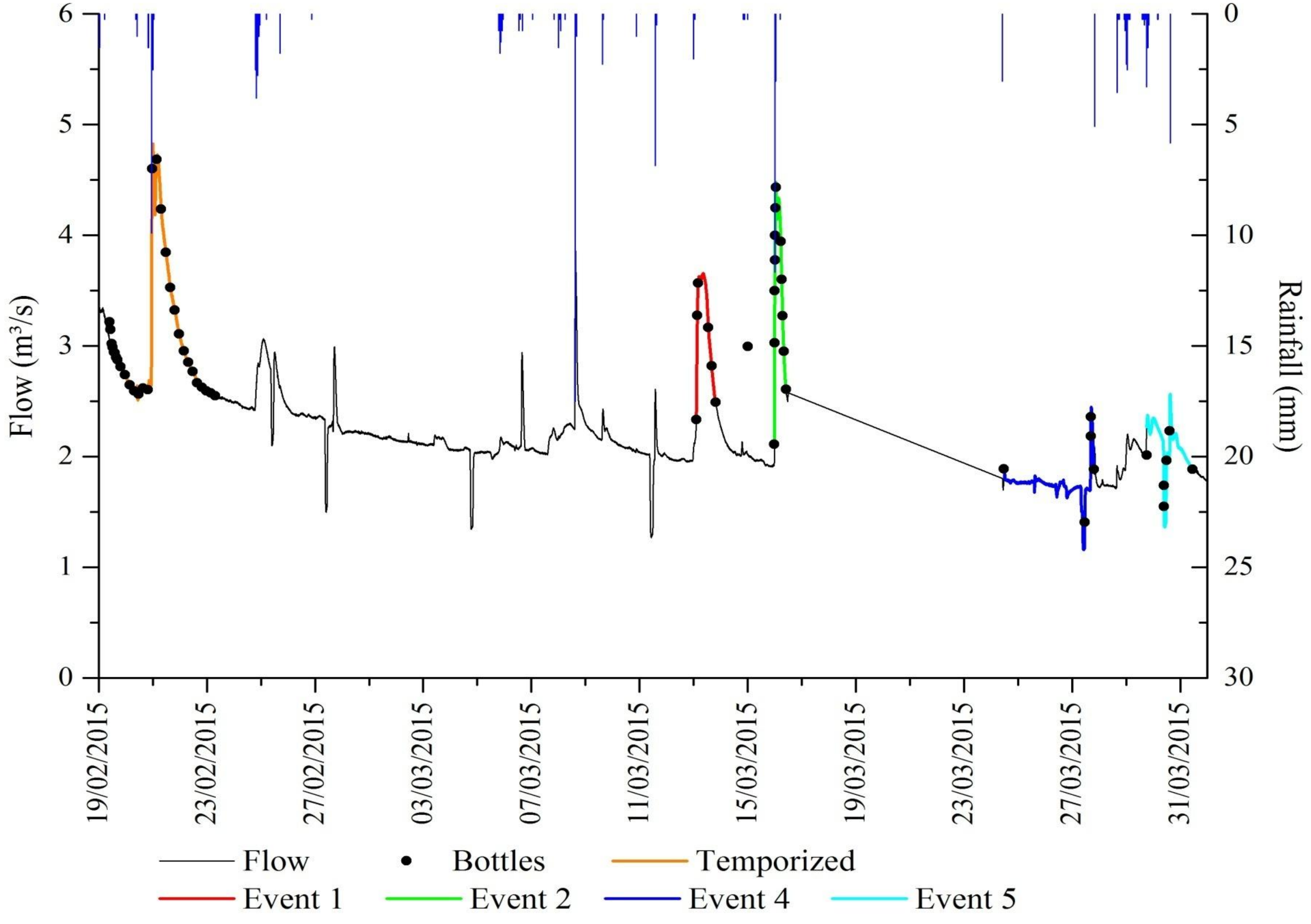


Figure 23 - Hydrograph with sampling performed between February and March

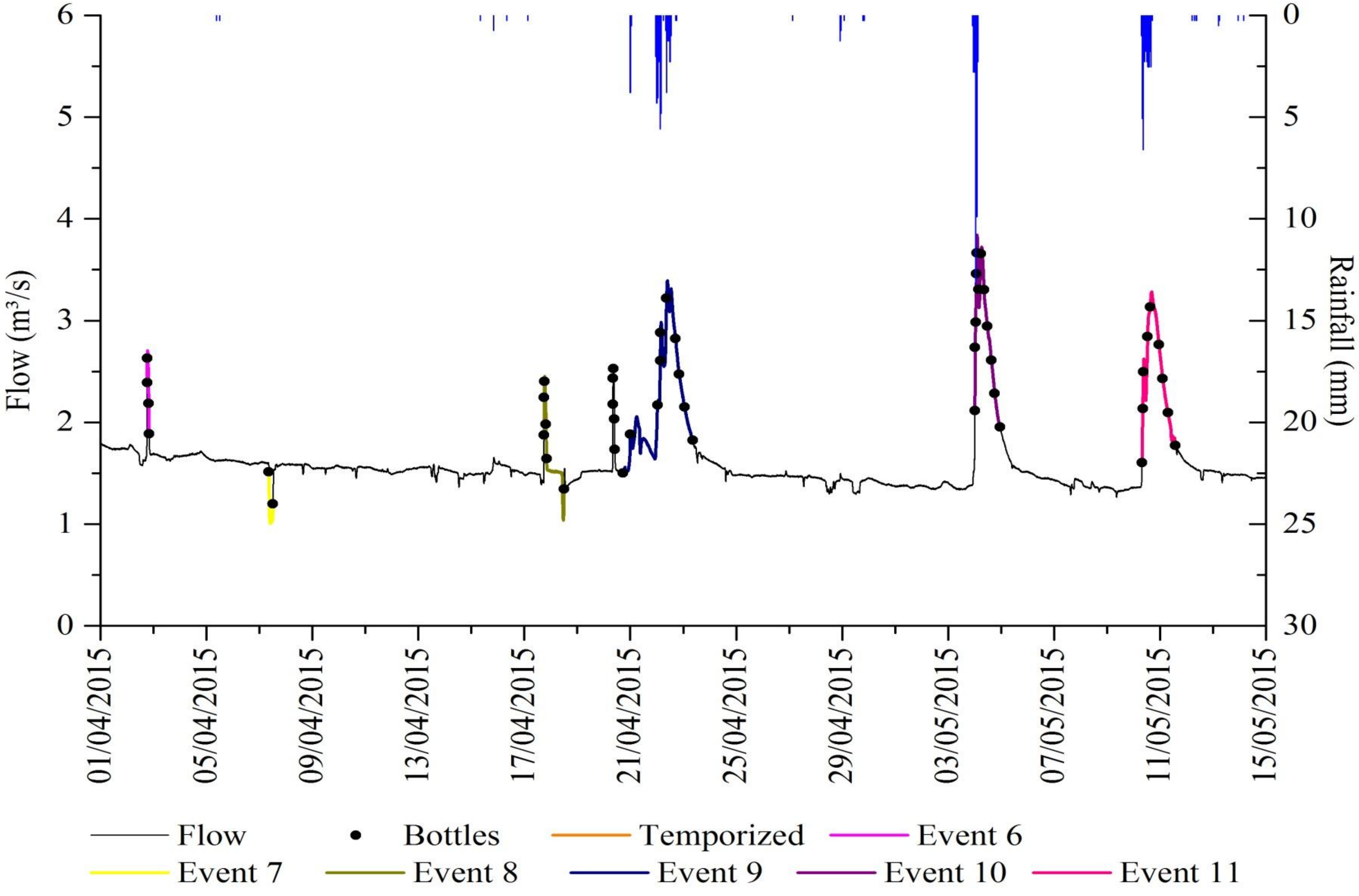


Figure 24 - Hydrograph with sampling performed between April and May

4.2. Baseline

The baseline event in February 19th was performed to simulate the traditional sampling. This event characterizes the Barigui River behavior. Before this campaign had rained, then the flow behavior was in decreasing scenario, ranging between first and last bottle sampling from 3,09 to 2,89 $m^3 s^{-1}$ in approximately 8 hours. Figure 25 shows temporized event.

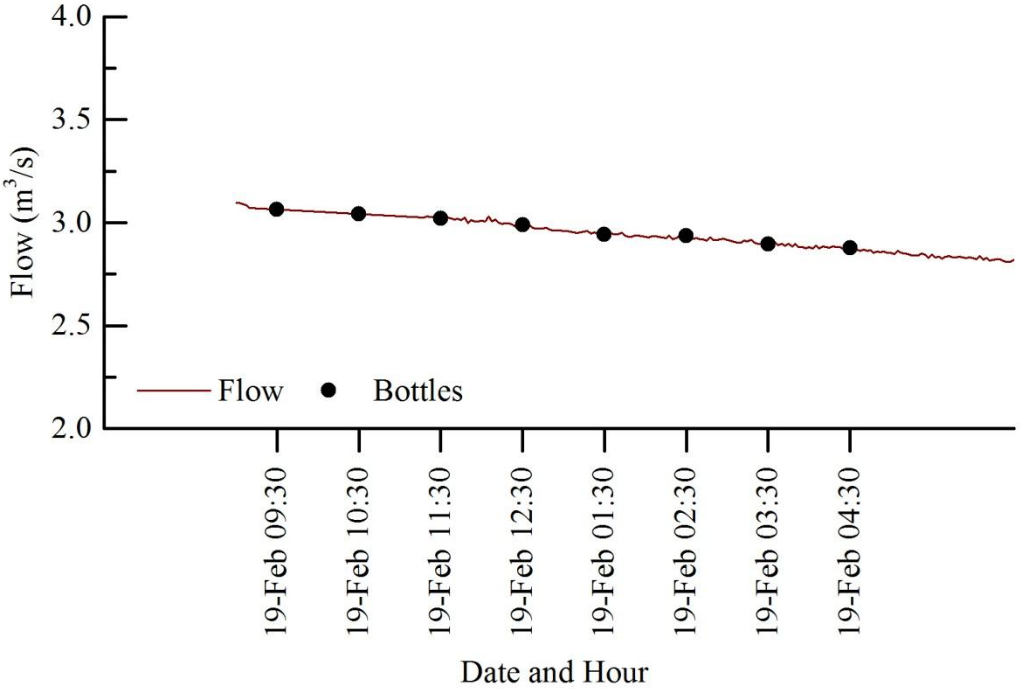


Figure 25 - Baseline event

For parameters of conductivity, pH, DO and temperature, standard deviation had not significantly values and the mean concentration for the event remained as expected. These parameters did not change influence during the day. Figure 26 shows the pollutographs for conductivity (270 ± 2.0 $\mu S\ cm^{-1}$), pH (7,79 ± 0,04), DO (7.18 $mgO_2\ L^{-1}$ ± 0.16), and temperature (20.56 ± 0.50°C), indicating a stable behavior of the system with concentration mean values concentration as expected with no significant changes during the sampling period. Clearly very oxygenated water, with more basic composition due to the geological nature of the watershed.

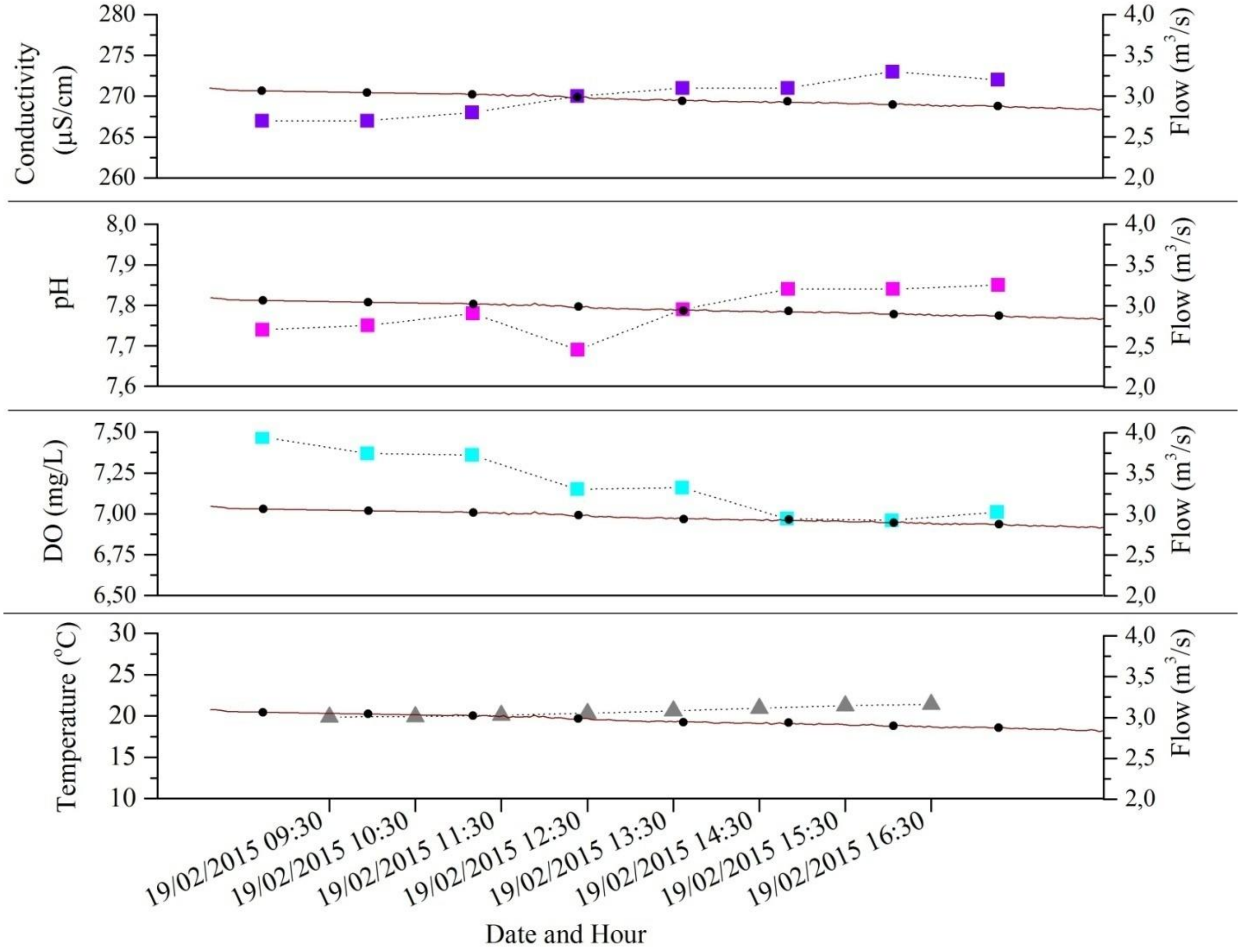


Figure 26 - Distribution of conductivity, DO, pH and temperature for baseline event

DOC, COD, TN and TP, chemical water quality parameters, had an almost linear distribution (Figure 27). DOC and COD had an average concentration about 3.23 ± 1.30 mg C L^{-1} and 6.90 ± 2.99 mgO_2 L^{-1}, respectively. For TN and TP average concentration and standard deviation was, respectively, 0.45 ± 0.06 mg N L^{-1} and 0.08 ± 0.01 mg P L^{-1}.

For the physical parameters such as TS and SS with their fractions (fixed and volatile) and turbidity indicates a more dynamic characteristics of the concentration (

Figure 28). For baseline analyses, these parameters did not have significantly changes along the day. The average concentrations and standard deviation to TS (FTS and VTS) was 164 ± 12 mg L^{-1} (143 ± 13 and 21 ±10 mg L^{-1}); For SS (FSS and VSS) was 44 ± 8 mg L^{-1} (30 ± 2 and 13 ± 6 mg L^{-1}), and turbidity as 35,59 ± 5,28 NTU.

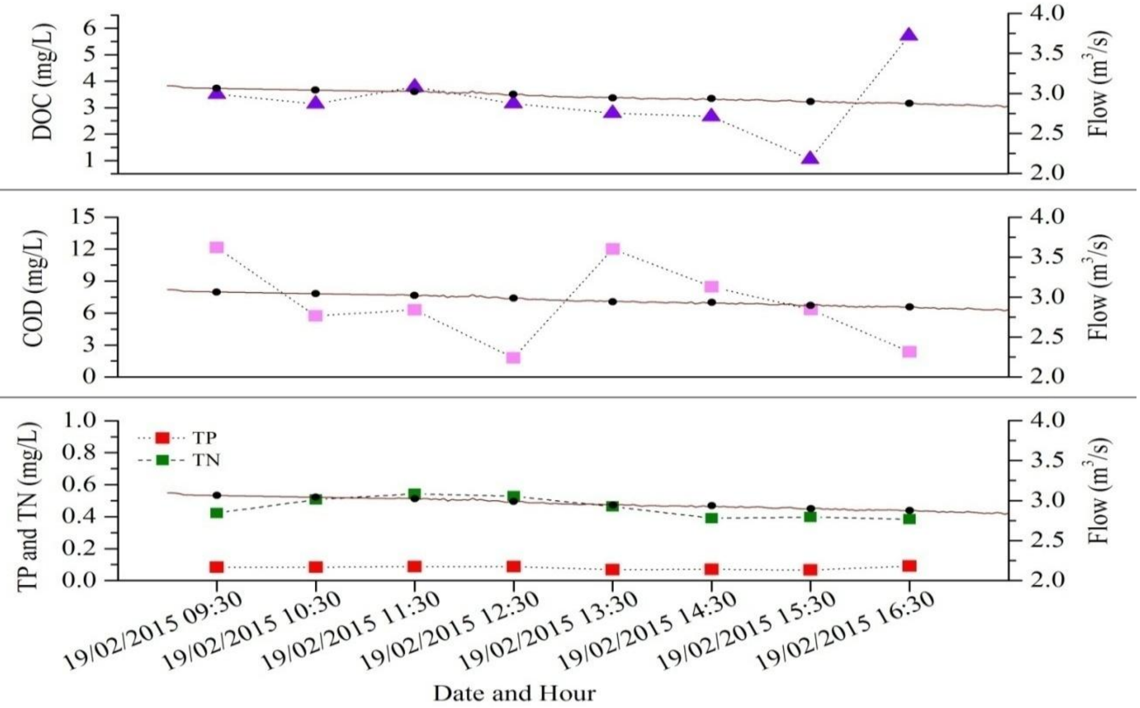


Figure 27 – Distribution of DOC, COD, TN and TP for baseline event

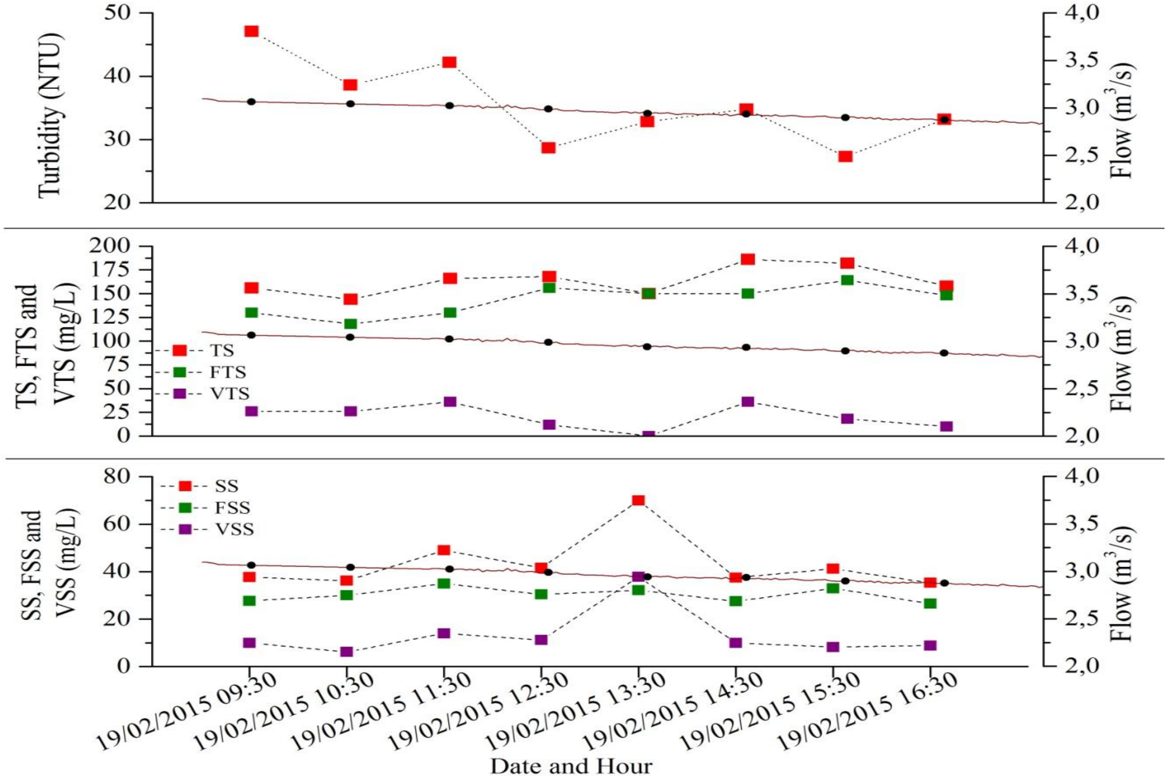


Figure 28 - Distribution of turbidity, TS (VTS and FTS), and SS (VSS and FSS) for baseline event

4.3. Temporized Event

The temporized event started on 19th February at 12:30 a.m. and finished on 23rd February at 8:30 a.m (Figure 29). This event collected 24 bottles every four hours, in order to simulate the traditional temporized sampling s presented in the literature. During this period, six rainfall events occurred. The first two, one with 0,508 mm/h and other with 0,762 mm/h, did not produce significant changes on river flow (Q ~ 2,60 m³ s^{-1}). After that, one biggest rainfall happened, that accumulated a 14,22 mm and caused a flow variation from 2,60 m³ s^{-1} to 4,82 m³ s^{-1} in 5 hours. It can be highlighted that bottles 10 and 11 represent the sampling for the event peak.

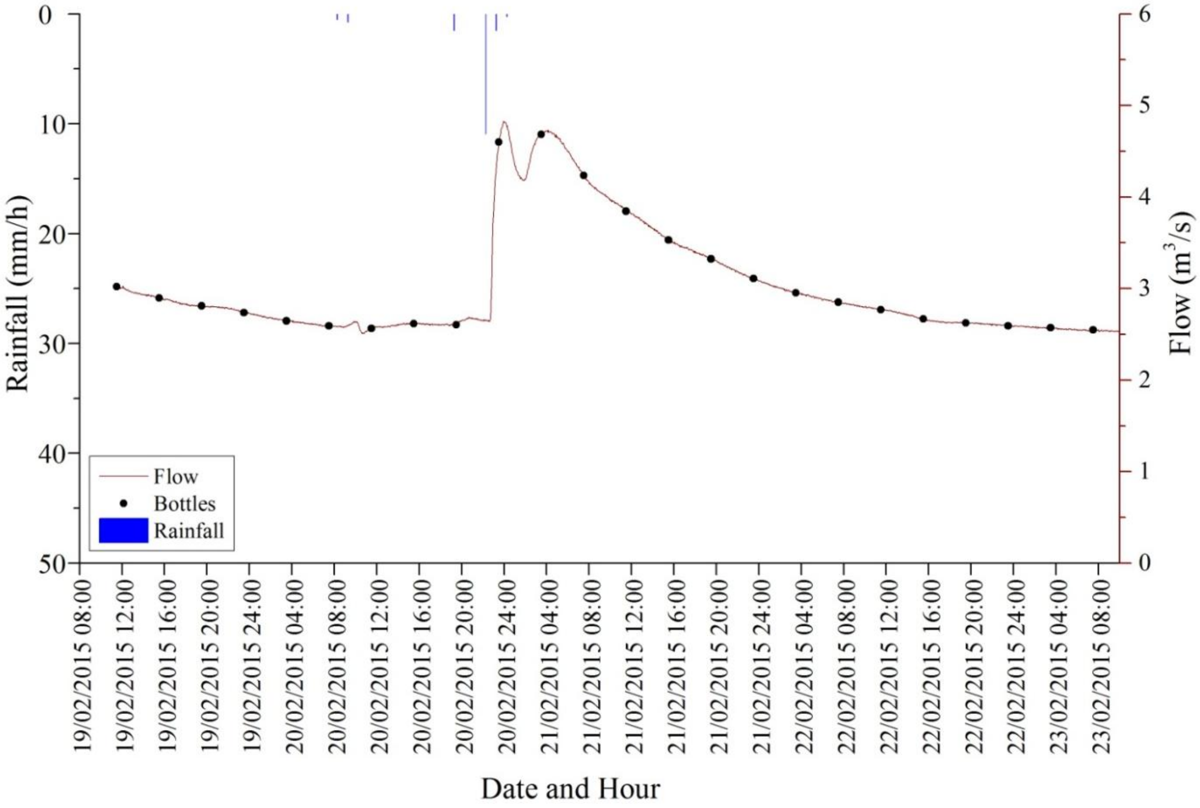


Figure 29 - Temporized event

Conductivity had decreased in concentrations in peak event bottles; this parameter started with 231 µS cm^{-1} in first bottle, decreasing to 194,1 µS cm^{-1} in bottle 10 and 190,7 µS cm^{-1} in bottle 12, then increasing again to 230 µS cm^{-1} in last bottle (24). The pH values did not have wide variation during this campaign, with slight decreasing in peak bottles, keeping always more alkaline (pH values approximately 8,0). The temperature had variation ranging from 23 to almost 25 °C. The DO concentration, had stable behavior, ranging about 7,73 ± 0,13 mgO$_2$ L^{-1}, therefore the values were always good. The average concentrations were, 221,15 ± 11,07 µS cm^{-1}, 8,08 ± 0,17 and 23,53 ± 0,73 °C, respectively for conductivity, pH and temperature. Figure 30 shows behavior of conductivity, DO, pH and temperature during temporized event.

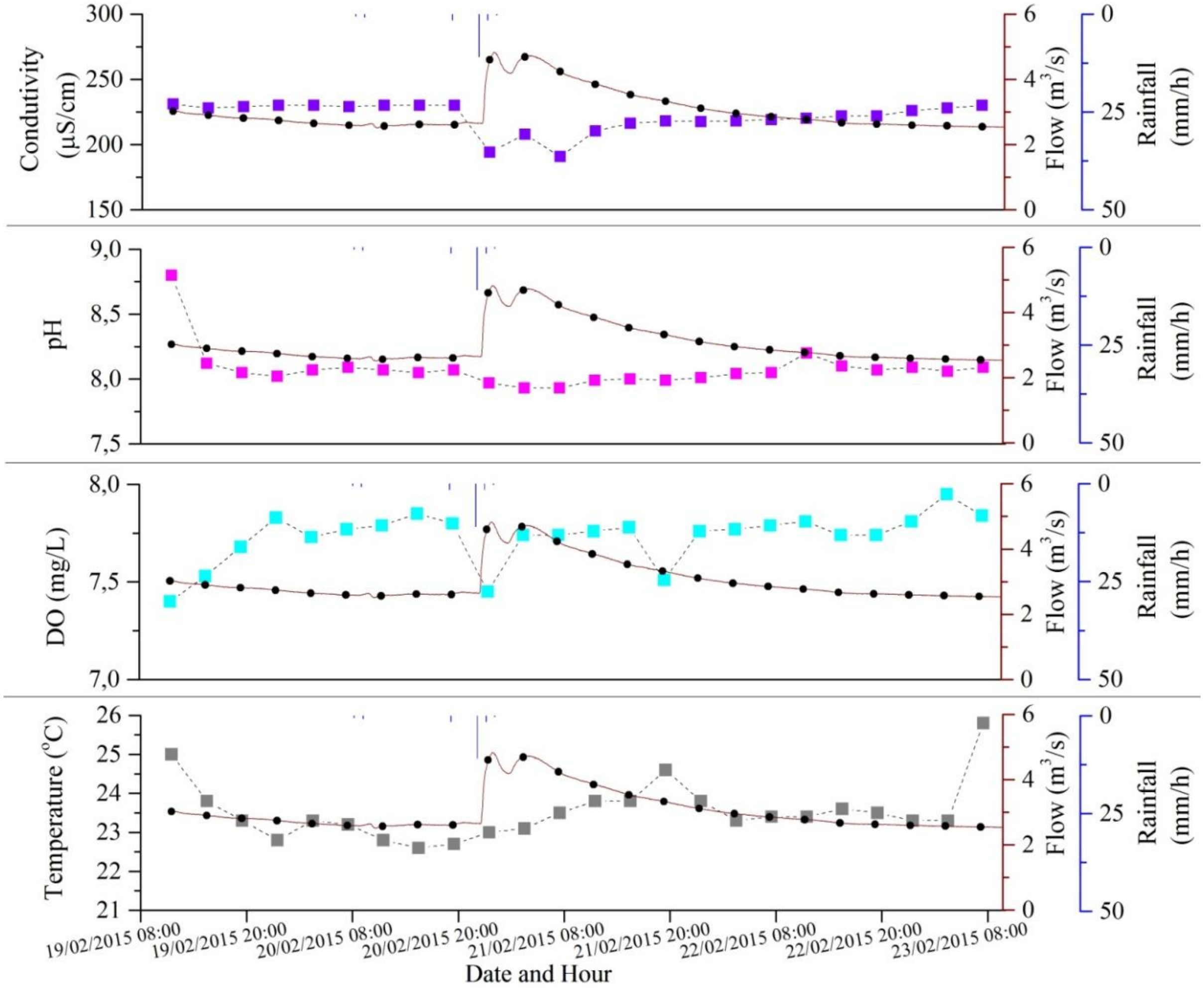


Figure 30 – Distribution of conductivity, DO, temperature and pH for temporized event

The chemical parameters, as COD, TN and TP had behavior following the dynamic of the events as can be seen in Figure 31, with increasing concentration with the flows positive increments. For all this water quality parameters bottle 10 offered the samples for the analysis, with concentration about 75,50 mgO$_2$ L^{-1} for COD, 0,58 mg N L^{-1} for TN and 0,63 mg P L^{-1} for TP.

The TP variation was wider than TN, starting in 0,08 mg P L^{-1} on first bottle, arriving to peak of hydrograph and decreasing to 0,02 mg P L^{-1} in last bottle, while the TN started in 0,50 mg N L^{-1} in first bottle, increasing to peak of hydrograph and then decreasing to 0,42 mg N L^{-1} in last bottle (24). It can be indicated that the N/P ratio is 5,1, revealing an particular interesting result with nitrogen as limiting nutrient; even that nitrogen concentration was bigger than phosphorus in all bottles (expect bottle 10). Nitrogen showed a limiting factor because is more available than phosphorus nutrient into the river ecosystem.

For DOC, the behavior was random, not following a pattern according hydrograph as others parameters. The maximum value found was 6,78 mg L^{-1} in bottle 13, after flow increase. Considering the event start and finish the values for DOC are close with 1,44 mg L^{-1} for first bottle and 1,84 mg L^{-1} for last one, possibly returning to balance. Figure 31 shows the pollutographs performed for DOC (3,19 ± 1,53 mg C L^{-1}), COD (14,26 ± 14,61 mg O_2 L^{-1}), TN (0,46 ± 0,04 mg N L^{-1}) and TP (0,09 ± 0,14 mg P L^{-1}).

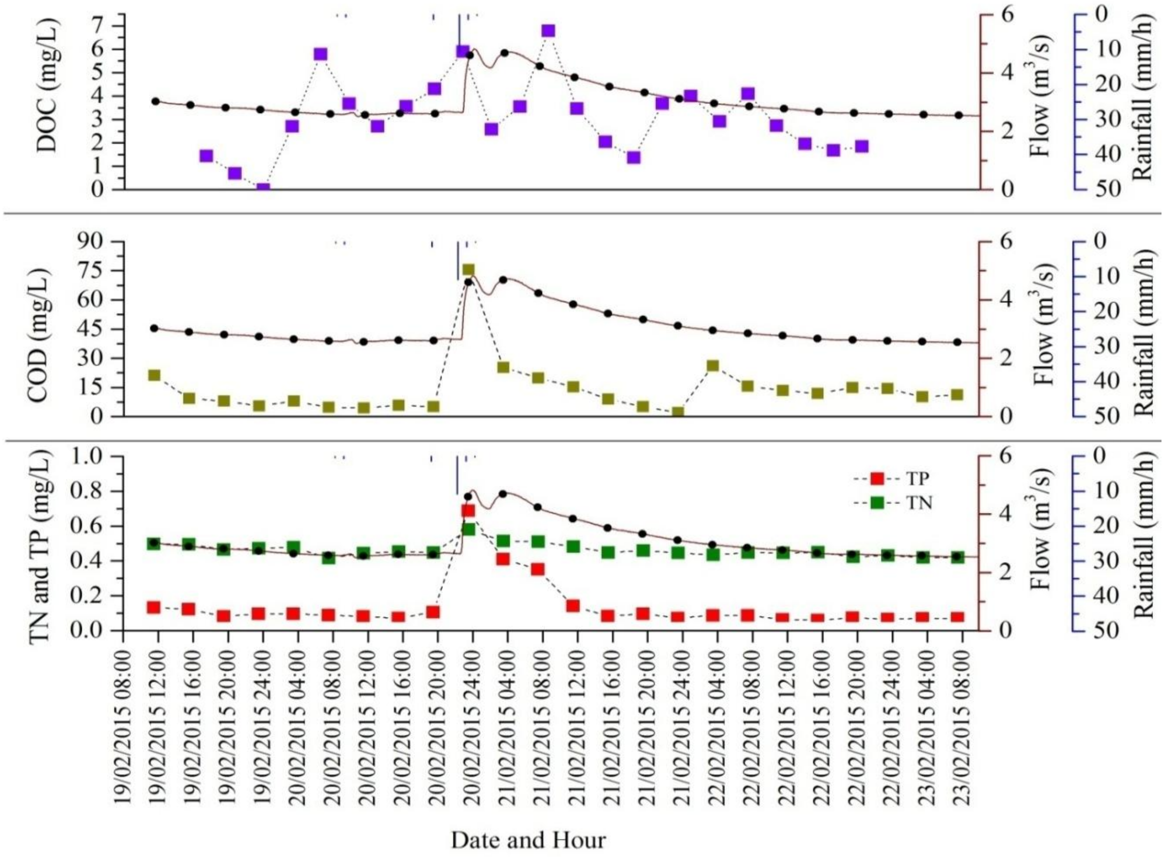


Figure 31 - Distribution of COD, TN and TP for temporized event

The physical parameters followed the hydrograph with the rainfall and flow increase. Turbidity, TS (FTS and VTS) and SS (FSS and VSS) had the concentration peak in bottle 10 with values about 1730 NTU, 2180 (1880 and 300) mg L^{-1} and 2124 (1852 and 272) mg L^{-1} respectively. The average for them was 138,35 ± 350,42 NTU for turbidity; 299 ± 408 (202 ± 362 and 98 ± 70 mg L^{-1}) for TS (FTS and VTS); and 148 ± 428 (140 ± 398 and 26 ± 59 mg L^{-1}) for SS (FSS and VSS). Turbidity, ST and SS (with their fractions) concentrations are show in Figure 32.

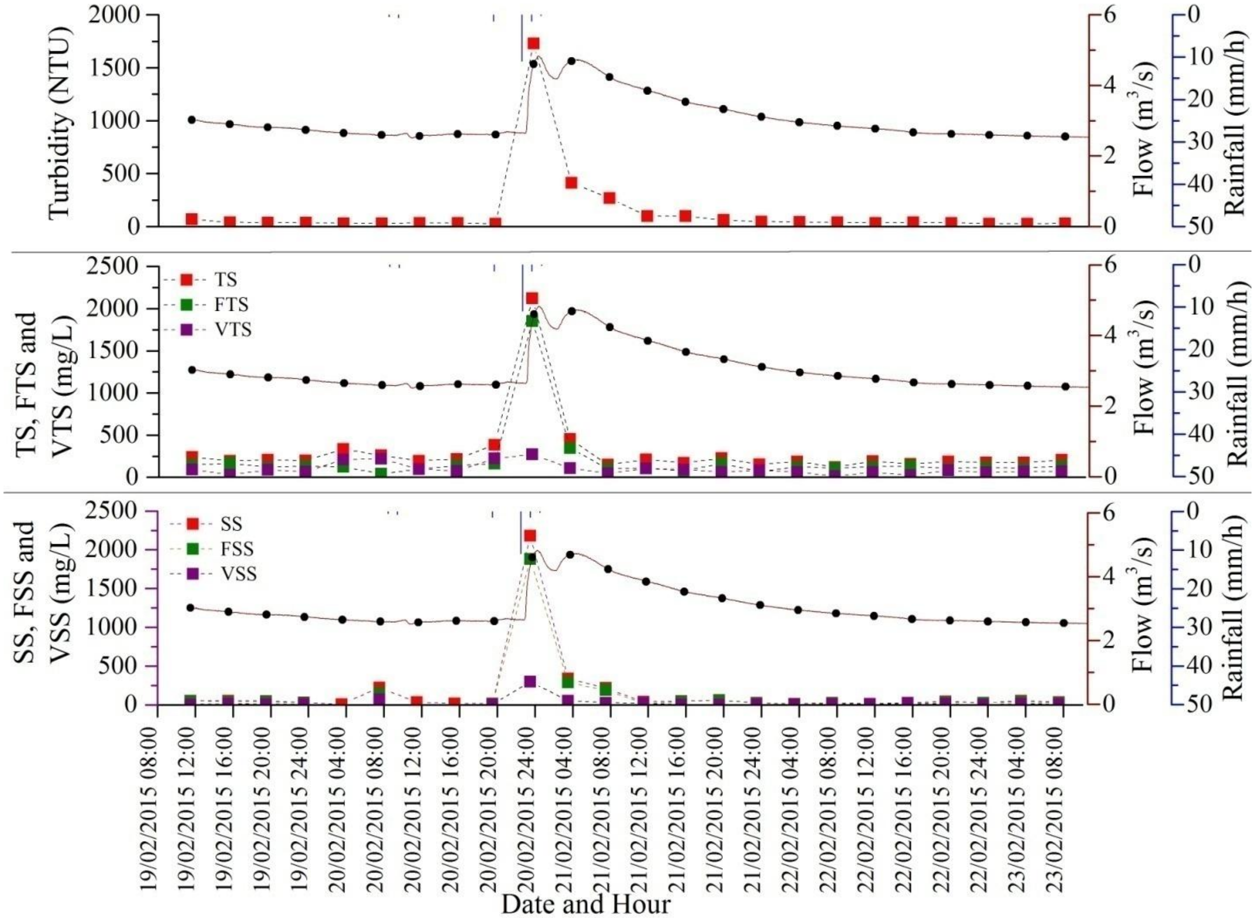


Figure 32 - Distribution of turbidity, TS (VTS and FTS), and SS (VSS and FSS) for temporized event

4.4. Diffuse Pollution Events

Diffuse pollution events are excess of precipitation which causes water runoff over the overall watershed, drained to water bodies carrying mass pollutant. In this study, events 1, 2, 9, 10 and 11, allowed to have an overlook in this aspect (see Figure 33 to Figure 54). When the soil capacity of retention and infiltration is exceeded runoff takes place and causes strong river level variation into the river. However, this water contains compounds that can produce water quality degradation or an impact from the pollution matrix with increase in pollutant loading. The pollution by diffuse sources and the results are shown next.

Table 10 indicates hydrological characteristics of the main events that were classified as diffuse sources in this research. Because of the rainfall episodes, changes in flow and water volume were observed. The hydrological characteristics reflects the event duration, maximum flow (Q_{max}), accumulated precipitation (P_{acum}), Superficial Flow volume (V_{trans}) during the event and, critical time that happened when the maximum flow was reached.

Table 10 - Hydrological characteristics of diffuse pollution events performed

Event - Hydrological Characteristics					
	1	*2*	*9*	*10*	*11*
Event Duration (h)	17,16	30,33	56,83	22,67	30,33
Q_{max} ($m^3 s^{-1}$)	3,66	4,48	3,30	3,85	3,28
P_{acum} (mm)	2,29	14,73	38,61	31,50	28,70
V_{trans} ($10^5 m^3$)	1,99	1,48	4,56	2,35	2,74
Critical Time (2015)	13/03 08:37:30	16/03 01:00:00	22/04 09:32:30	04/05 02:12:30	10/05 16:37:30

4.4.1. Event 1

The event 1 started on 13th March at 2:20 a.m. and ended in the same day at 7:30 p.m. 7 bottles were collected in 17,16 hours. The rain started on 12th March at 11:02 p.m. and after 3 hours and 17 minutes SBN equipment did the first sampling. The rain event lasted around one hour. The initial flow (before rainfall) was approximately 1,96 $m^3 s^{-1}$ and increased until 3,65 $m^3 s^{-1}$ (peak). Figure 33 represents event 1.

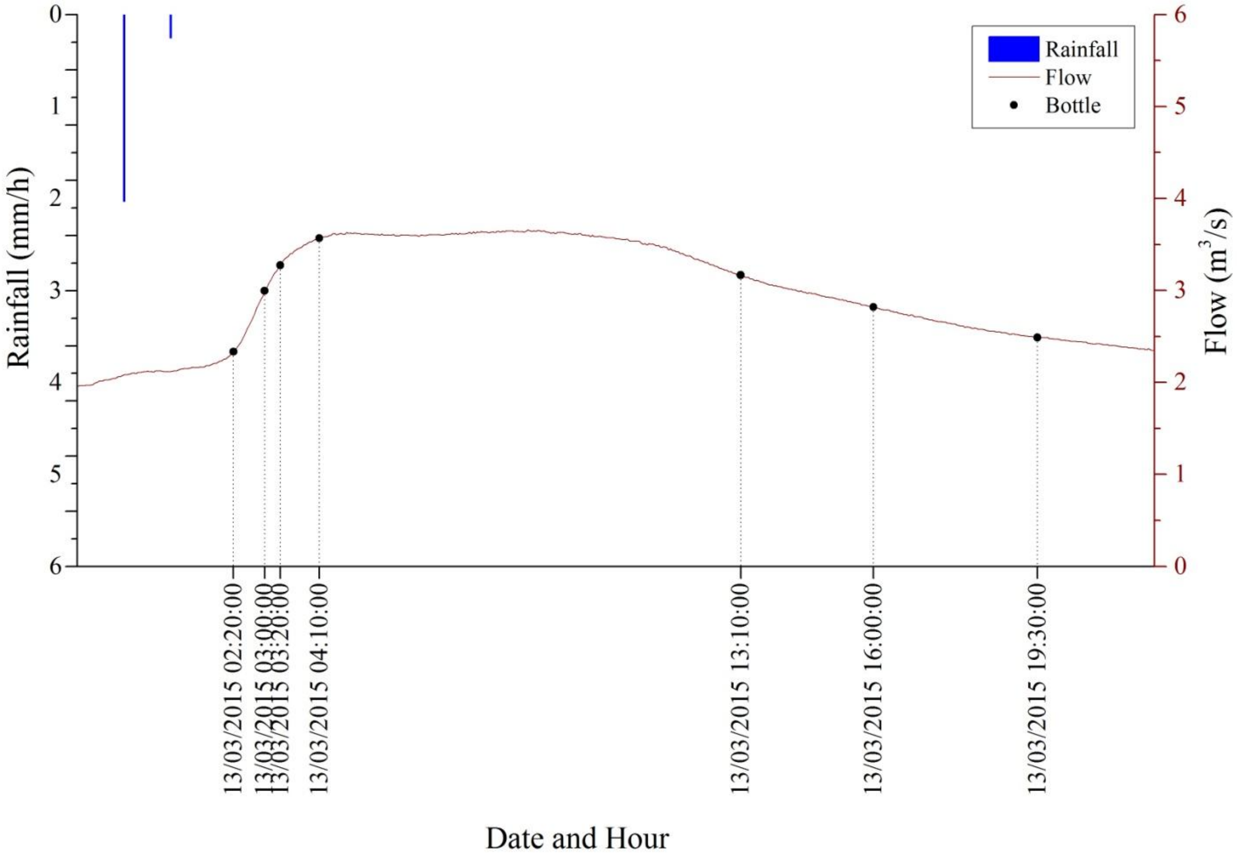


Figure 33 - Event 1

Alkalinity peak was registered in bottle 4 with 169,12 mg $CaCO_3$ L^{-1}. The average concentration (± standard deviation) is 158,40 ± 9,61mg $CaCO_3$ L^{-1}. For the conductivity, peak occurs on first bottle with 275 µS cm^{-1}; the average is 259 ± 14,67 µS cm^{-1}. For the temperature, DO and pH the concentrations did not have wide variations. The average concentrations were respectively 23,55 ± 0,20 °C, 7,31 ± 0,10 mg O_2 L^{-1} and 8,05 ± 0,06. Behavior of these water quality parameters are show in Figure 34, indicating a more stable characteristic of these parameters.

DOC, COD, TP and TN, as indicated in figure 13, had average concentrations of 5,74 ± 3,83 mg L^{-1}, 31,60 ± 4,51 mg O_2 L^{-1}, 0,14 ± 0,15 mg P L^{-1} and 0,55 ± 0,05 mg N L^{-1} respectively. COD peak was in first bottle with 40,82 mg L^{-1}. TP peak was in bottle 5, increasing

0,07 mg L^{-1} to 0,46 mg L^{-1}; TN peak was in bottle 3 with 0,27 mg/L; In all bottles the TN concentrations was greater than TP concentrations. Interestingly, for this event, DOC decreases when flow increase and had a peak just in bottle 5 with 10,21 mg L^{-1}, at the recession of the hydrograph. The DOC, COD, TN and TP distribution along event 1 are shown in Figure 35.

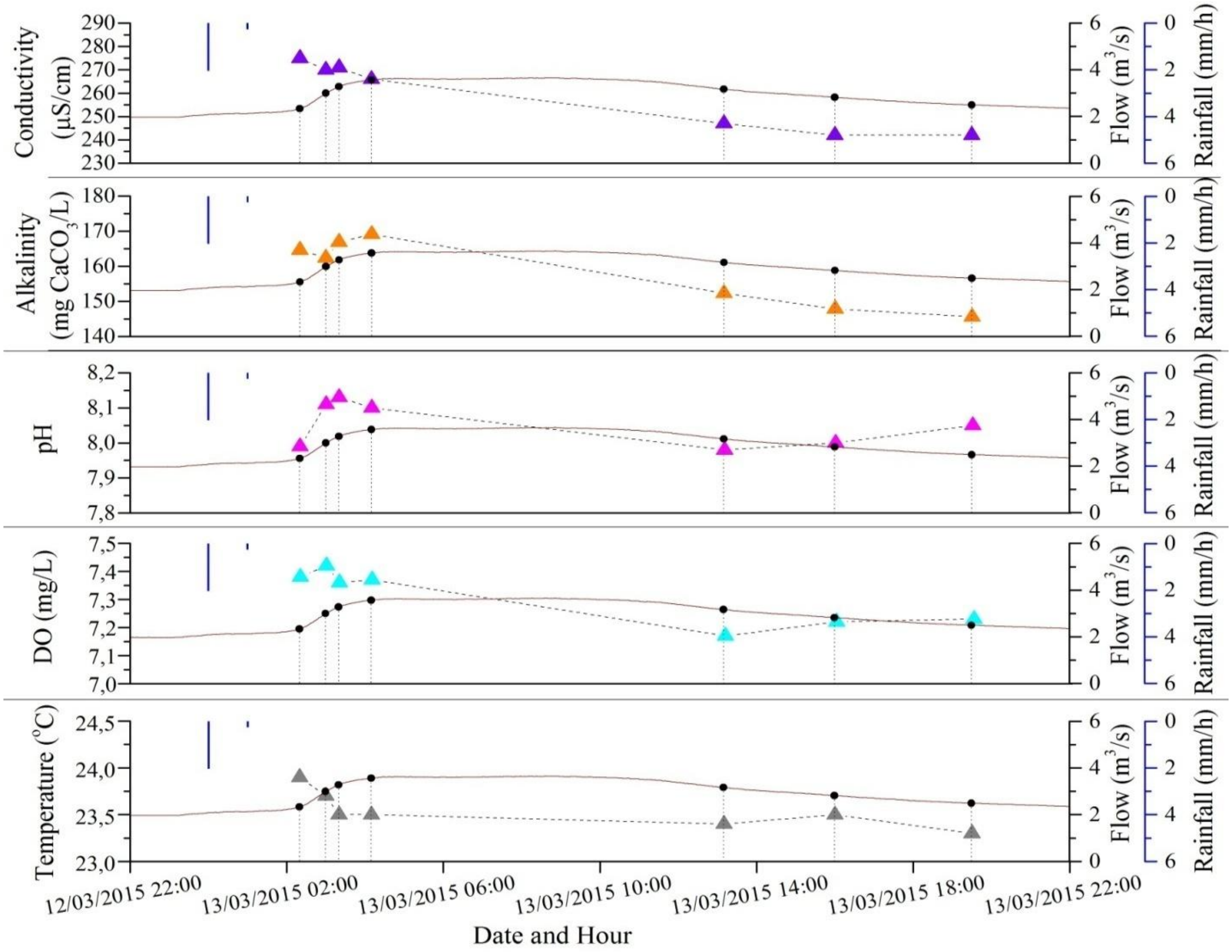


Figure 34 - Distribution of conductivity, alkalinity, pH, DO and temperature along event 1

The physical parameters (turbidity, TS, SS and their fractions) had similar behavior with each other. Turbidity initial was 66,7 increasing until 212 NTU on peak bottle (fourth bottle).The TS peak was in bottle four, with concentrations of 350, 228 and 79 mg L^{-1} for respectively to TS, FTS and VTS; On bottles 4 and 7 the VTS concentrations was greater than FTS. For SS peak was verified in bottle 6 with concentrations of 235, 156 and 79 mg L^{-1} respectively to SS, FSS and VSS; Only the bottle 7 the VSS concentration was greater than FSS. Figure 36 shows turbidity, ST and SS pollutographs for event 1.

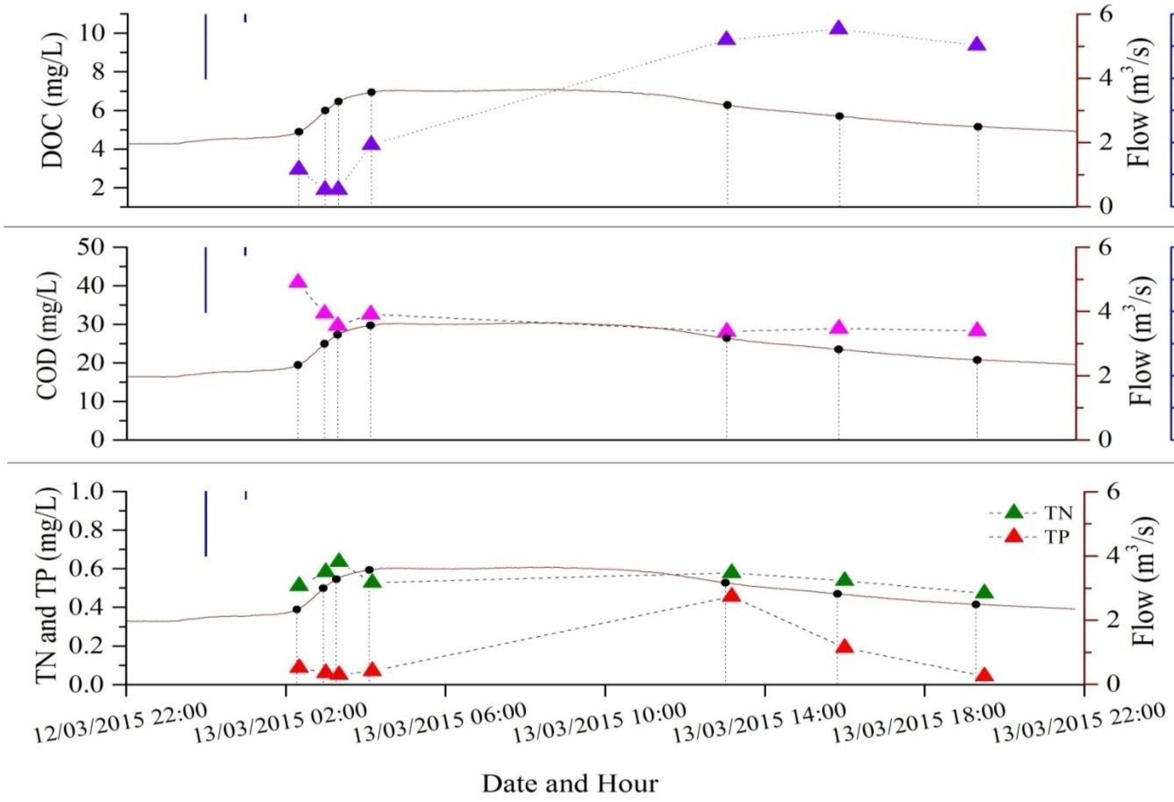


Figure 35 - Distribution of DOC, COD, TN and TP along event 1

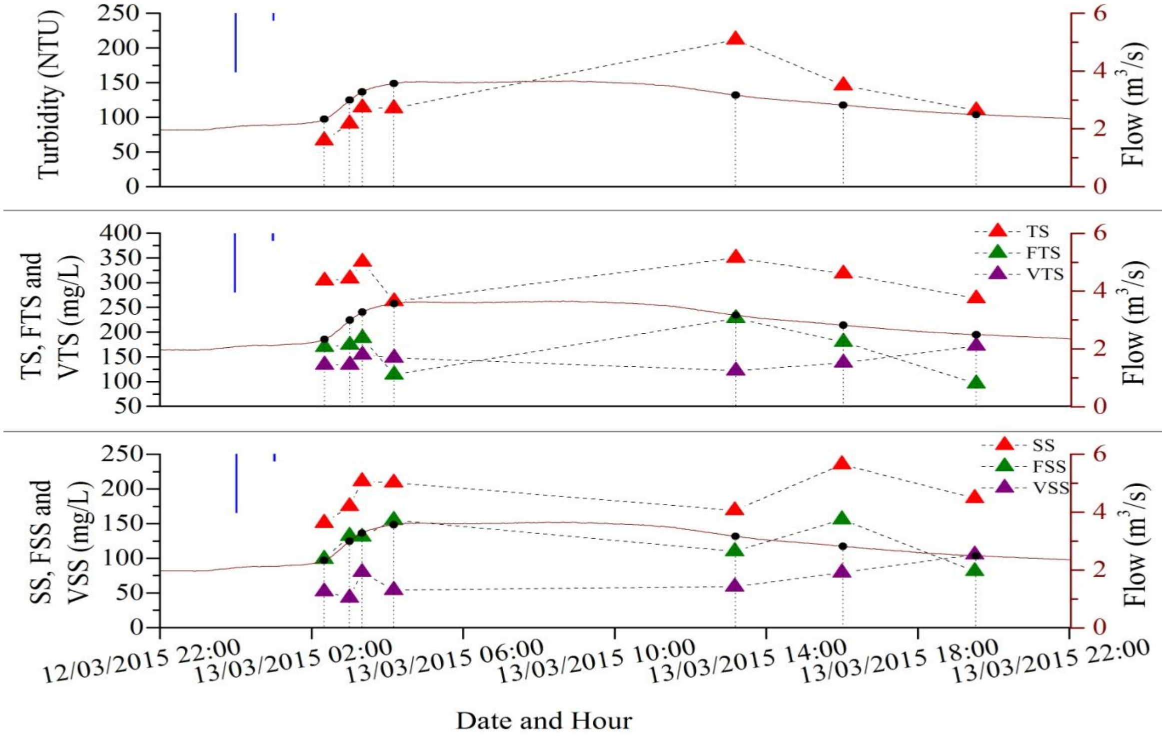


Figure 36 - Distribution of turbidity, TS (VTS and FTS), and SS (VSS and FSS) along event 1

4.4.2. Event 2

The event 2 started on 15th March at 11:40 p.m. and ended on 17th March at 6:00 a.m. collecting 12 bottles, with a duration of 30.33 hours. The rain started on 15th March at 11:27 p.m. and after 13 minutes SBN equipment did the first sampling. The rain event lasted around 12,37 hours. The initial flow (before rainfall) was approximately 1,90 m³ s^{-1} and increase until 4,48 m³ s^{-1} (peak). Figure 37 represent event 2.

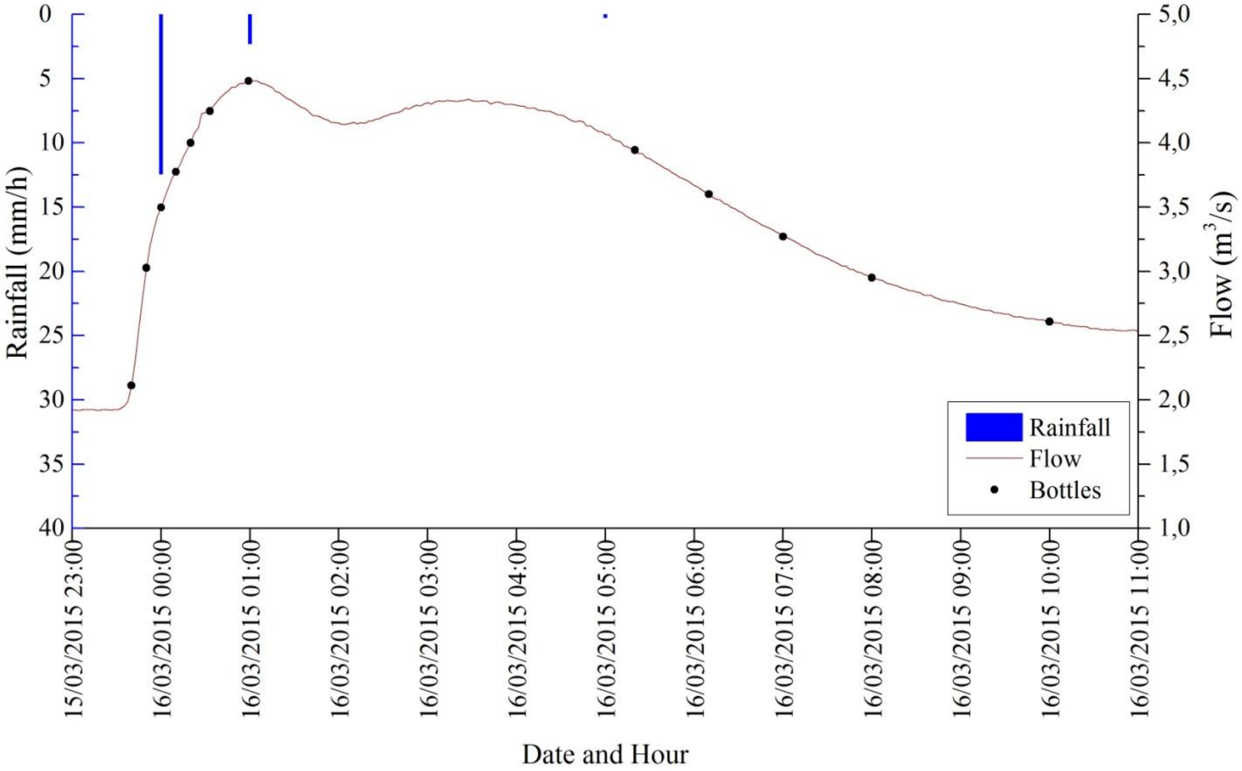


Figure 37 - Event 2

Alkalinity concentrations started in 161,28 mg $CaCO_3$ L^{-1} in first bottle, decreasing until 107,52 mg $CaCO_3$ L^{-1} in bottle 4 (maximum decrease) and return to 141,12 mg $CaCO_3$ L^{-1} in last bottle (17). This behavior following the hydrograph also is observed for conductivity concentrations: started in 264 µS cm^{-1} in first bottle, decreasing to 175,5 µS cm^{-1} in bottle 7 and return to 269 µS cm^{-1} in last bottle. The pH values increasing according the flow, with 7,77 in bottle 2 to 8,18 in bottle 7 (peak concentration). The temperature was stable. The DO concentrations was reduction in peak bottles (2 to 7), with the lowest concentration in bottle 7

(6,24 mg O_2 L^{-1}), returning to 7,94 mg O_2 L^{-1} in bottle 17. The average for alkalinity was 129,20 ± 14,38mg $CaCO_3$ L^{-1}; for conductivity was 236,44 ± 25,17 µS cm^{-1}; for pH, temperature and DO was, respectively, 7,97 ± 0,12; 21,08 ± 0,68 °C and 7,69 ± 0,22 mg O_2 L^{-1}. Figure 38 represent these parameters during event 2.

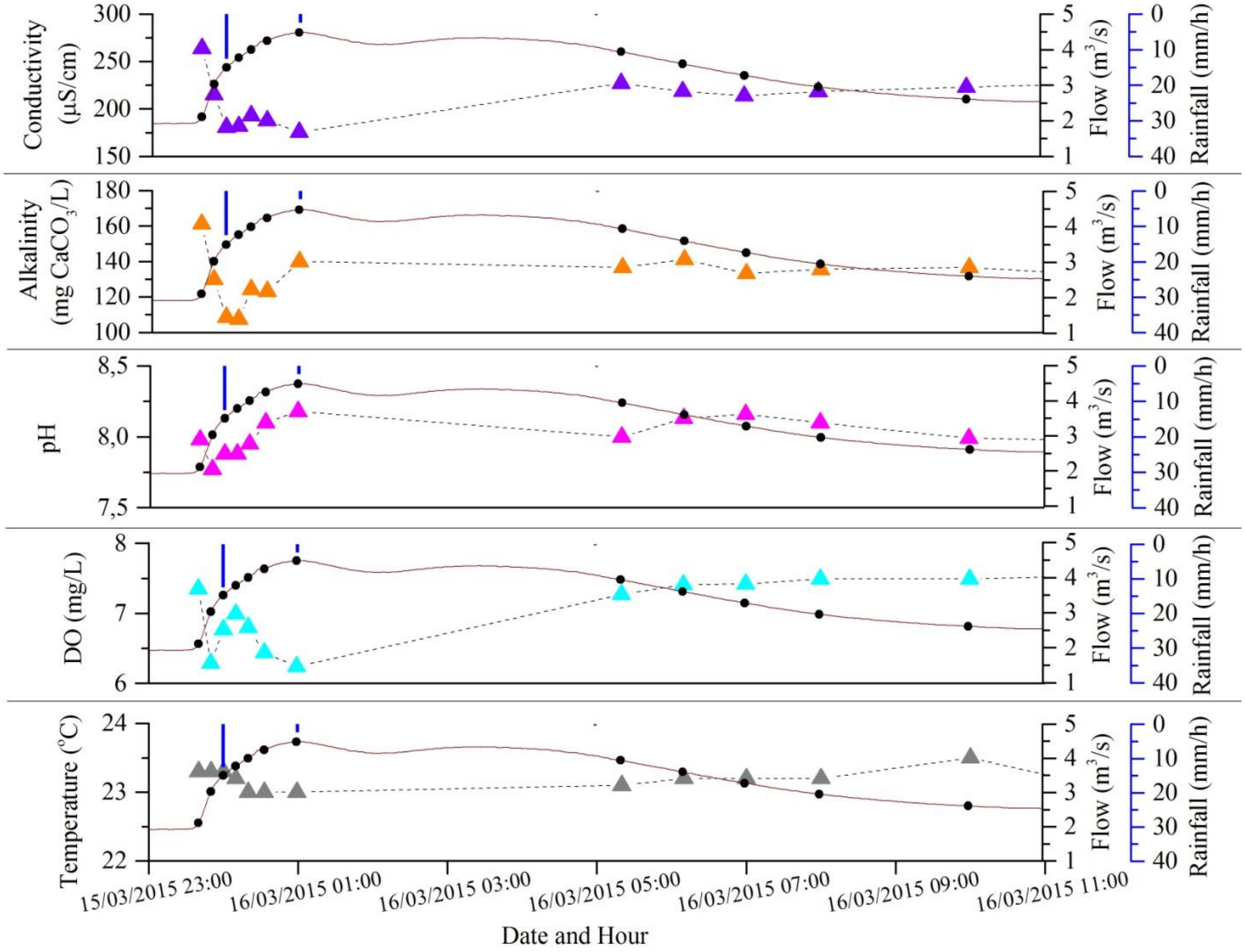


Figure 38 - Distribution of conductivity, alkalinity, pH, DO and temperature along event 2

Figure 39, as follows, shows DOC, COD, TN and TP pollutographs. DOC had a more stable behavior, with one peak in bottle 4 (16,77 mg L^{-1}). After that, the values decrease without wide range. The average and standard deviation for DOC was 5,51 ± 4,08 mg L^{-1}. COD concentrations had a behavior following hydrograph, where the peak was found in bottle 6 with 85,69 mgO_2 L^{-1}, decreasing until 3,37 mgO_2 L^{-1} in last bottle (17). TN concentrations did not wide variation, with peak in bottle 7 (0,62 mg N L^{-1}). Instead, for TP concentrations had wide variation, following hydrograph; started in first bottle with 0,09mg P L^{-1}, increasing until 1,60 mg P L^{-1} in bottle 7 (peak), and then returning to 0,07 mg P L^{-1} in last bottle. The average for COD, TN and TP concentrations was, respectively, 43,26 ± 25,44 mgO$_2$ L^{-1}, 0,51 ± 0,06 mg N L^{-1} and 0,50 ± 0,46 mg P L^{-1}.

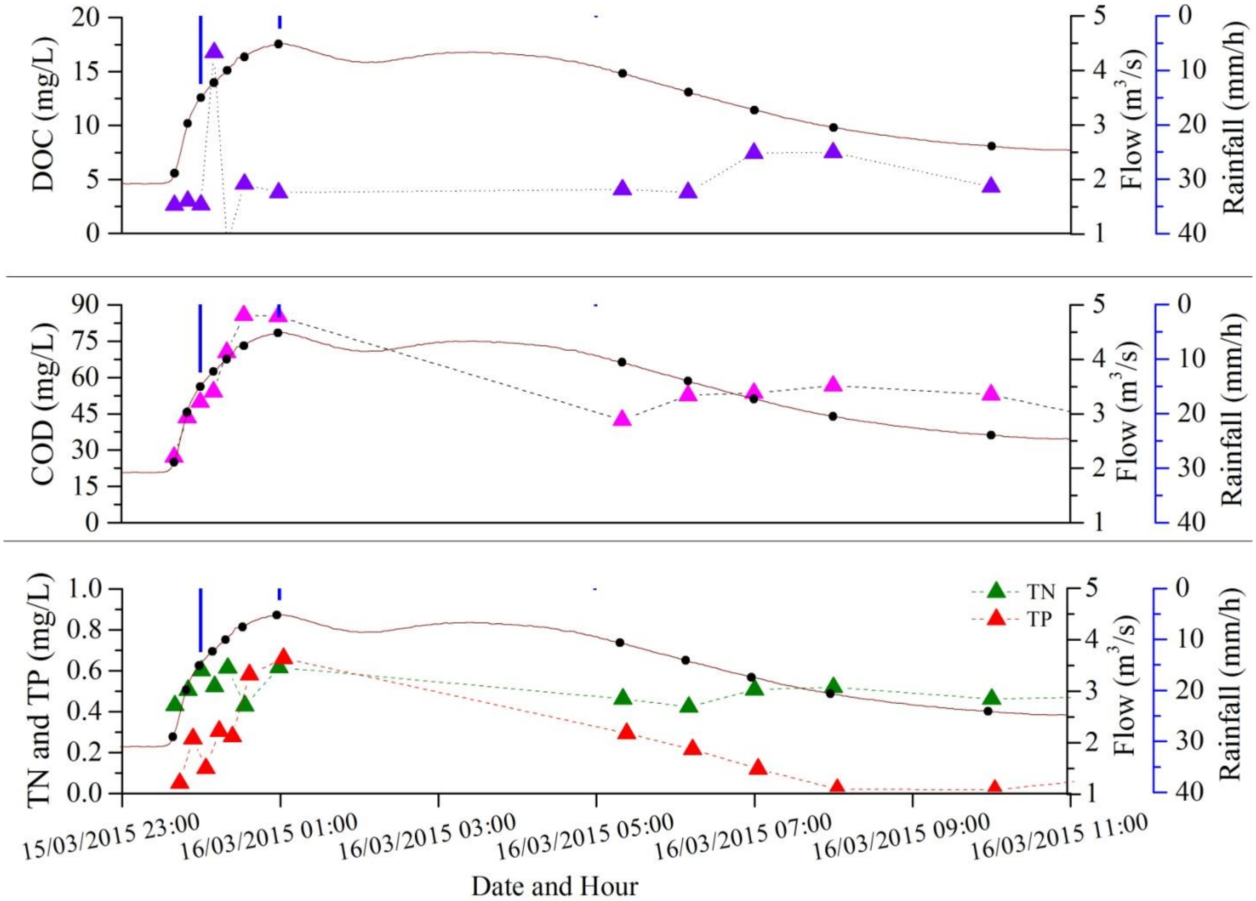


Figure 39 - Distribution of DOC, COD, TN and TP along event 2

For turbidity the peak happened in bottle 7 with 1970 NTU, started with 44,1 in bottle one, increasing until peak and decreasing to 54 NTU in event end. For TS:FTS:VTS and SS:FSS:VSS the peak also happens in bottle 7, with concentration of 1878:1468:410 and 1768:1386:381 mg L^{-1} respectively. Any bottle had volatile concentration bigger than fixed concentration of solids. The average for turbidity, TS (FTS and VTS) and SS (FSS; VSS) was 509,20 ± 555,16 NTU, 695 ± 566 mg L^{-1} (505 ± 495 and 190 ± 106 mg L^{-1}) and 540 ± 601 mg L^{-1} (429 ± 512 and 111 ± 103 mg L^{-1}). Figure 40 show turbidity, TS and SS pollutographs.

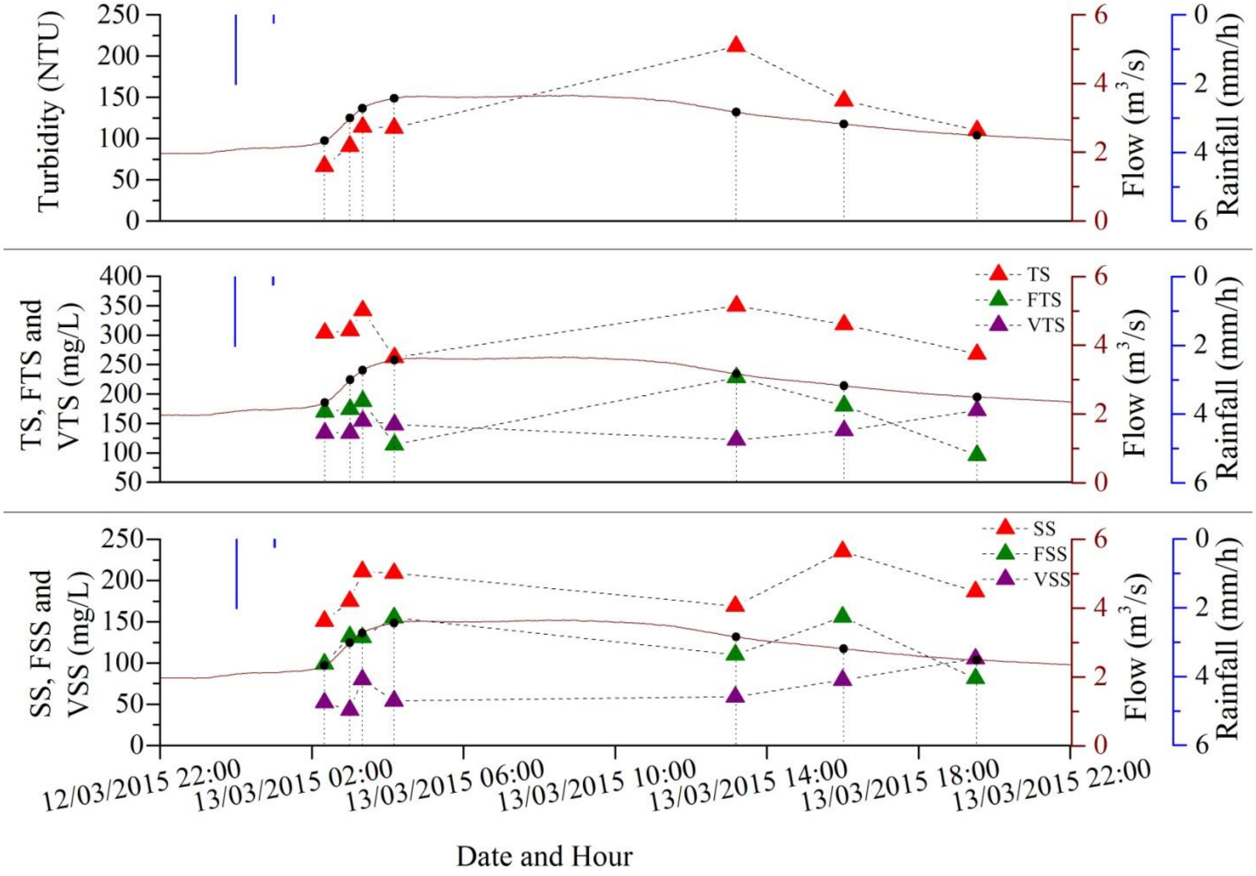


Figure 40 - Distribution of turbidity, TS (VTS and FTS), and SS (VSS and FSS) along event 2

4.4.3. Event 9

The event 9 started on 20th April at 11:50 p.m. and ended on 23rd April at 08:40 a.m. collecting 9 bottles, with duration of 56,83 hours. The rain started on 20th April at 23:25p.m. and after 25 minutes approximately SBN equipment did the first sampling. The rain event lasted around 41,62h. The initial flow (before rainfall) was approximately 1,52 m³ s^{-1} increasing until 3,30 m³ s^{-1} on event peak. Figure 41 represent event 9.

As indicated in Figure 42, alkalinity and conductivity had the same behavior, decreasing during the event peak. The alkalinity concentration was 169,29 mg $CaCO_3$ L^{-1} in first bottle, decrease to 125,40 mg $CaCO_3$ L^{-1} in bottle 3 and returning to 153,62 mg $CaCO_3$ L^{-1} in last bottle. Conductivity started with 299 µS cm^{-1} in first bottle, decreasing to 237 µS cm^{-1} in bottle 4 and increasing to 273 µS cm^{-1} in bottle 9. The pH values did not have much variation, however the values are always more alkaline. Temperature was stable. The DO concentration was low, with 4,95 mgO_2 L^{-1} in first bottle and was increasing during the event reaching 8,19 mgO_2 L^{-1} in bottle 9. The average for alkalinity, conductivity, pH, temperature and DO, respectively, was 150,38 ± 16,24 mg $CaCO_3$ L^{-1}; 268,80 ± 23,11 µS cm^{-1}; 8,02 ± 0,16; 20,21 ± 0,10 °C; and 7,59 ± 0,96 mg O_2 L^{-1}.

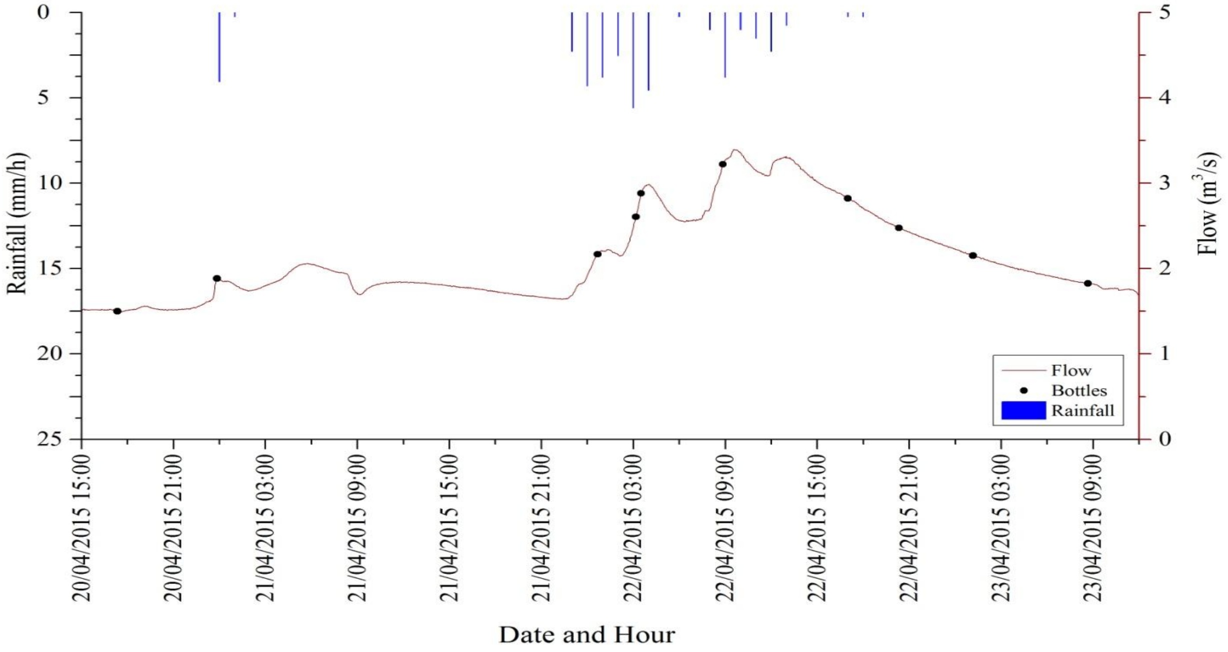


Figure 41 - Event 9

DOC had a peak in bottle 3, with 4,39 mg L^{-1}. The behavior was without wide ranges. The higher COD concentrations happened during the event peak, then decreasing with the flow. The COD peak was in bottle 3 with 16,91 mg O_2 L^{-1}. For TP concentrations the behavior follows the hydrograph. In first bottle the concentration was 0,63 mg L^{-1}, decreasing until the rain start again. The TP peak was in bottle 4 with 0,49 mg L^{-1} and finishing with 0,10 mg L^{-1} in bottle 9. TP was higher than TN in all bottles, except the last one. Figure 43 shows DOC, COD, TN and TP pollutographs.

TN concentrations showed stable, but considering their fractions, nitrite and ammonia nitrogen had high concentration during the event peak. The nitrogen ammonia peak was in first bottle with 229,64 µg L^{-1} (NO_2^- = 9,38µg L^{-1} and nitrate could not detectable) and nitrite peak was in bottle 4 with 10,32 µg L^{-1} (NH_3 = 105,50 µg L^{-1} and nitrate could not detectable). The nitrate was present at the end of the event, with peak in last bottle (1,67 µg L^{-1}); the NH_3 concentrations in this bottles decreasing. This values and differences between nitrogen fractions can be due to occurrence of nitrogen cycle. The average for TN was 0,42 ± 0,02 mg L^{-1}, for nitrite was 7,26 ± 2,04 µg L^{-1}, for nitrogen ammonia was 76,74 ± 64,16 µg L^{-1} and for nitrate did not possible calculate (Figure 44).

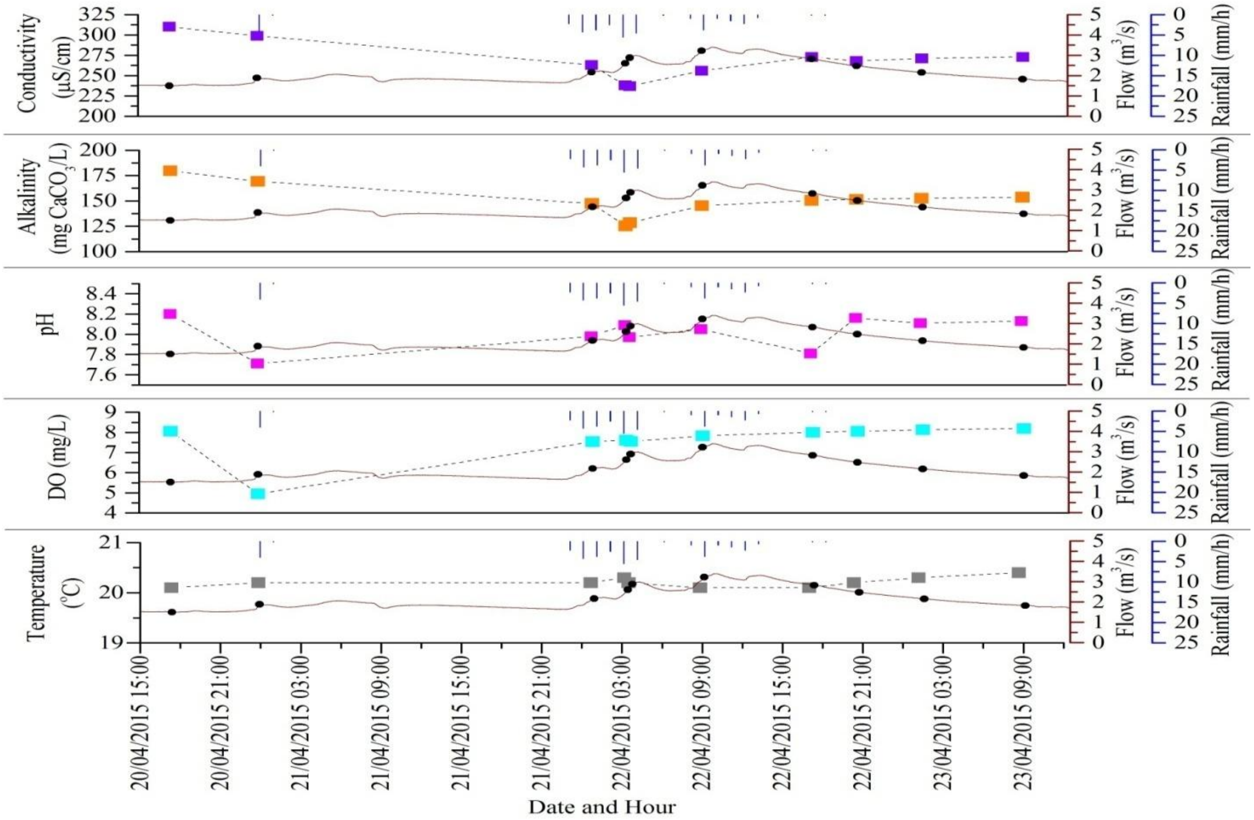


Figure 42 - Distribution of conductivity, alkalinity, pH, DO and temperature along event 9

For physical water quality parameters, all of them followed the hydrograph, in other words, increasing and decreasing with the flow. Turbidity, TS and SS peak was in bottle 4 with 163 NTU; 952 mg L^{-1} for TS, 382 mg L^{-1} for FTS, and 570 mg L^{-1} for VTS. For suspended solids and fractions was 233 mg L^{-1} for SS, 199 mg L^{-1} for FSS, and 34 mg L^{-1} for VSS. The average values for turbidity was 88,46 ± 48,74 NTU, for TS (FTS and VTS) was 336 ± 221 mg L^{-1} (174 ± 85 and 161 ± 145 mg L^{-1}), and for SS (FSS and VSS) 112 ± 70 mg L^{-1} (92 ± 63 and 20 ± 8 mg L^{-1}). Figure 45 shows turbidity, TS and SS pollutographs.

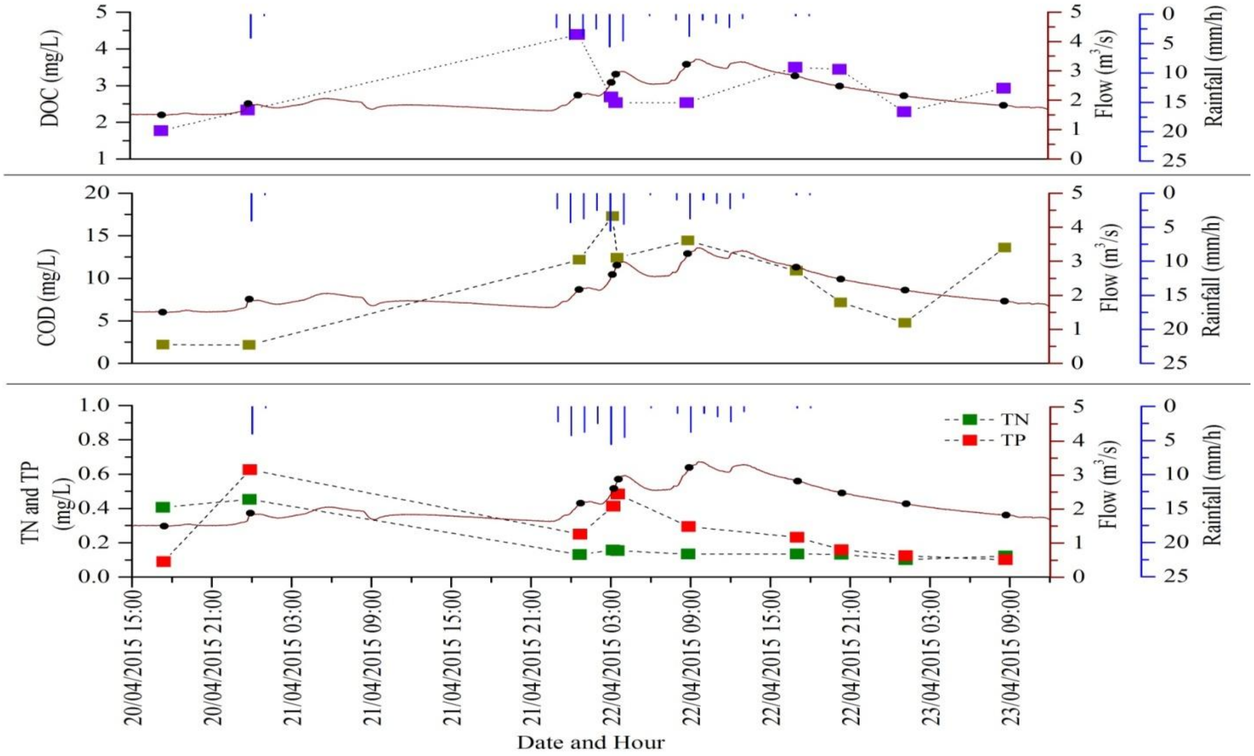


Figure 43 - Distribution of DOC, COD, TN and TP along event 9

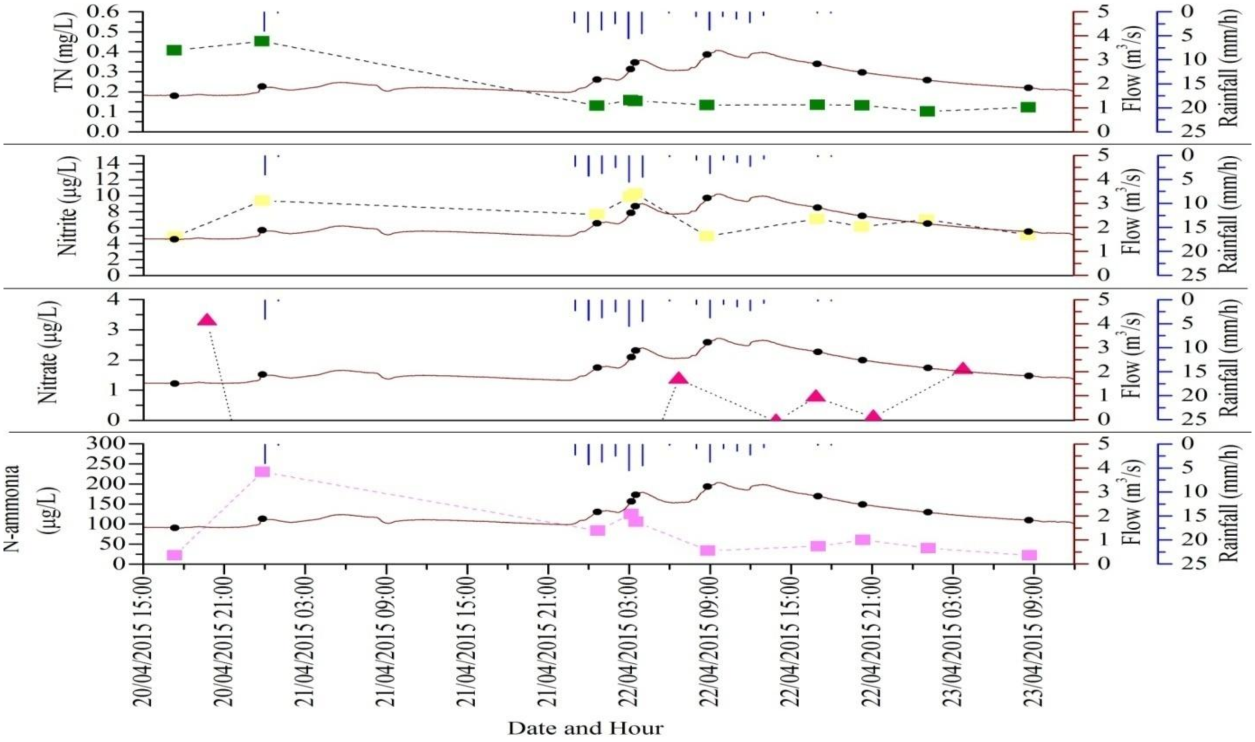


Figure 44 - Distribution of total nitrogen, nitrite, nitrate and ammonia nitrogen for event 9

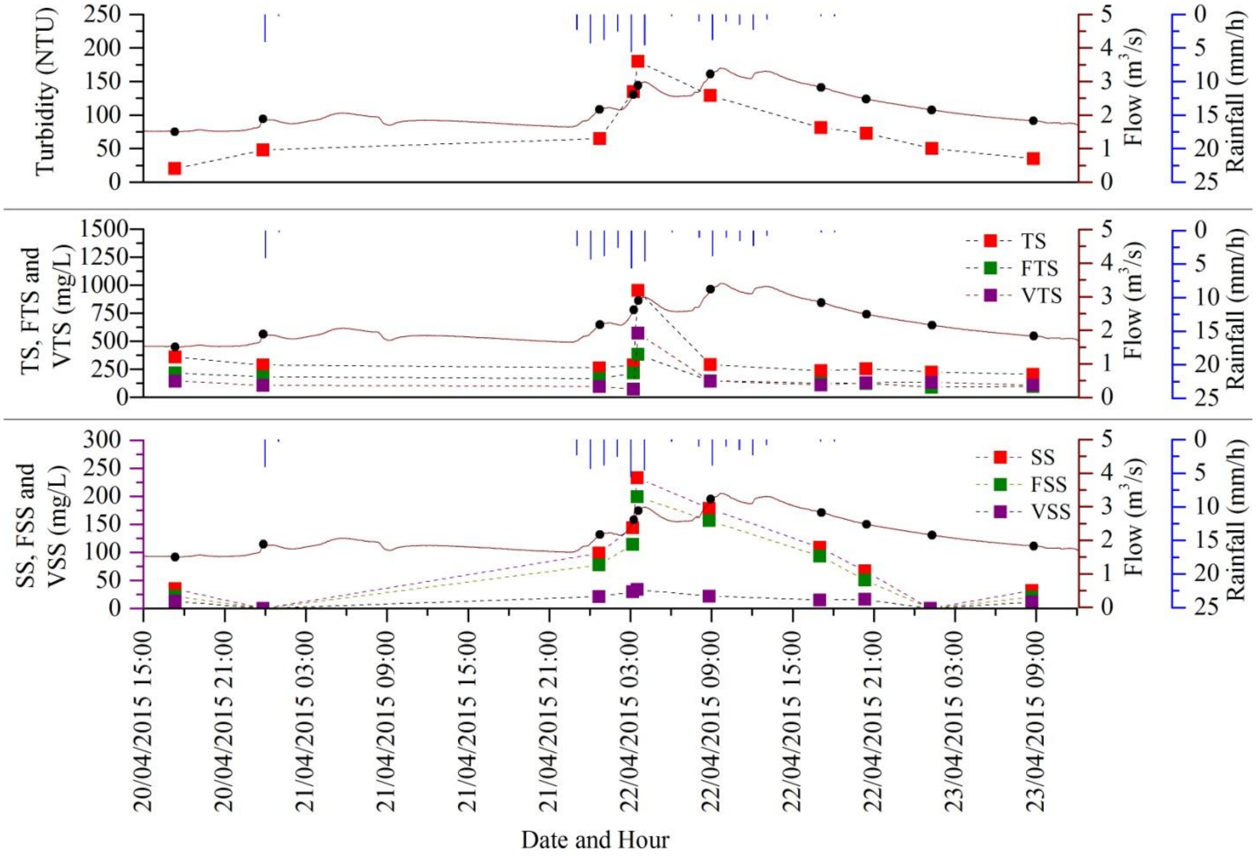


Figure 45 - Distribution of turbidity, TS (VTS and FTS), and SS (VSS and FSS) along event 9

4.4.4. Event 10

The event 10 started on 4th May at 00:20 a.m. and ended in the same day at 11:00 p.m. collecting 12 bottles, with duration of 22.67 hours. The rain started on 3rd May at 9:30 p.m. and after 2 hours and 50 minutes SBN equipment did the first sampling. The rain event lasted around five hour. The initial flow (before rainfall) was approximately 1,38 $m^3\ s^{-1}$ increasing until 3,85 $m^3\ s^{-1}$ on event peak. The critical time happen on 4th May at 02:12 a.m. Figure 46 represents event 10**.**

Alkalinity peak was in bottle 5 with 190,19 mg $CaCO_3$ L^{-1}. The average concentration was 152,57 ± 19,36 mg $CaCO_3$ L^{-1}. Temperature and pH did not have much variation among the bottles, with average about 14,23 ± 1,70 °C and 7,96 ± 0,15 respectively. The DO and conductivity behavior were similar, having lower values in the bottles of the event ascent (bottles 2 to 5). The lowest concentrations for DO was found in bottle 2 (6,80 $mgO_2\ L^{-1}$) and for conductivity was in bottle 5 (191,4 $\mu S\ cm^{-1}$). The average concentrations for the both water quality parameters were, respectively, 8,13 ± 0,92 $mgO_2\ L^{-1}$ and 215,48 ± 23,74 $\mu S\ cm^{-1}$. Figure 47 shows the pollutographs of water quality parameters mentioned above.

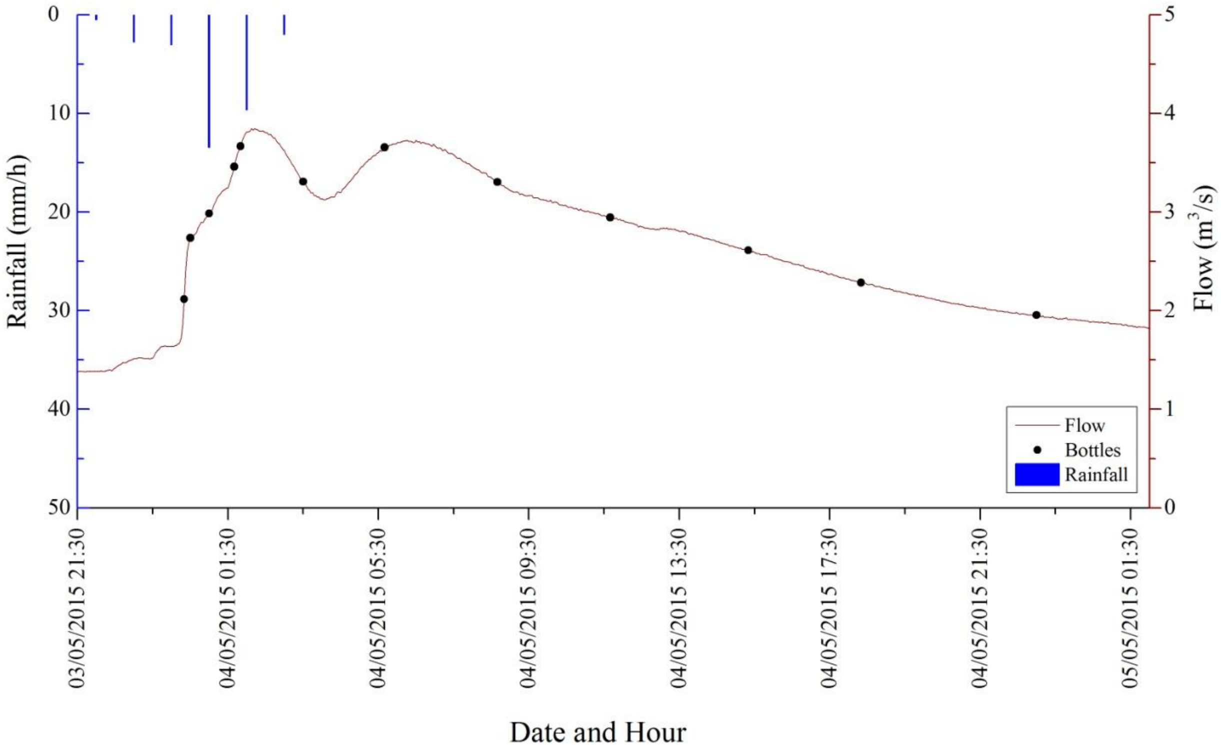


Figure 46 - Event 10

The parameters COD, TN and TP had behavior similar to pollutograph, increasing during the ascent flow and then decreasing with river normal course return. COD was the peak in bottle 2 (74,97 $mgO_2\ L^{-1}$), TP was the peak in bottle 7 (0,62 $mg\ P\ L^{-1}$, increasing from 0,17 $mg\ L^{-1}$) and TN was the peak in bottle 4 (0,26 $mg\ N\ L^{-1}$). Just on last 3 bottles the TN > TP concentrations. DOC was more stable with two significantly peaks, in bottle 6 (9,44 $mg\ L^{-1}$) and bottle 12 (11,34 $mg\ L^{-1}$). The average concentrations were 3,80 ± 3,41 $mg\ L^{-1}$, 34,95 ± 32,76 $mgO_2\ L^{-1}$, 0,17 ± 0,05 $mg\ N\ L^{-1}$ and 0,28 ± 0,19 $mg\ P\ L^{-1}$ respectively for DOC, COD, TN and TP. Figure 48 shows DOC, COD, TN and TP pollutographs.

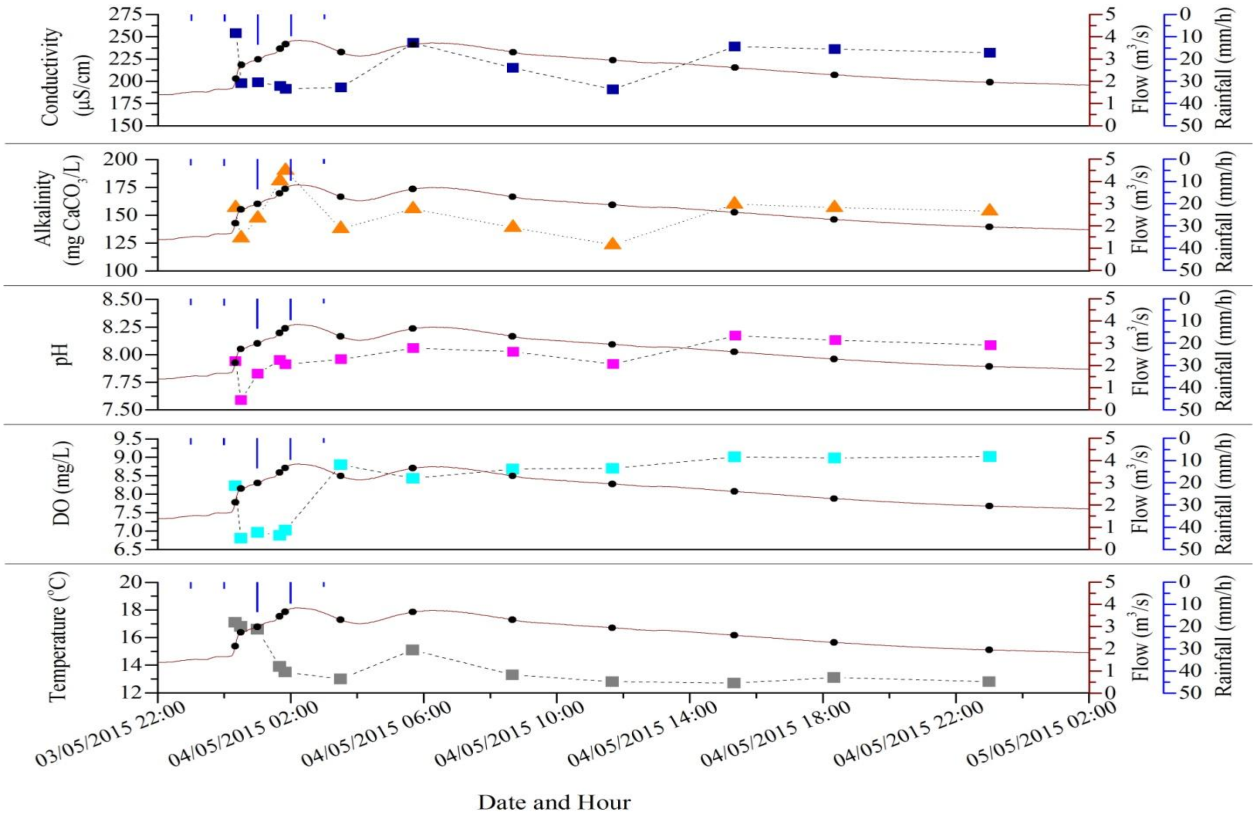


Figure 47 - Distribution of conductivity, alkalinity, pH, DO and temperature along event 10

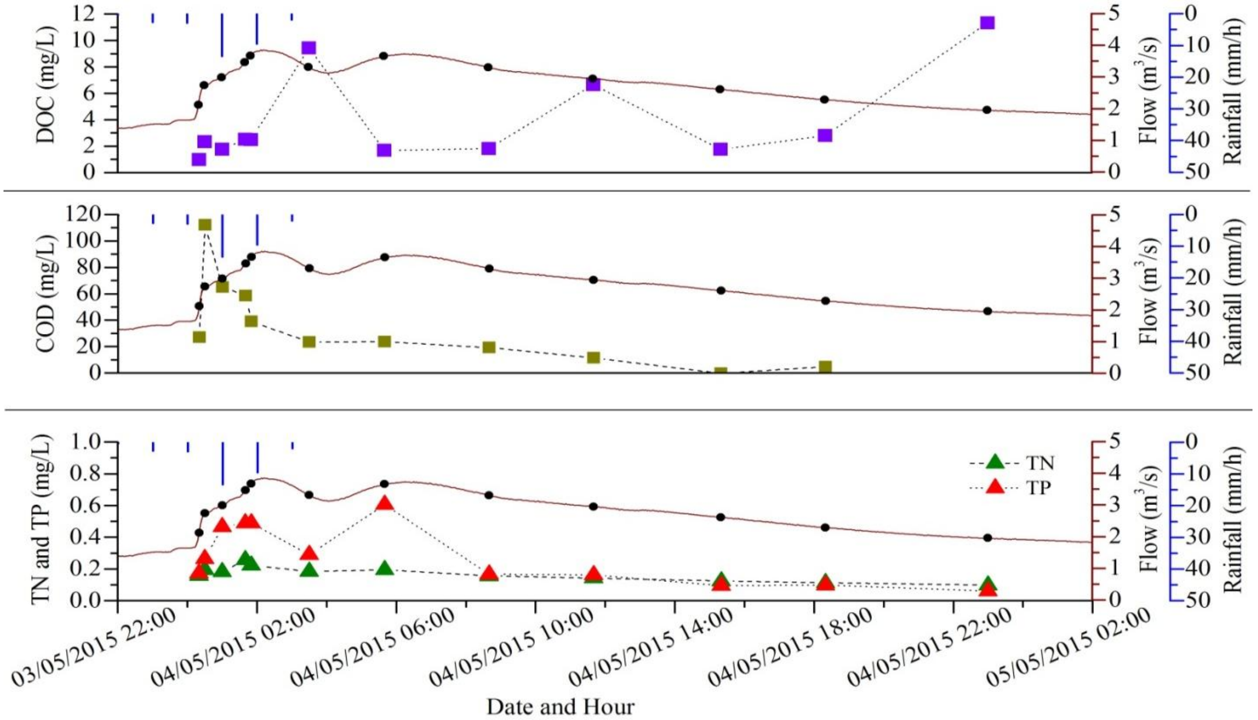


Figure 48 - Distribution of DOC, COD, TN and TP along event 10

It was observed that concentration distribution on nitrogen fraction can be associated to cycle nitrogen. When the N-ammonia concentrations were high, the nitrite concentrations were high too; however the nitrate concentrations were below of detection limit. In bottle 4 had the concentrations peak for NH_3 and NO_2^-, respectively 235,43µg N L^{-1} and 134,20 µg N L^{-1}; nitrate concentration can´t be measured. So, when had N-ammonia decreased the nitrate concentrations increased; on bottle 10 was the nitrate peak concentration with 105,72 µg N L^{-1} while for the same bottle, the NH_3 concentration was 32,73µg N L^{-1} and NO_2^- was 15,07 µg N L^{-1}. Figure 49 show potentially fractions nitrogen transformation along event 10.

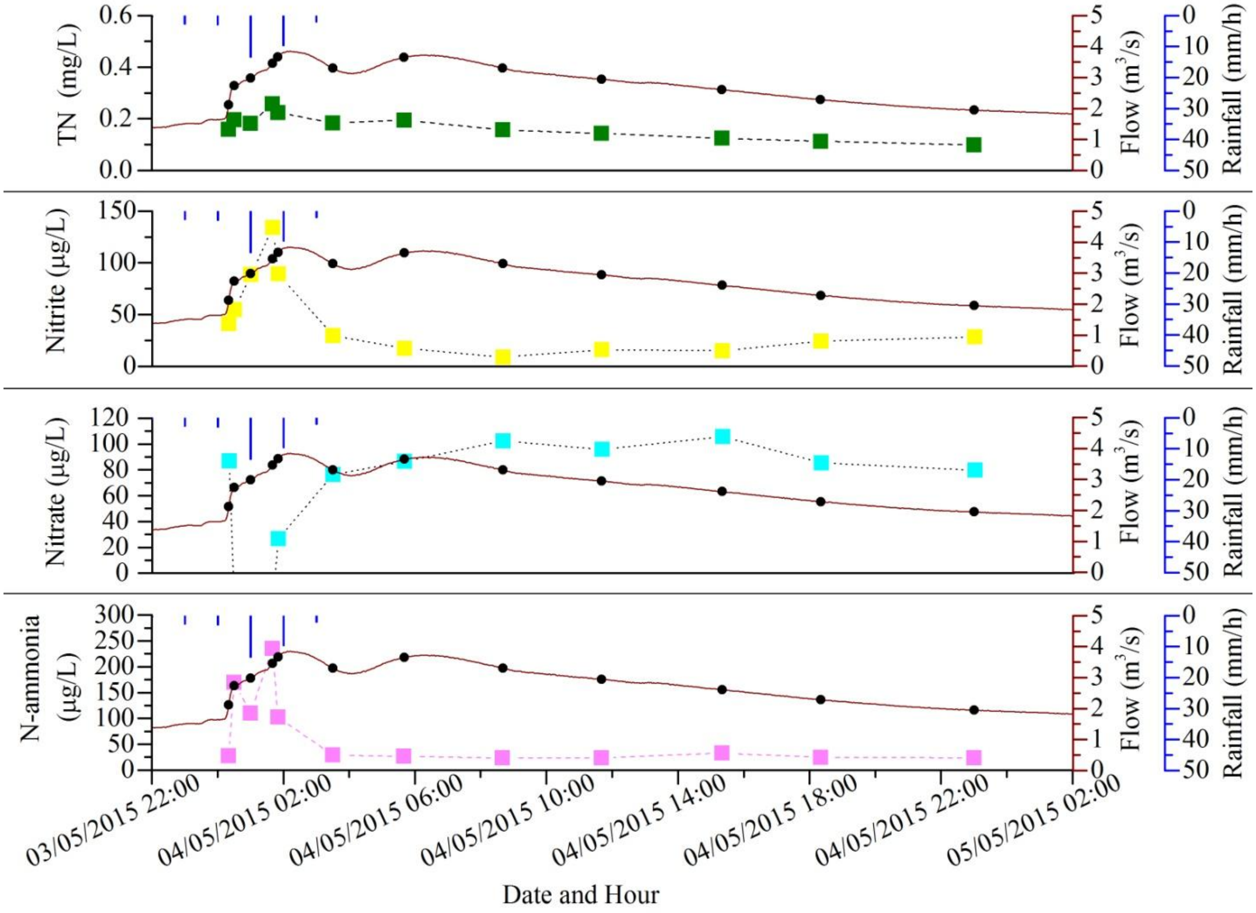


Figure 49 - Distribution of total nitrogen, nitrite, nitrate and ammonia nitrogen along event 10

The physical parameters (turbidity, TS, SS and their fractions) had similar behavior among each other and hydrograph. The solids carrying happens according the rainfall event and flow increase. Turbidity peak was in bottle four with 1100 NTU. For TS and SS the peak happened in bottle four too, with concentration of 1306, 1034 and 272 mg L^{-1} for respectively to TS, FTS and VTS, and 1073, 924 and 149 mg L^{-1} respectively to SS, FSS and VSS. The average values for turbidity was 405,13 ± 389,95 NTU, for TS (FTS and VTS) was 618 ± 363 mg L^{-1} (458 ± 312 and 160 ± 52 mg L^{-1}), and for SS (FSS and VSS) 345 ± 332 mg L^{-1} (298 ± 293 and 47 ± 40 mg L^{-1}). Figure 50 shows turbidity, TS and SS pollutographs along event 10.

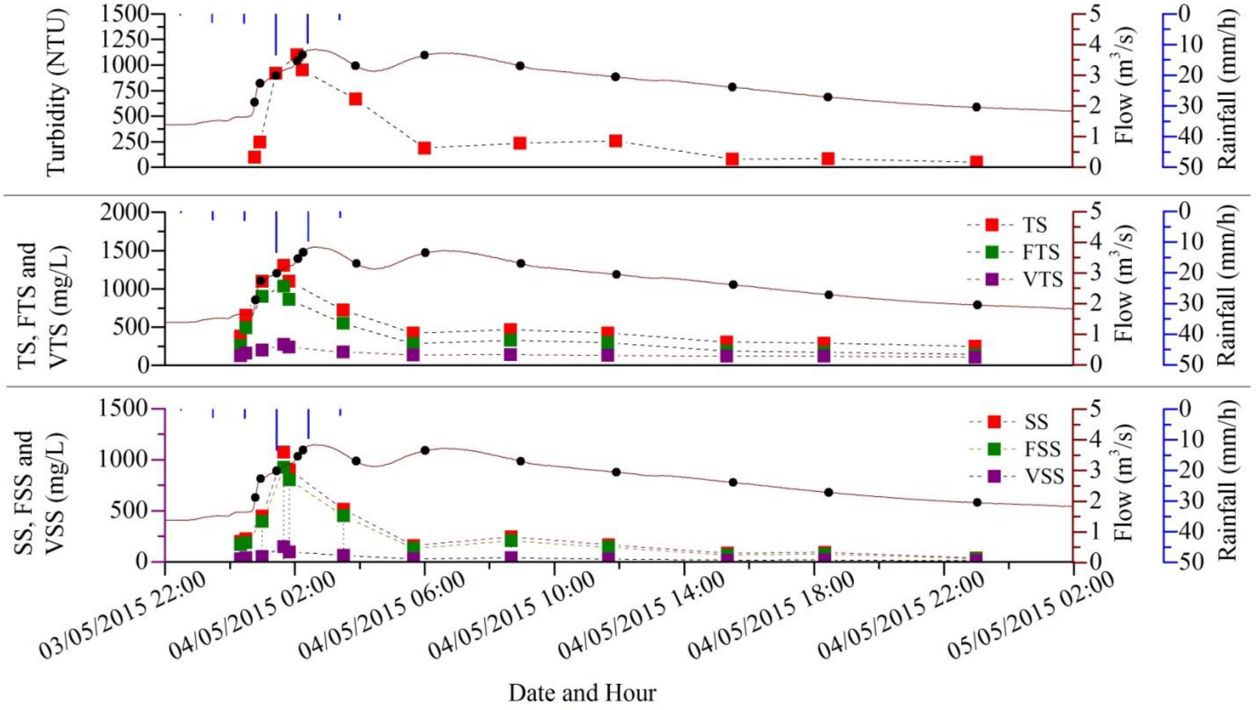


Figure 50 - Distribution of turbidity, TS (VTS and FTS), and SS (VSS and FSS) along event 10

4.4.5. Event 11

The event 11 started on 10th May at 07:50 a.m. and ended on 11th May at 02:10 p.m. collecting 9 bottles. The rain started on 10th May at 06:12 a.m. and after 1 hour and half approximately SBN equipment did the first sampling. The rain event lasted around 9,83h. The initial flow (before rainfall) was approximately 1,36 m^3 s^{-1} increasing until 3,28 m^3 s^{-1} on event peak. Figure 51 represents event 11.

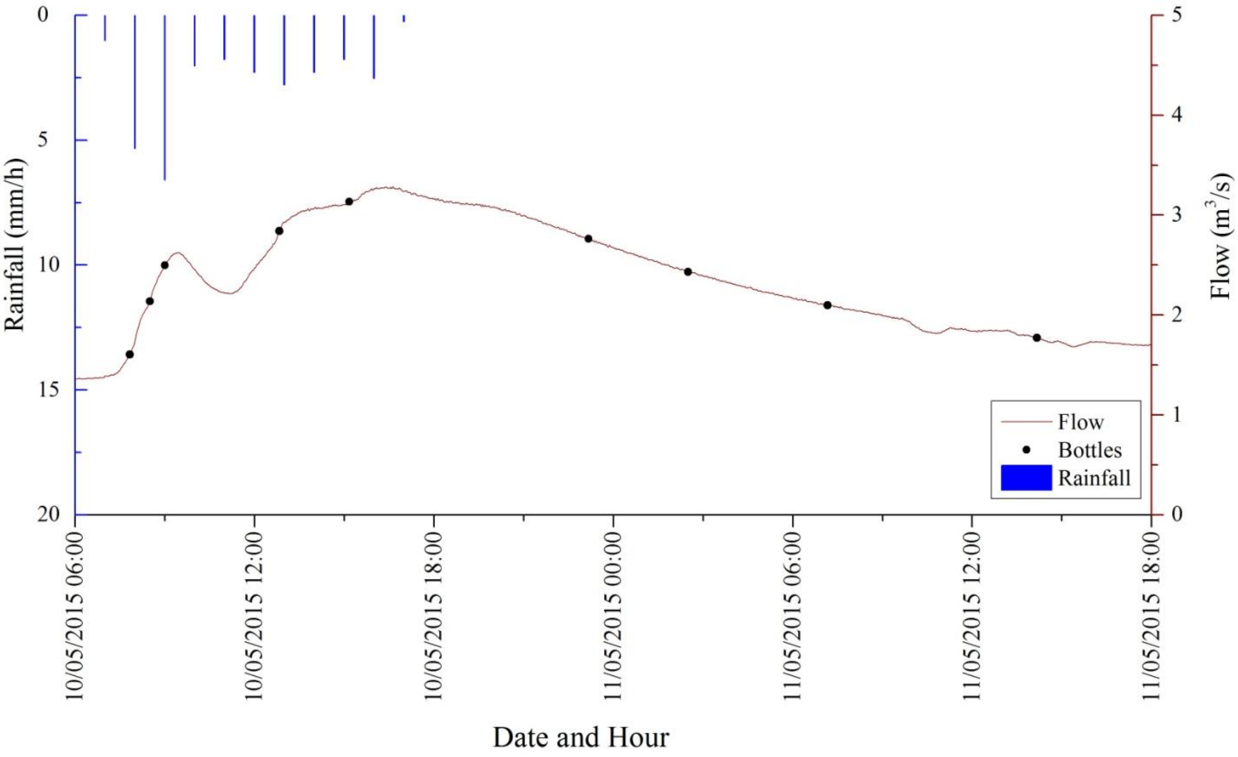


Figure 51 - Event 11

Alkalinity and conductivity did not have much variation among the bottles, and the concentration peak happened on first bottle, with 167,20 mg $CaCO_3$ L^{-1} and 250 µS cm^{-1} respectively. At the same bottle (1) the DO concentration was the lowest, with 7,79 mgO_2 L^{-1}, however increase until 8,72 mgO_2 L^{-1} on bottle 9. The temperature remained stable. pH behavior followed hydrograph, starting at 7,79 in bottle 1, increasing until 8,08 in bottle 5 and returning to 7,86 in bottle 9. The average for this water quality parameters, respectively, was 150,02 ± 8,18 mg $CaCO_3$ L^{-1}; 225,78 ± 12,89 µS cm^{-1}; 8,45 ± 0,36 mg O_2 L^{-1}; 13,88 ± 0,73 °C; and 7,94 ± 0,08. Figure 52 shows pollutographs of water quality parameters mentioned above.

COD peak was in bottle 8 with 15,27 mg L^{-1} and their behavior followed hydrograph. For TN and TP the concentration remained stable around 0,10 mg L^{-1}. DOC was more stable and not followed hydrograph behavior. The peak happened in bottle 6 with 11,87 mg L^{-1}. The average for DOC, COD, TN and TP was respectively 4,66 ± 3,08 mg L^{-1}; 14,98 ± 8,05 mgO_2 L^{-1}; 0,11 ± 0,02 mg N L^{-1} and 0,10 ± 0,04 mg P L^{-1}. Figure 53 shows COD, TN and TP pollutographs.

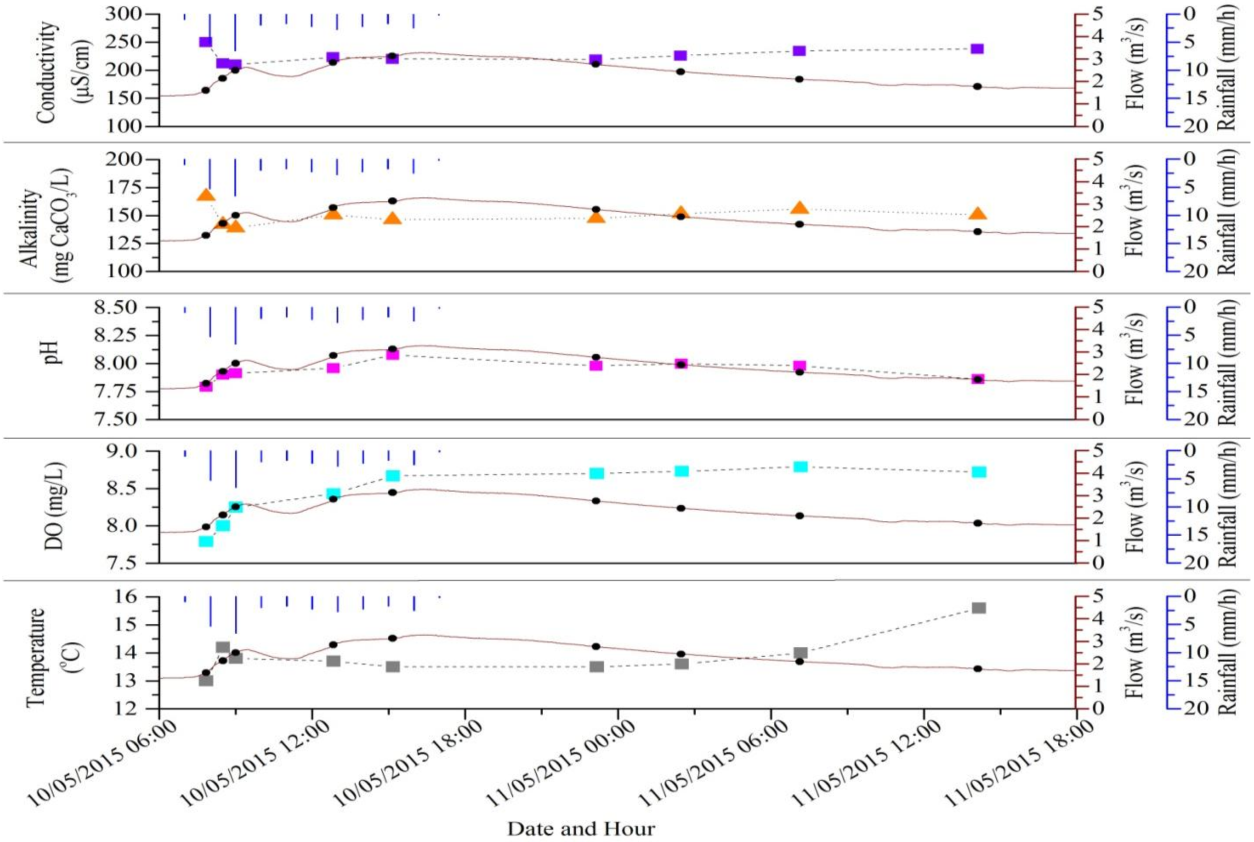


Figure 52 - Distribution of conductivity, alkalinity, pH, DO and temperature along event 11

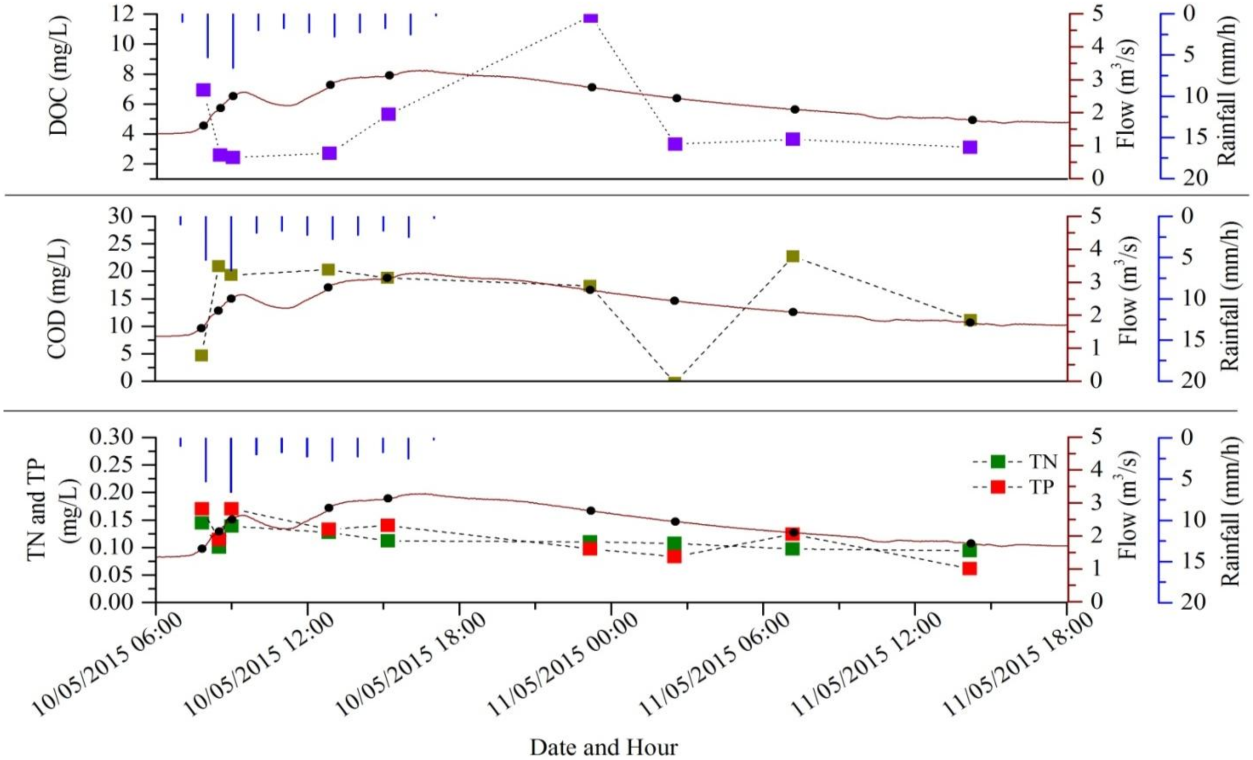


Figure 53 - Distribution of DOC, COD, TN and TP along event 11

For physical water quality parameters, all of them followed the hydrograph, in other words, increasing and decreasing with the flow. Turbidity peak was in bottle three with 163NTU.The TS peak was in bottle three, with concentrations of 370, 250 and 120 mg L^{-1} for respectively to TS, FTS and VTS. For SS the peak occurs in bottle five with concentrations 119, 96 and 23 mg L^{-1} respectively to SS, FSS and VSS. The average values for turbidity was 92,51 ± 49,74 NTU, for TS (FTS and VTS) was 291 ± 44 mg L^{-1} (180 ± 40 and 111 ± 10 mg L^{-1}), and for SS (FSS and VSS) 70 ± 35 mg L^{-1} (56 ± 29 and 14 ± 6 mg L^{-1}). Figure 54 shows turbidity, TS and SS pollutographs for event 11.

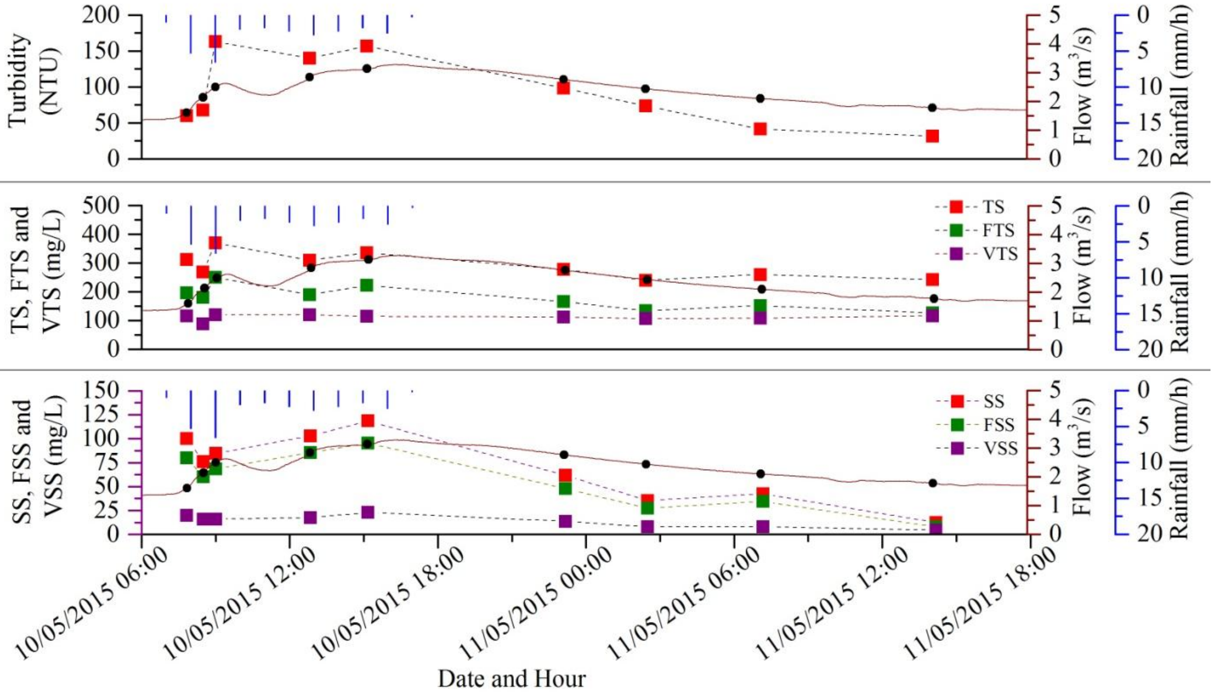


Figure 54 - Distribution of turbidity, TS (VTS and FTS), and SS (VSS and FSS) along event 11

4.5. Summary of Diffuse Pollution Events

Table 11, as follows, summarizes hydrological characteristics and the range of water quality parameters for each event. Event 1 was shorter (17,16 h) and less rainfall volume (2,29 mm), but brought the bigger amount of nitrogen ammonia (189,72 ± 284,31μg N L^{-1}) and DOC (5,74 ± 3,83 mg C L^{-1}) among all events. Event 9 was longer (56,83 h) and more rainfall volume

(38,61 mm) but DOC and COD concentrations had the lowest value among all events, with respectively 2,84 ± 0,76 mg C L^{-1} and 9,68 ± 5,16 mg O_2 L^{-1}. This fact can be function of the characteristics rainfall that produces a dilution of this substance due a big water volume during a long time space.

Events 2 and 11 had the same duration (30,33 h), however event 2 had the lowest rainfall volume (14,73 mm against 28,70 of event 11) and collect more bottles (12 against 9 of event 11). This situation can be explained due flow ranging that was bigger for event 2 (about 2,58 m^3 s^{-1} [1,90 – 4,48]) and consequently causing strong discharge into the river. Wide variations of water column level during short time generate fast and numerous triggers for the SBN sampled. Rainfall in event 9 was more distributed along the time producing slow response into the water column level and, consequently, for SBN trigger. Differences in event 2 and 11 can be show in Figure 37 and Figure 51, respectively.

Conductivity and DO were stable among events. DO have concentration above 8 mg L^{-1} in events 10 and 11 (8,13 ± 0,92 mg L^{-1} and 8,45 ± 0,36 mg L^{-1}) while temperature had the lowest values (14,23 ± 1,70 °C for event 10 and 13,88 ± 0,73 °C for event 11). According Silva et al. (2008), rainfall can contribute to increase in temperature, conductivity and dissolved oxygen. Alkalinity had the lowest concentration in event 2 (129,20 ± 14,38 mg $CaCO_3$ L^{-1}) while for the other events the averages was 152,84 ± 13,35 mg $CaCO_3$ L^{-1}. pH remained stable among events, that differs of Silva et al (2008) that found the lowest values (~5,0) when had the biggest rainfall observed (436mm) in study period.

TN and TP had close concentrations in events 2, 10 and 11, and for event 1 and 9 the TN was bigger than TP values, as found in Gao et al. (2014). N:P ratio was bigger for event 1 (3,92) that had a rainfall short-duration, and was less for event 10 (0,94) where the rainfall was more intense. Events 2 and 9, that had same rainfall duration, have similar N:P ratio (1,02 and 1,1, respectively), while event 9 (longer and more intense) had a N:P intermediate (1,5) among all events. All N:P ratio indicates nitrogen as limiting factor, according Chapra (1997) classification. In study of Gao et al. (2014) N:P ratio were low under extreme rainfall events (4 and 50) in comparison with N:P ratio under low rainfall or base flow conditions (about 35 and 600). These authors justify the N:P ratio decrease to the downward trend in N losses. Rainstorms occurred in rainy season will alter nutrient stoichiometry, probably conditioned nutrients availability in aquatic systems to seasonal changes (Gao et al., 2014).

Table 11 - Summary of events characteristics and range of water quality parameters

	Events				
	1	**2**	**9**	**10**	**11**
Duration	17,16	30,33	56,83	22,67	30,33
P_{acum}	2,29	14,73	38,61	31,50	28,70
NB	7	12	9	12	9
ΔQ	1,96 – 3,65	1,90 – 4,48	1,52 – 3,30	1,38 – 3,85	1,36 – 3,28
Cond	259,00 ± 14,67	236,44 ± 25,17	268,80 ± 23,11	215,48 ± 23,74	225,78 ± 12,89
Alka	158,40 ± 9,61	129,20 ±14,38	150,38 ± 16,24	152,57 ± 19,36	150,02 ± 8,18
Temp	23,55 ± 0,20	21,08 ± 0,68	20,21 ± 0,10	14,23 ± 1,70	13,88 ± 0,73
pH	8,05 ± 0,06	7,97 ± 0,12	8,02 ± 0,16	7,96 ± 0,15	7,94 ± 0,08
DO	7,31 ± 0,10	7,69 ± 0,22	7,59 ± 0,96	8,13 ± 0,92	8,45 ± 0,36
DOC	5,74 ± 3,83	5,51 ± 4,09	2,84 ± 0,76	3,80 ± 3,41	4,66 ± 3,08
COD	31,60 ± 4,51	43,26 ± 25,44	9,68 ± 5,16	34,95 ± 32,76	14,98 ± 8,05
TN	0,55 ± 0,05	0,51 ± 0,06	0,42 ± 0,02	0,17 ± 0,05	0,11 ± 0,02
NH_4^+	189,72 ± 284,31	72,02 ± 104,12	76,74 ± 64,16	69,12 ± 70,81	72,61 ± 30,95
NO_2^-	9,09 ± 6,79	12,29 ± 4,59	7,26 ± 2,04	45,64 ± 38,96	14,11 ± 1,68
NO_3^-	-	-	1,44 ± 3,15	56,22 ± 52,06	82,58 ± 3,10
TP	0,14 ± 0,15	0,50 ± 0,46	0,28 ± 0,18	0,18 ± 0,19	0,10 ± 0,04
Turb	139,00 ± 43,36	509,20 ± 555,16	88,46 ± 48,74	405,13 ± 389,95	92,51 ± 49,74
TS	307,43 ± 33,54	694,82 ± 565,83	335,80 ± 220,84	618,00 ± 362,56	290,67 ± 44,34
FTS	164,29 ± 45,07	505,06 ± 495,29	174,40 ± 85,41	458,33 ± 311,84	179,56 ± 40,36
VTS	143,14 ± 16,41	189,76 ± 105,70	161,40 ± 85,41	159,67 ± 52,09	111,11 ± 9,91
SS	190,99 ± 29,00	539,00 ± 600,61	112,04 ± 70,33	345,15 ± 332,43	70,45 ± 35,19
FSS	123,46 ± 28,08	428,71 ± 512,33	91,82 ± 63,37	298,49 ± 292,86	56,38 ± 29,20
VSS	67,54 ± 21,70	110,89 ± 103,03	20,23 ± 7,98	46,47 ± 40,36	14,08 ± 6,12

Duration (hours); P_{acum} – precipitation accumulated (mm h^{-1}); NB – number of bottles; ΔQ – flow range (m^3 s^{-1}); Cond – conductivity (µS cm^{-1}); Alka – alkalinity (mg $CaCO_3$ L^{-1}); Temp – temperature (°C); DO (mg L^{-1}); DOC (mg C L^{-1}); COD (mg O_2 L^{-1}); TN (mg N L^{-1}); $NH4^+$ - nitrogen ammonia (µg L^{-1}); NO_2^- - nitrite (µg L^{-1}); NO_3^- - nitrate (µg L^{-1}); TP (mg P L^{-1}); Turb – turbidity (NTU); TS (FTS:VTS) and SS (FSS:VSS) (mg L^{-1}).

DOC concentrations had bigger values in event 1 (5,74± 3,83 mg C L^{-1}) and less values in event 9 (2,84 ± 0,76 mg C L^{-1}). In slow rainfall the concentrations increase, while in intensive rainfall concentrations decrease can be due to dilution by amount of water discharged into the river. The values measured are similar to found by Gao et al. (2014) and Oh et al. (2013), but DOC concentrations increase in rainfall event. For Gao et al (2014), average DOC concentration range from 2,49 ± 1,41 mg L^{-1} in base flow to 4,72 ± 3,30 mg L^{-1} during rainstorm event. In Oh et al (2013) study, DOC concentrations increase up to 10,1 mg L^{-1} during storm event (base flow concentration about 1,1 ± 3,8 mg L^{-1}). Equally, Butturini et al. (2006) also found DOC concentrations increasing in all storm events measured in research of them.

For physical parameters, event 2 carried the biggest pollutant mass in comparison to others events, which can be due the specifics characteristics for this event. Turbidity has average about 509,20 ± 555,16 NTU, total solids and suspended solids has concentrations about 694,82 ± 565,83 and 539,00 ± 600,61 mg L^{-1}, respectively. Similarly, Oliveira and Cunha (2014) showed that during dry periods turbidity values are less than in rainy periods (< 60 NTU) in Lower Jari River (Amapá State, Brazil). Nevertheless, rainfall also can favor turbidity decrease (Silva et al, 2008) according rainfall characteristics, as long-duration or high-intensity. This can be observed in event 9 and 11 that had the lowest values of turbidity and serial solids due high-intensity with long-duration rainfall, and rainfall distributed along event duration, respectively. Silva et al. (2008) observed increase in suspended solids due influences of precipitation.

Event 10 brought lower values than event 2 for physical parameters, but similar when compared with other events, because some of its characteristics were the same of event 2 like high intensity in short time space (duration of 22,67 hours and rainfall volume of 31,50 mm). Besides, event 10 had the lowest nitrogen ammonia concentration (69,12 ± 70,81 µg N L^{-1}) and the biggest values of nitrite (45,64 ± 38,96 µg N L^{-1}) among all events.

4.6. Special Events

Special events are classified due to changes in water column level without rainfall interferences. The change occurs in a range that the equipment interprets as "change caused by rain" and then collected a sample. Some variations were by flow increase as extra water in the system, so denominated as water discharge, and another, flow decrease, classified as water sink, as indicated in Table 12. For each condition are indicated the number of bottles collected, the volume of water removed or discharge in river, flow range between the lowest and highest flow value observed (ΔQ), and the duration of this condition.

Table 12 - Characteristics of specials events performed

Special Events								
Events	*Additional Discharge*				*Water sink*			
	Bottles collected	Volume (10^4 m^3)	ΔQ (m^3 s^{-1})	Duration (h)	Bottles collected	Volume (10^4 m^3)	ΔQ (m^3 s^{-1})	Duration (h)
5	3	5,36	1,71 – 2,45	7,53	1	2,87	1,73 - 1,16	5,58
6	-	-	-	-	3	1,80	2,12 – 1,36	3,13
7	4	2,96	1,68 – 2,71	3,96	2	3,29	1,60 – 1,01	7,08
8	5	2,66	1,40 – 2,46	3,83	1	1,24	1,50 – 1,03	2,66
	6	2,96	1,51 – 2,54	4,36				

4.6.1. Event 5

The event 5 started in 27th March colleting 4 bottles. This event happened without rain, so can be characterized by water output and input. The SBN equipment cannot identify if it was raining or not, just can identify the difference of level water column. Figure 55 represents event 5, also sampled by SBN.

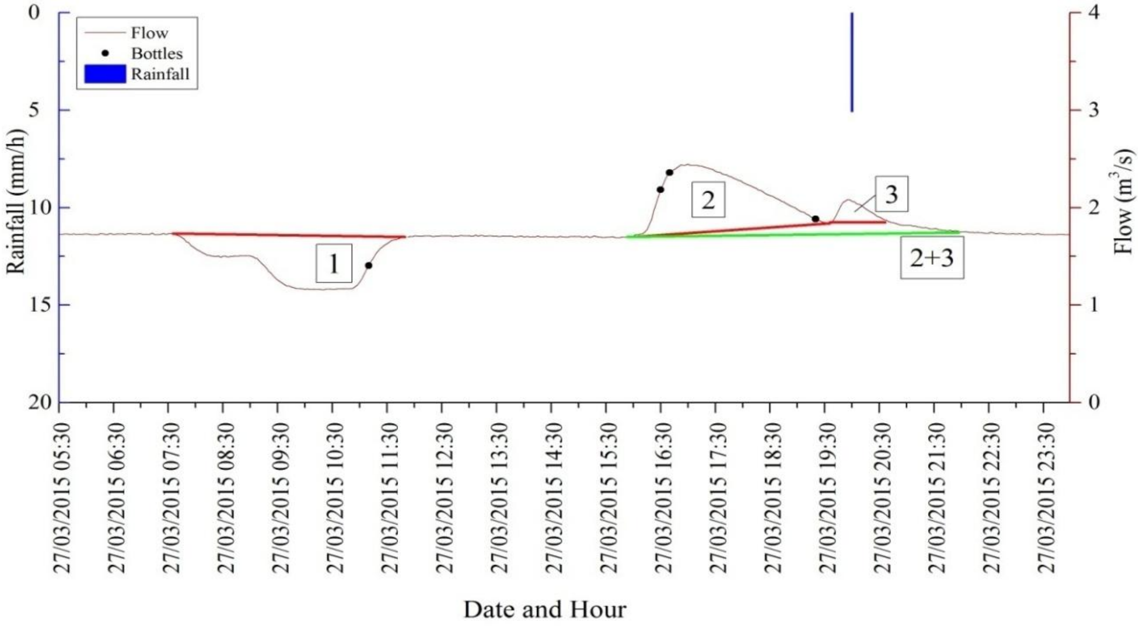


Figure 55 - Event 5

The part 1 is characterized by a water removal. The initial flow was approximately 1,73 m³ s^{-1} decreasing until 1,16 m³ s^{-1}. When the flow was being reestablished the SBN identify a variation in water column and did another sampling. The flow returns to 1,70 m³ s^{-1}. This event had a duration about 5,58h and had a removal approximately of 2,87.10^{4} m³ of water.

The parts 2 and 3 characterizes a water discharge. The flow increased until 2,18 m³ s^{-1} collecting a samples, then increasing more to 2,35 m³ s^{-1} collecting again, reaching until 2,45 m³ s^{-1}. This discharge had a volume about 2,77.10^{4} m³ of water. Shortly thereafter other discharge occurs, part 3. This little event had a initial flow of 1,84 m³ s^{-1} increasing until 2,08 m³ s^{-1} with a duration about 1,25h. The part 2 had a volume discharged of 8,78.10^{3} m³ approximately. The part 2 plus part 3 had a discharged about 5,36.10^{4} m³ during 5,58h. After 3 hours the flow reestablishing to 1,72 m³ s^{-1}. It can be observed that occur a rainfall during the discharge in part 3. Therefore this rainfall not allows variation in flow rate.

For the water quality parameters, DO, pH, temperature and alkalinity had a little increase following the discharge, with peak in bottle 3. The conductivity stayed stable. The average for this parameters was, respectively, 8,67 ± 0,02 mg O_2 L^{-1}; 8,16 ± 0,05; 15,68 ± 0,26 °C; 170,00 ± 2,59 mg $CaCO_3$ L^{-1} and 261,25 ± 2,06 µS cm^{-1}. Figure 56 shows pollutographs of water quality parameters mentioned above.

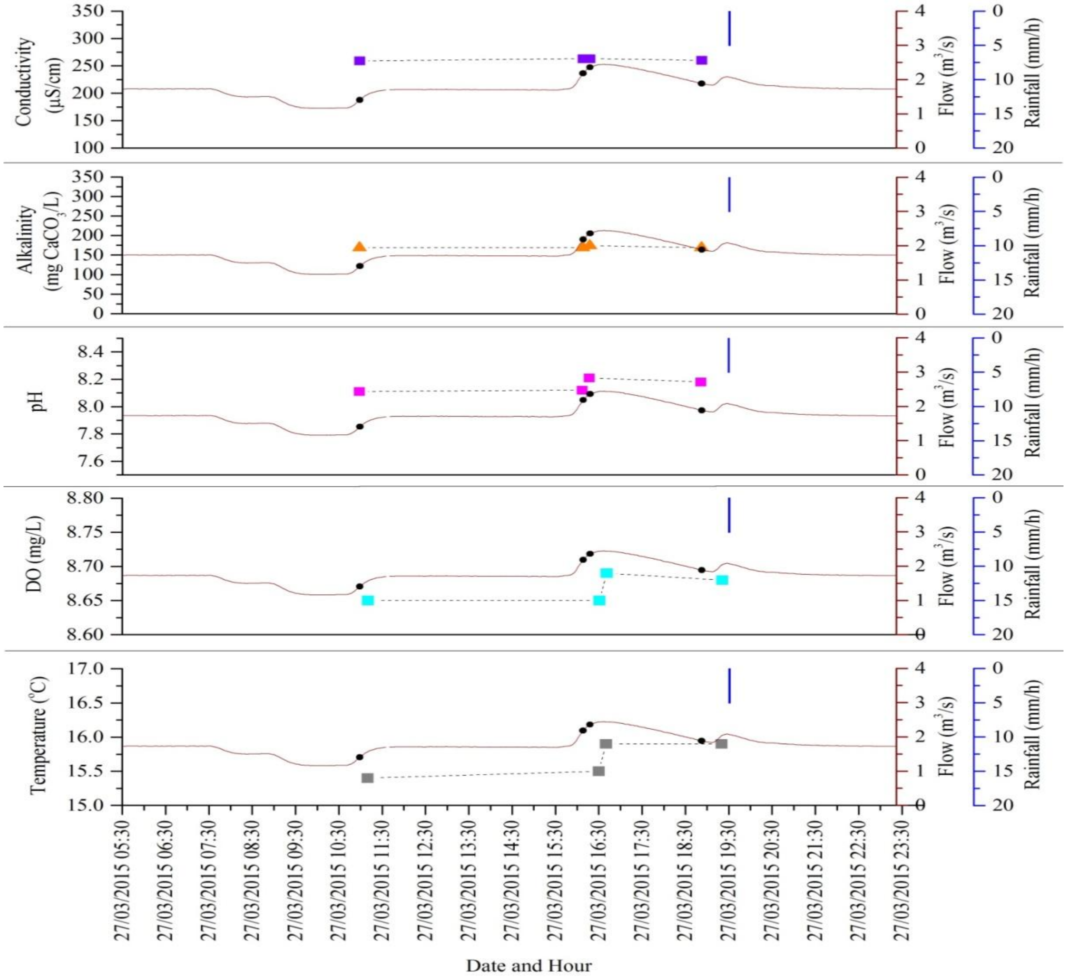


Figure 56 - Distribution of conductivity, alkalinity, pH, DO and temperature along event 5

COD and TP concentrations had a decrease followed discharge, instead the TN concentration that had an increase. TN > TP for all bottles. The average for COD, TP and TN was 10,10 ± 1,63 mgO$_2$ L^{-1}, 0,07 ± 0,03 mg P L^{-1} and 0,46 ± 0,02 mg N L^{-1}. Figure 57 shows COD, TN and TP pollutographs from event 5.

For physical parameters, turbidity and TS followed the discharge. The peak happened in bottle 3 with 83,6 NTU and 308:244:64 mg L^{-1} respectively to turbidity, TS:FTS:VTS. Instead of that behavior, SS decrease along the event, then the peak occurs in first bottle with 241:206:35 mg L^{-1}for SS:FSS:VSS. Figure 58 shows turbidity, TS and SS pollutographs from event 5. The average for turbidity was 64,35 ± 17,44 NTU, for TS (FTS and VTS) was 255 ± 37 mg L^{-1} (210 ± 27 and 45 ± 16 mg L^{-1}) and for SS (FSS and VSS) was 104 ± 93 mg L^{-1} (85 ± 82 and 19 ± 11 mg L^{-1}).

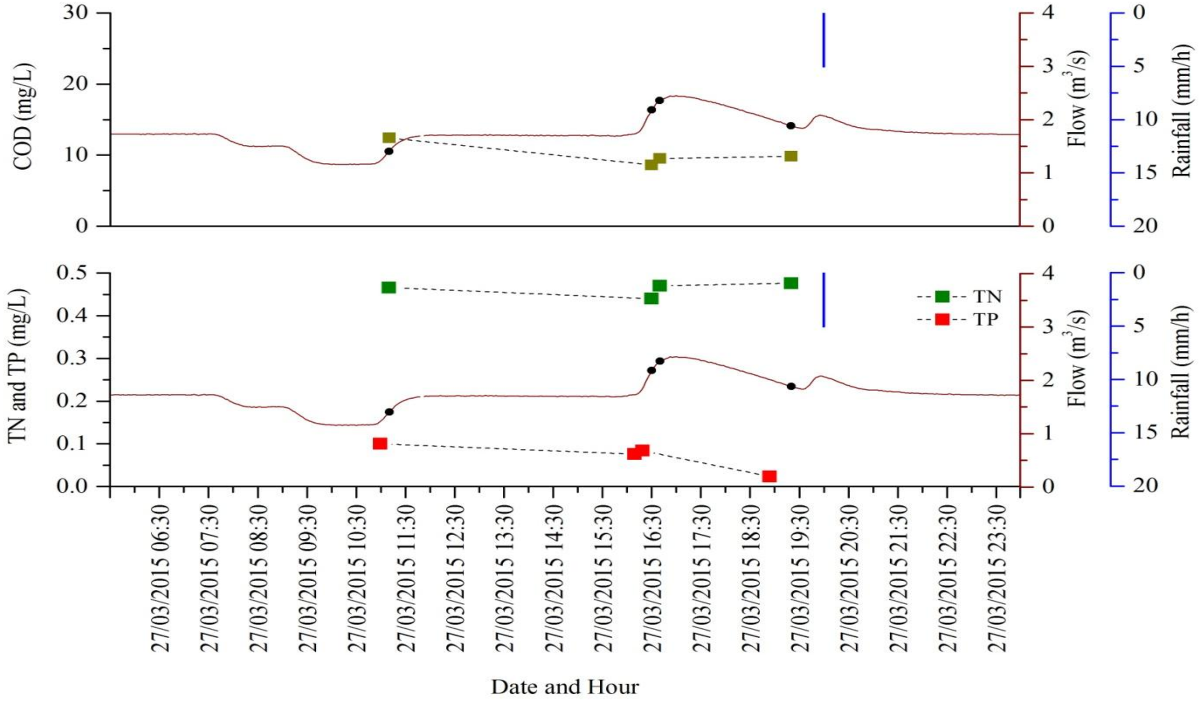


Figure 57 - Distribution of COD, TN and TP along event 5

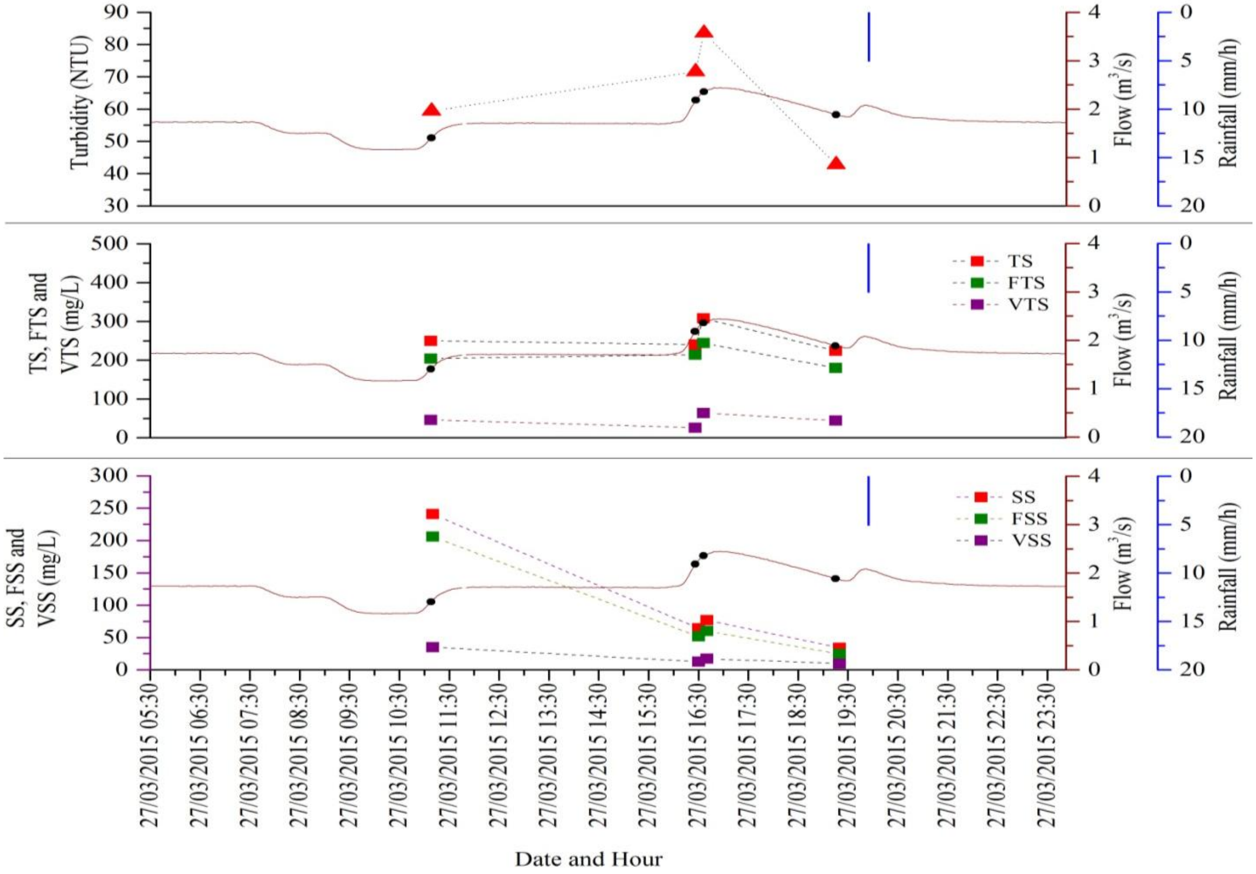


Figure 58 - Distribution of turbidity, TS (VTS and FTS), and SS (VSS and FSS) along event 5

4.6.2. Event 6

The event 6 started in 29th March and finished in 31st March, collecting 6 bottles, as presented in Figure 59. This event cannot be classified as pollution diffuse event, because there were some variations that can be classified as water removal.

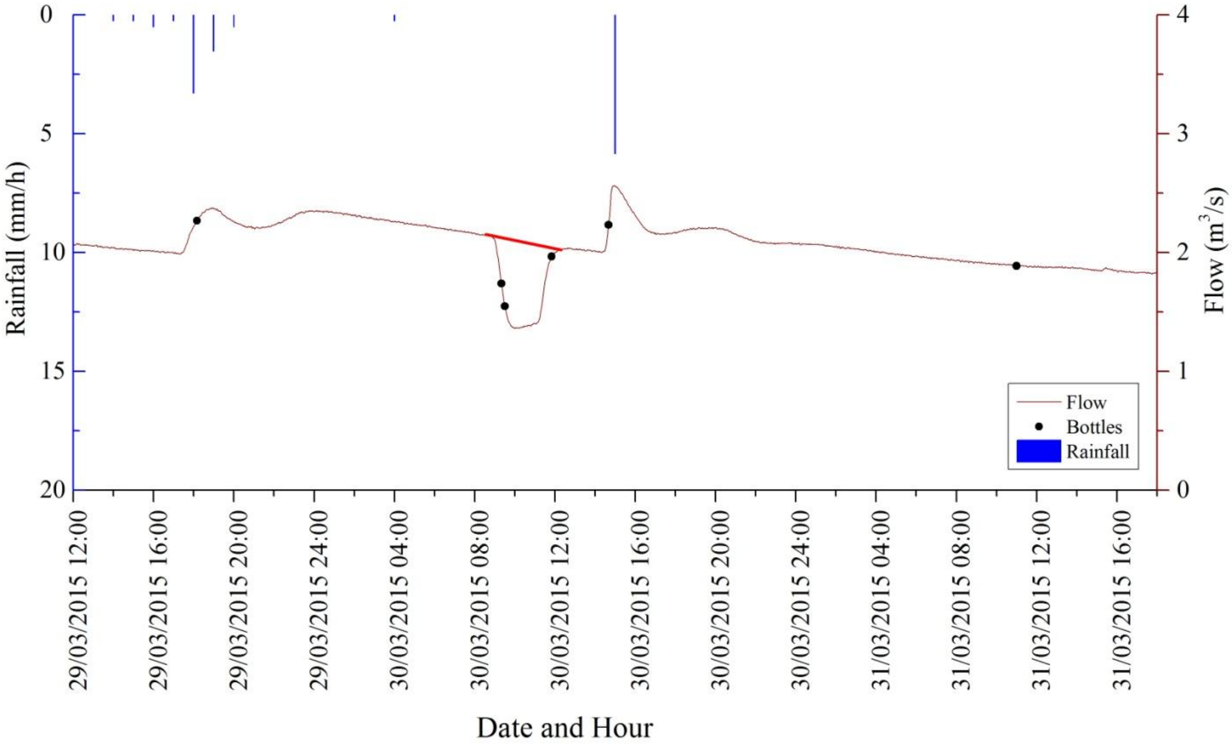


Figure 59 - Event 6

As can be observed, there was rainfall in beginning of the event, during 7 hours and accumulating 6,6 mm approximately. In general, the water body tends to assimilate water input by the rain with very few variations. Approximately 14 hours after the end of the event, there was a water removal event, producing a flow variation about 0,78 m³ s^{-1} (decreasing from 2,14 m³ s^{-1} to 1,36 m³ s^{-1}). During water removal, SBN was trigged twice (9:20 and 9:30 a.m.)

The water volume removed from the river was approximately $1{,}80.10^4$ m³ along 3 hours. Then, a rain happened but without promoting significantly changes in river flow that could induce SBN to collect.

For the water quality parameter: alkalinity and conductivity were stables. The average for this parameters were, respectively, 157,49 ± 4,74 mg $CaCO_3$ L^{-1} and 237,67 ± 8,76 µS cm^{-1}. For pH, DO and temperature the values had increase during the water removal, with average of 8,02 ± 0,13, 8,48 ± 0,44 mgO_2 L^{-1} and 15,22 ± 0,48 °C. Figure 60 shows pollutographs of water quality parameters mentioned above.

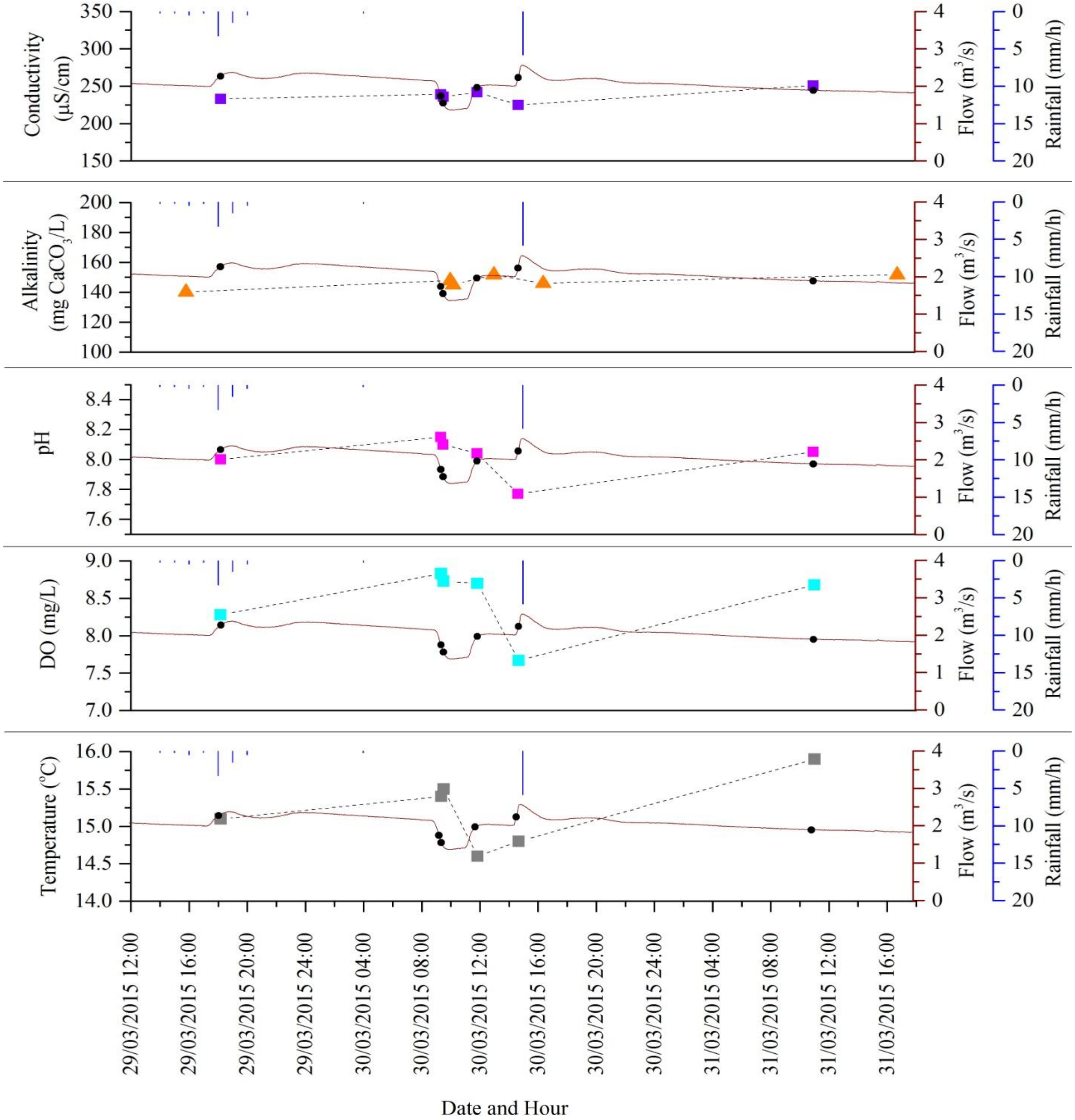


Figure 60 - Distribution of conductivity, alkalinity, pH, DO and temperature along event 6

The chemical parameters as COD and TP had decrease during the water removal, however the concentration increase in bottle 5 that represent the hydrograph ascent. For TP concentration peak occurred in bottle 5 with concentration of 0,23 mg P L^{-1}. TN concentration also had the peak in bottle 5 (0,55 mg L^{-1}), but during the event concentrations did not have much variations. DOC had a peak in bottle 3 with 3,50 mg L^{-1}, while for the last bottle DOC concentration cannot be measured. The average for DOC, COD, TP and TN concentration were, respectively, 2,16 ± 1,05 mg C L^{-1}, 14,53 ± 4,21 mgO_2 L^{-1}, 0,11 ± 0,06 mg P L^{-1} and 0,49 ± 0,03 mg N L^{-1}. Figure 61 shows DOC, COD, TN and TP pollutographs for event 6.

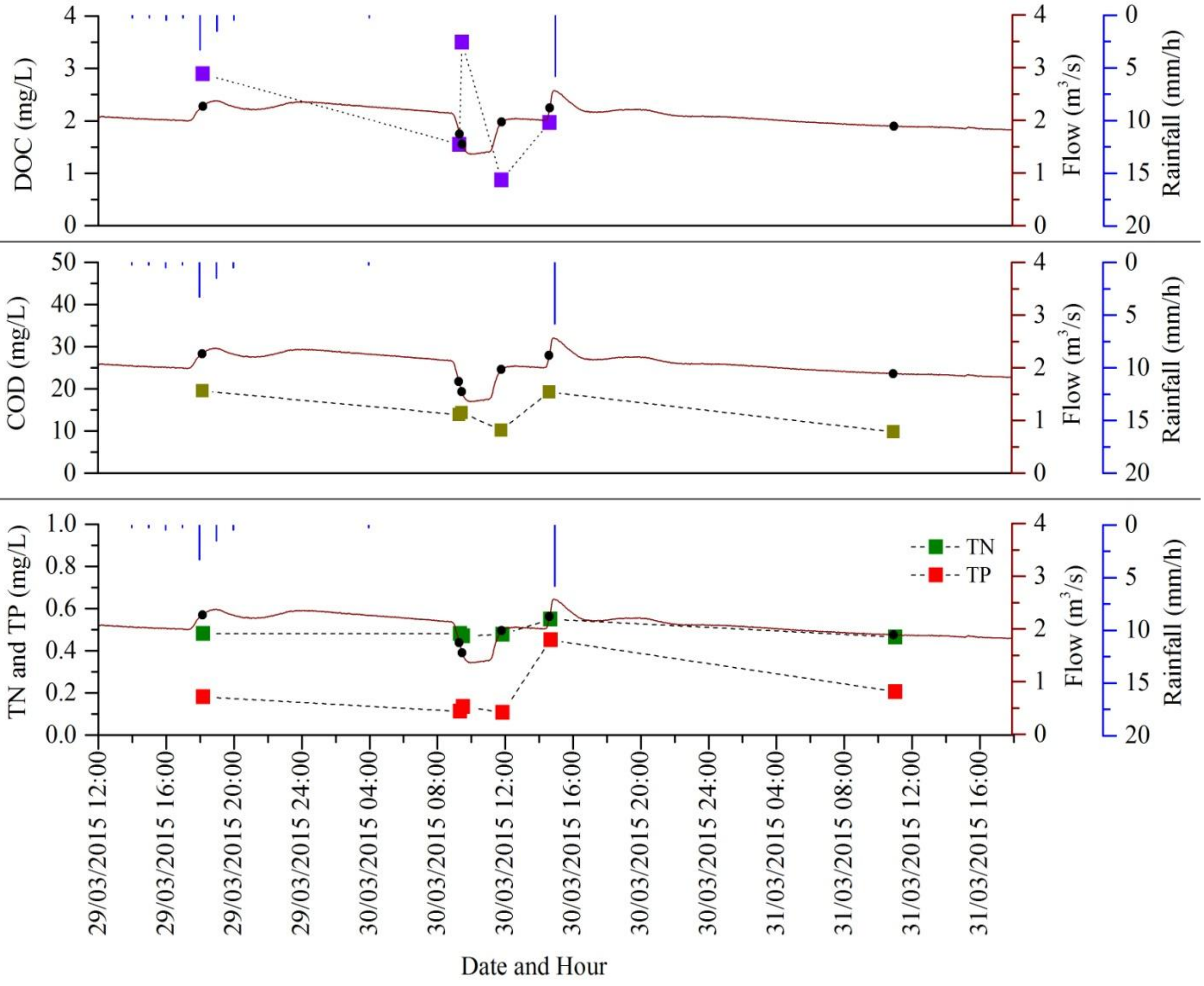


Figure 61 - Distribution of DOC, COD, TN and TP along event 6

Turbidity had a behavior similar to the flow, the values increase and decrease according the flow. The average for turbidity was 63,62 ± 17,07 NTU. TS also had a behavior similar to the flow, but during the water removal the concentration decreasing; the average for TS (FTS and VTS) was 213 ± 21 mg L^{-1} (186 ± 24 and 27 ± 16 mg L^{-1}). For SS the values decreasing during the water removal and then increased significantly following the hydrograph ascent, with peak in bottle 5 (100:75:25 mg L^{-1} for SS:FSS;VSS). The average for SS (FSS and VSS) was 63 ± 25 mg L^{-1} (48 ± 19 and 15 ± 6 mg L^{-1}).Figure 62 shows turbidity, TS and SS pollutographs from event 6.

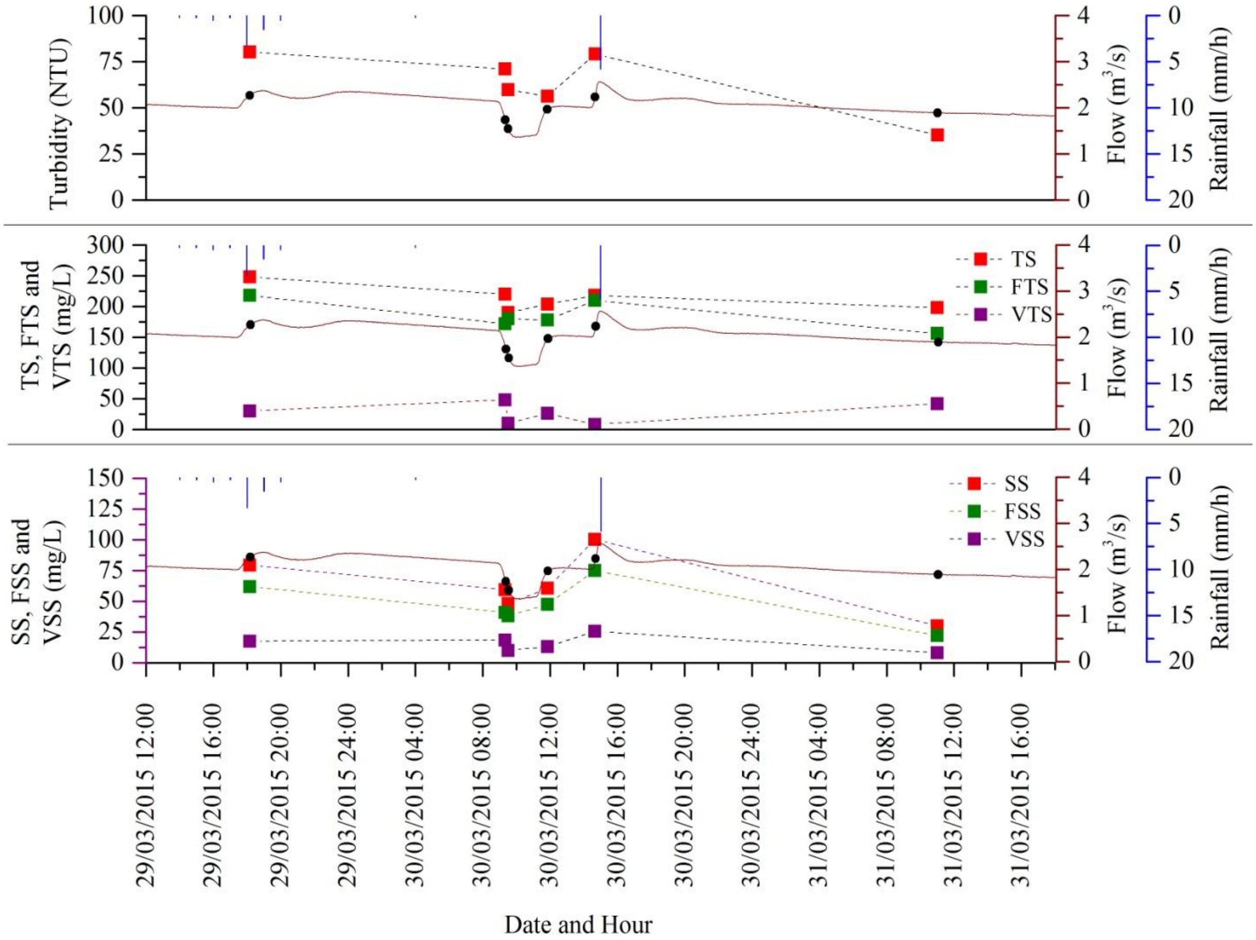


Figure 62 - Distribution of turbidity, TS (VTS and FTS), and SS (VSS and FSS) along event 6

4.6.3. Event 7

This event can be divided into 2 parts. The first one happened on 2nd April characterized as a water discharge event. The second one happened in 7th April characterized as a water removal event. Figure 63 represents event 7.

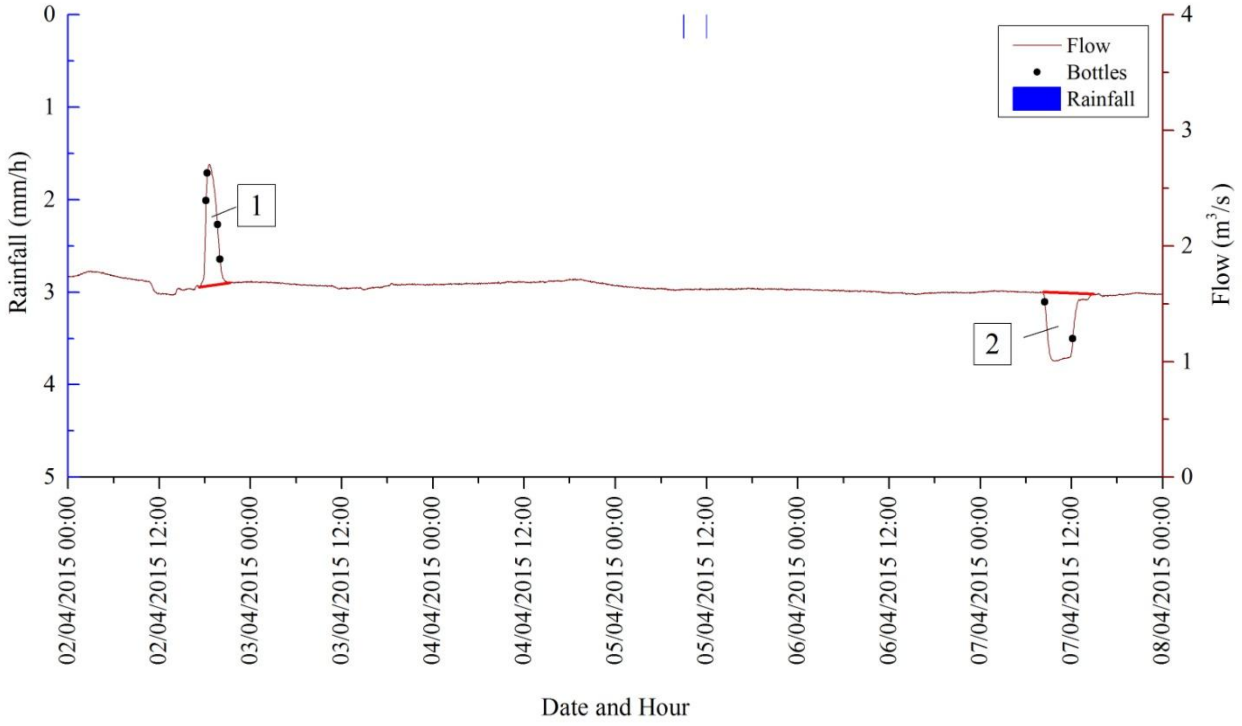


Figure 63 - Event 7

The event 7 part 1 had flow change with a water discharge. The flow was 1,68 m³ s^{-1} approximately, before discharge. After a hour the flow increase to 2,71 m³ s^{-1} that was peak flow. This part had a duration ~ 4 hours, with a volume of $2{,}96.10^4$ m³ discharged into the river and provided the level variation enough to SBN collected 4 bottles.

Considering the chemical water quality parameters, COD could not be measured (< detection limit); TN was bigger than TP in all bottles without much variations; for N fraction, N-NH_3 was found in most concentration. The average for TP, TN and N-NH_3 concentration was, respectively, 0,07 ± 0,02 mg P L^{-1}, 0,39 ± 0,005 mg N L^{-1} and 40,51 ± 10,25 µg N L^{-1}. For solids, the concentrations increased in ascent bottles, and decreased in bottles 3 and 4, but with significantly changes to SS. The peak occurred in bottle 2, with 292:220:72 mg L^{-1} for TS:FTS:VTS and 126:99:26 mg L^{-1} for SS:FSS:VSS. The average for TS (FTS and VTS) was 250 ± 45 mg L^{-1} (184 ± 38 and 65 ± 8 mg L^{-1}) and SS (FSS and VSS) was 77 ± 50 mg L^{-1} (59 ± 40 and 18 ± 9 mg L^{-1}). COD had a increase whit discharge, with peak in bottle 3 of 3,29 mg L^{-1}. Figure 64 show DOC pollutograph.

The event 7 part 2 had a flow change with water removal. Initial flow was approximately 1,60 m^3 s^{-1} at 07:55 a.m. and decrease until 1,01 m^3 s^{-1} (maximum decrease) in about 2 hours. Flow returns to 1,58 m^3 s^{-1} at 3:00 p.m. This event had a duration about 7,08 h with a removal volume of 3,29.10^4 m^3. For water quality parameters, COD could not be measured (< detection limit); For N fraction, N-NH$_3$ had most present and TN > TP. The average for TN was 0,39 ± 0,004 mg N L^{-1} and TP was 0,07 ± 0,01 mg P L^{-1}. TS concentrations was bigger than SS concentrations, with an average of 221 ± 10 mg L^{-1} for TS, 164 ± 3 mg L^{-1} for FTS, 57 ± 13 mg L^{-1} for VTS, 43 ± 9 mg L^{-1} for SS, 27 ± 7 mg L^{-1} for FSS and 16 ± 2 mg L^{-1} for VSS. Figure 65 and Figure 66 shows TP, nitrogen series, TS and SS pollutographs for all event 7. COD decrease together water sink, and maximum concentration decrease was 0,92 mg L^{-1} (Figure 64).

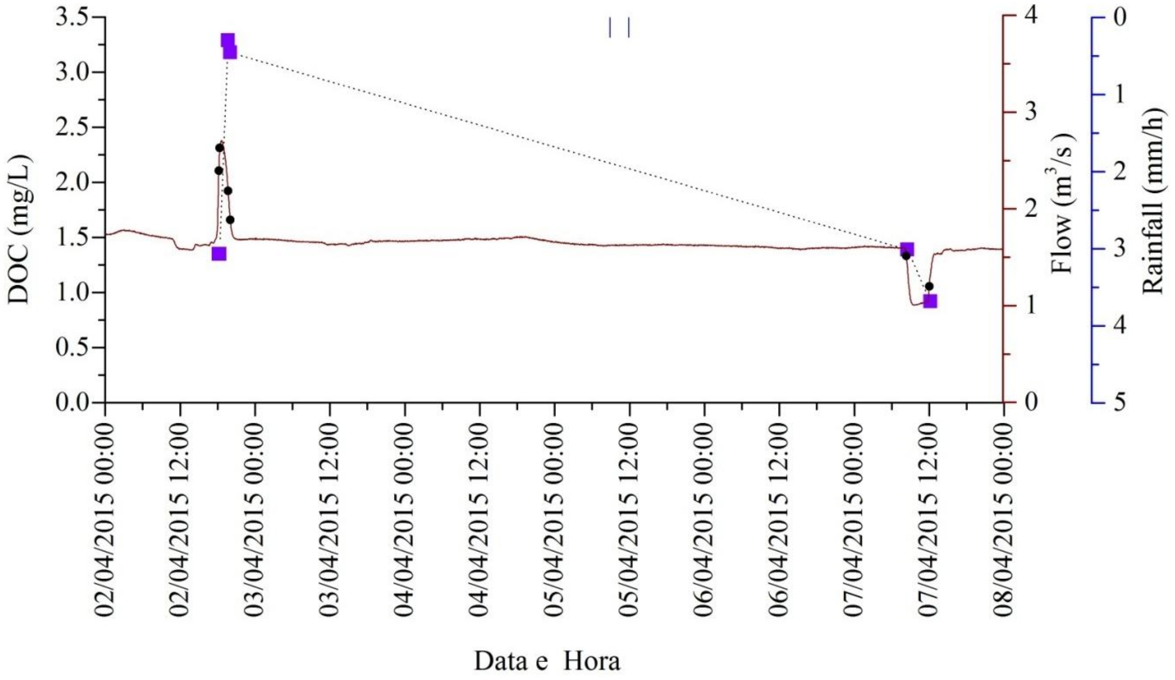


Figure 64 - Distribution of DOC for event 7

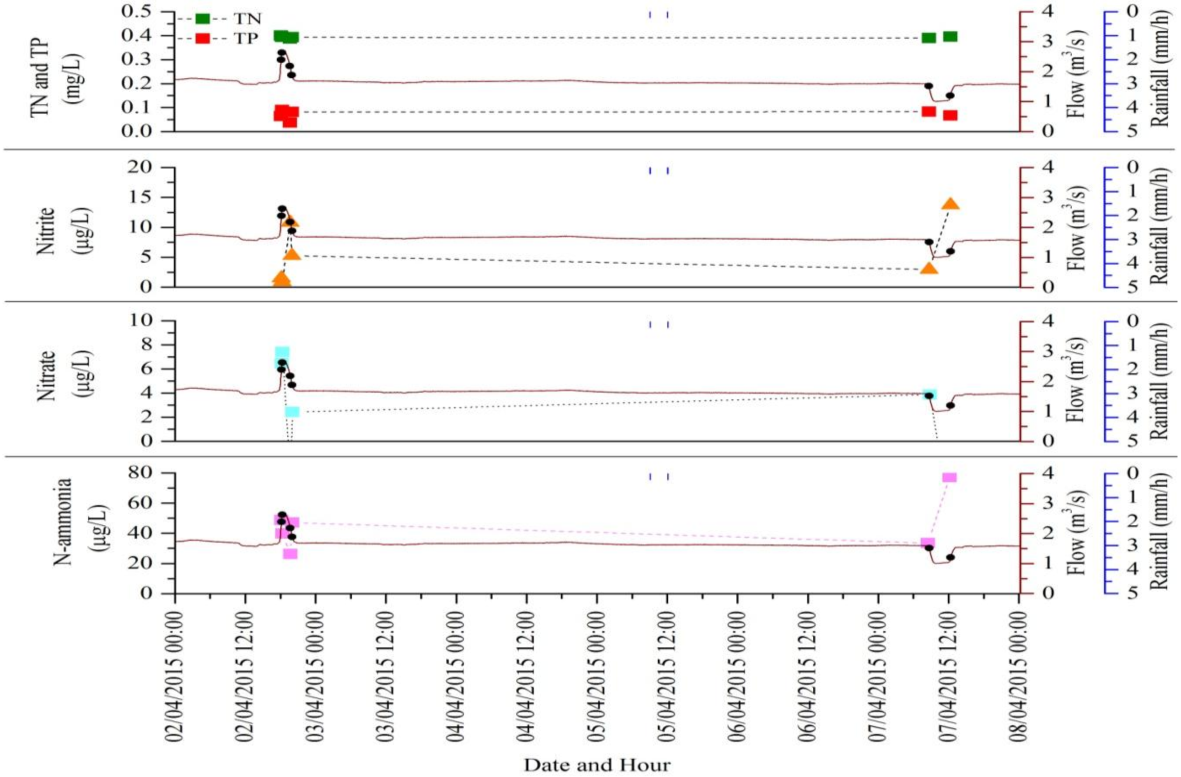


Figure 65 - Distribution of TP and nitrogen series for event 7

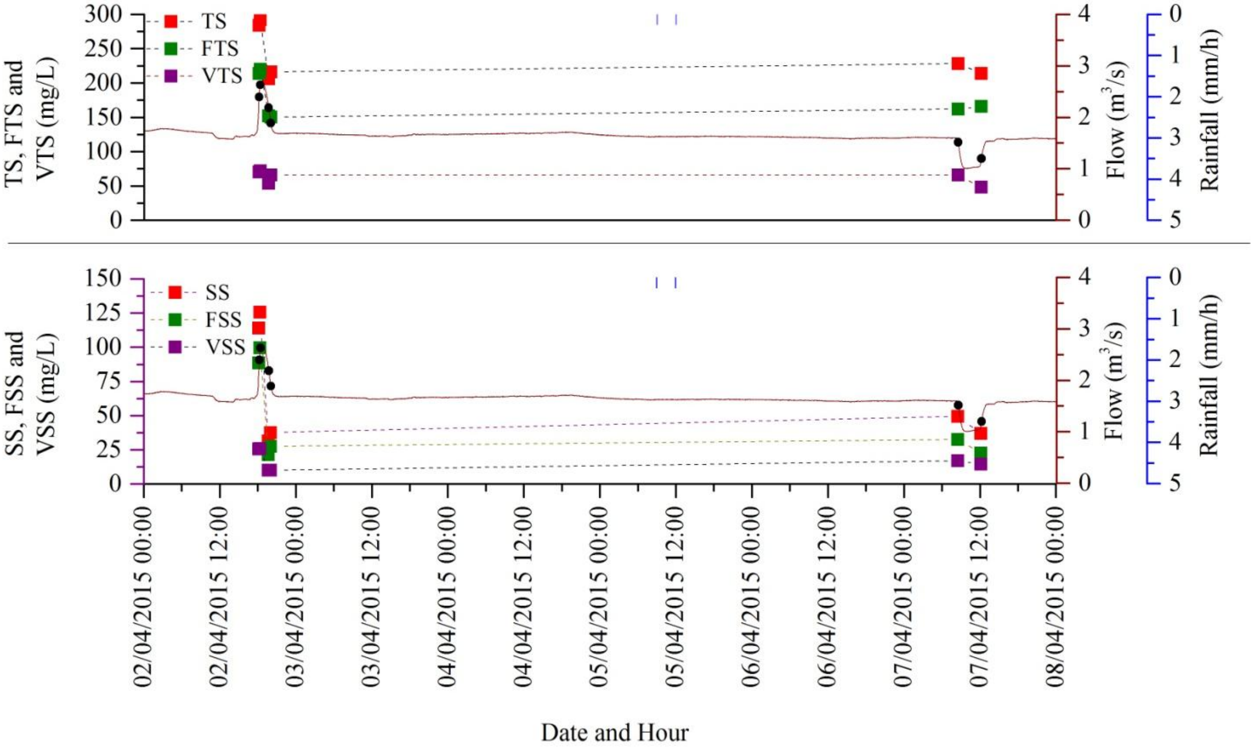


Figure 66 - Distribution of TS (VTS and FTS), and SS (VSS and FSS) along event 7

4.6.4. Event 8

This event was divided in 3 parts. The first one is characterized as a water discharge event happened in 17th April. The second is characterized as a removal event happened in 18th April, and the last on happened in 20th April being characterized as a water discharge event. Figure 67 represents event 8.

Event 8 part 1 collected 5 bottles during the flow ascent and decrease without rainfall occurrence, because that was classified as water discharge. The initial flow was 1,40 m³ s^{-1} at 5:25p.m., increasing until 2,46 m³ s^{-1} at 6:20 p.m. (peak flow). After this, in approximately 3 hours the flow returns to 1,53 m³ s^{-1}. The water discharge volume was $2{,}66.10^4$ m³.

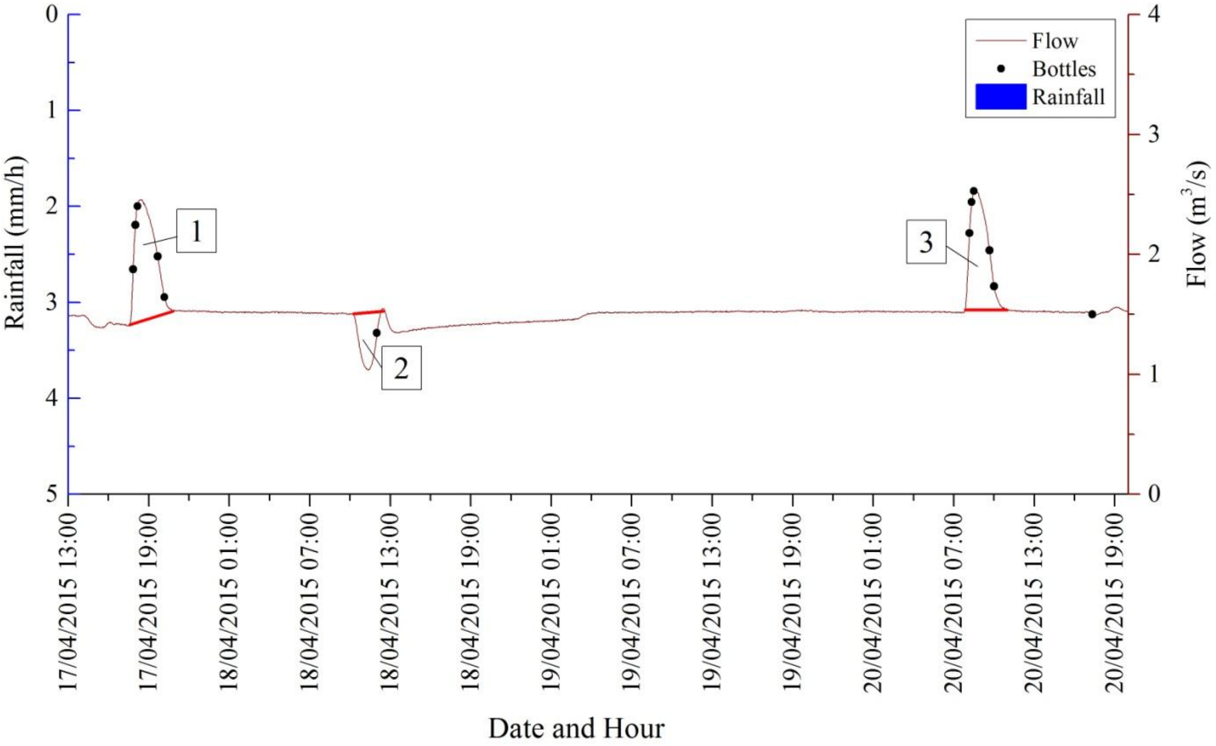


Figure 67 - Event 8

Alkalinity, conductivity, pH, DO and temperature remained with stable values among the bottles. The average for this water quality parameters was, respectively, 175,77 ± 5,35 mg $CaCO_3$ L^{-1}, 309,00 ± 3,67 µS cm^{-1}, 8,26 ± 0,03, 8,01 ± 0,14 mg O_2 L^{-1} and 20,68 ± 0,59 °C. For the chemical parameters, as COD, TN and TP, the behavior followed the discharge, increase and decrease along the flow. COD peak occurred in bottle 2 with 18,78 mg O_2 L^{-1}. TN concentrations was more stable than TP concentrations, that had more variation during the flow ascent; and TN>TP in all bottles. Considering the N fraction, nitrate was found more than ammonia nitrogen and nitrite. The average for COD, TP, TN (N-NH_3; NO_2^-; NO_3^-) was, respectively, 7,47 ± 7,15 mg O_2 L^{-1}; 0,22 ± 0,10 mg P L^{-1}; 0,41 ± 0,01 mg N L^{-1} (3,55 ± 4,54 µg N-NH_3 L^{-1}; 2,96 ± 2,29 µg NO_2^- L^{-1}; and 6,51 ± 2,85 µg NO_3^- L^{-1}). Similarly, the physical parameters followed the discharge behavior and the peak was in bottle 3: 101 NTU for turbidity, 332:242:90 mg L^{-1} for TS:FTS:VTS and 207:170:38 mg L^{-1} for SS:FSS:VSS. The average for turbidity was 59,06 ± 35,06 NTU, for TS and their fractions (FTS and VTS) was 273 ± 59 mg L^{-1} (197 ± 49 and 76 ± 11 mg L^{-1}) and for SS and their fraction (FSS and VSS) was 122 ± 80 mg L^{-1} (99 ± 67 and 23 ± 13 mg L^{-1}). DOC had concentration decrease with water sink. The minimum value measured was 1,29 mg L^{-1}. The average for DOC was 3,31 ± 2,09 mg L^{-1}; All pollutographs for these parameters are show in Figure 68 to Figure 71.

The part 2 correspond a water removal event due the flow decrease under the values normally expect. This event happened in 18th April with duration about 3 hours. Initial flow was 1,50 m^3 s^{-1} at 10:00 a.m. decreasing to 1,03 m^3 s^{-1} at 11:20 a.m. and reestablishing the flow initial at 12:40 a.m. The amount of water removed was approximately $1{,}24.10^4$ m^3.

Event 8 part 3 correspond a second water discharge and SBN collected 6 bottles. This part happened in 20th April, with initial flow 1,51 m^3 s^{-1} at 07:45 a.m. increase to 2,54 m^3 s^{-1} at 08:37 a.m. (peak flow). Around 12:07 p.m. the flow returns to the normal (1,52 m^3 s^{-1}) in that day. The volume of water discharged was approximately $2{,}96.10^4$ m^3.

For alkalinity and conductivity the values decrease while the flow increase, with maximum decrease in bottle 3 (175,56 mg $CaCO_3$ L^{-1} for alkalinity and 308 µS cm^{-1} for conductivity). The average for alkalinity and conductivity was, respectively, 179,57 ± 2,84 mg $CaCO_3$ L^{-1} and 312,00 ± 3,03 µS cm^{-1}. Temperature remained stable with average of 20,15 ± 0,15 °C. Equally, pH remained stable with alkaline values and average of 8,21 ± 0,04. DO concentrations had an increase behavior during the water discharge. The lower value happened in first bottle (7,87 mg O_2 L^{-1}), increasing until 8,13 in bottle 4 (peak). The average for DO concentrations was 8,05 ± 0,09 mg O_2 L^{-1}.

DOC had a peak in bottle 2 with 3,19 mg L^{-1}, while values measured in others bottles was around 1,5 mg L^{-1}. COD had peak in bottle 4 with 11,34 mg O_2 L^{-1}, while the TP peak happened in bottle 2 (0,26 mg P L^{-1}) and TN did not wide variation among the bottles collected. TN > TP in all bottles. Observing the N fractions, values possibly indicate the nitrogen cycle occurrence, whereas while nitrate concentration was larger, nitrite and ammonia nitrogen was less. For example in bottle 2 that represent the nitrate peak with 8,27 µg N L^{-1}, 1,01 µg N L^{-1} for nitrite and ammonia nitrogen below detection limit. Reverse was observed in bottle 5 (ammonia nitrogen peak) with 23,23 µg N L^{-1}, 7,45 µg L^{-1} for nitrite and 1,11 µg L^{-1} for nitrate. The average for DOC, COD, TP, TN (nitrate, nitrite and ammonia nitrogen) was, respectively: 1,96 ± 0,62 mg L^{-1}; 4,15 ± 6,31 mgO$_2$ L^{-1}; 0,17 ± 0,08 mg P L^{-1}; 0,41 ± 0,01 mg N L^{-1} (5,74 ± 2,95 µg L^{-1}; 3,14 ± 2,59 µg L^{-1}; and 13,76 ± 14,75 µg L^{-1}). Pollutographs are show in Figure 68 to Figure 71.

Physical parameters followed discharge behavior, increasing with ascent flow. The peak happened in bottle 2 with 70,5 NTU for turbidity, 360:208:152 mg L^{-1} for TS:FTS:VTS and 176:140:36 mg L^{-1} for SS:FSS:VSS. The average for turbidity in this part was 38,68 ± 22,63 NTU, for TS was 292 ± 59 mg L^{-1}, for FTS and VTS was respectively, 193 ± 29 mg L^{-1} and 99 ± 39 mg L^{-1}; for SS was 102 ± 69 mg L^{-1}, for FSS was 79 ± 59 mg L^{-1} and for VSS was 22 ± 10 mg L^{-1}.

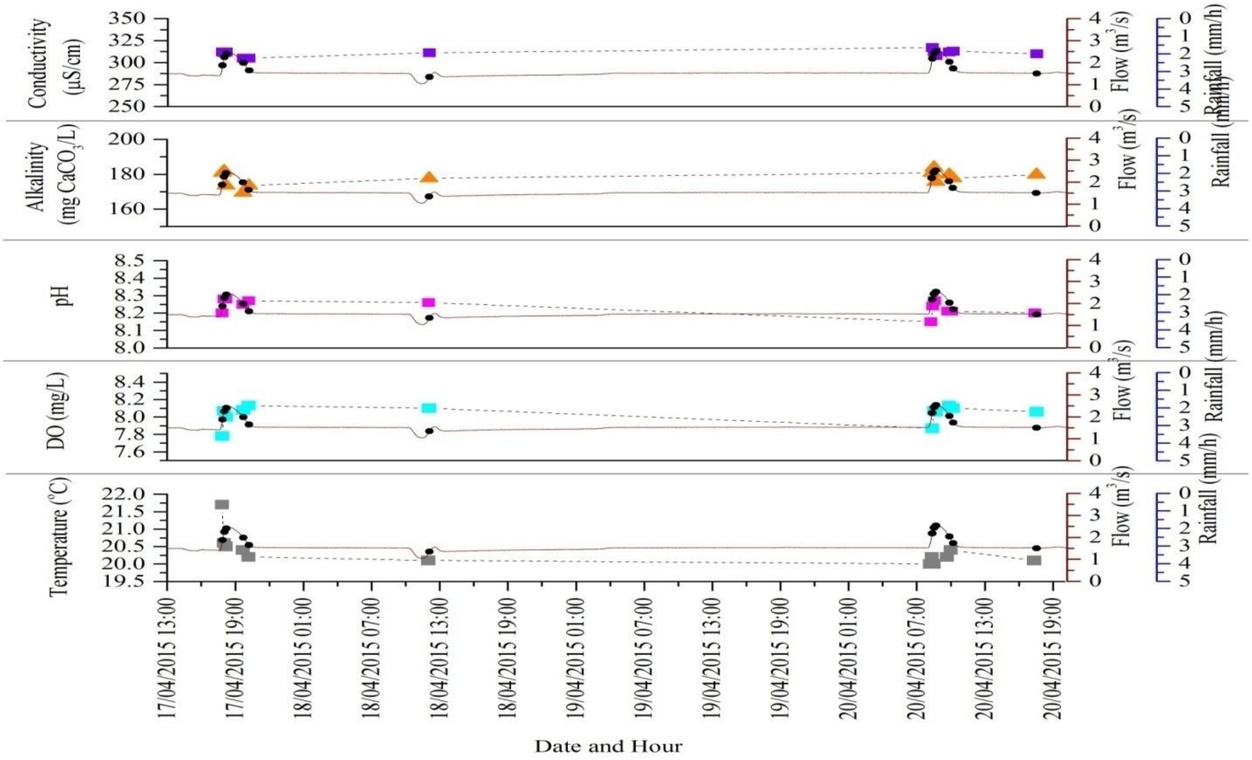


Figure 68 - Distribution of conductivity, alkalinity, pH, DO and temperature along event 8

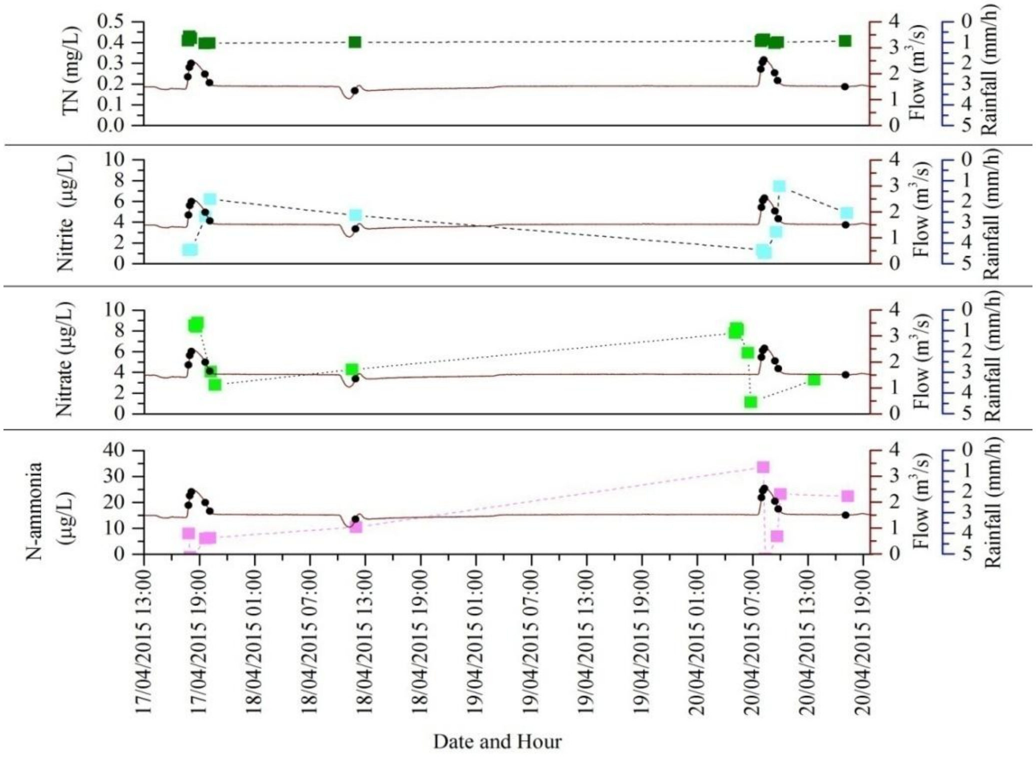


Figure 69 - Distribution of nitrogen cycle for event 8

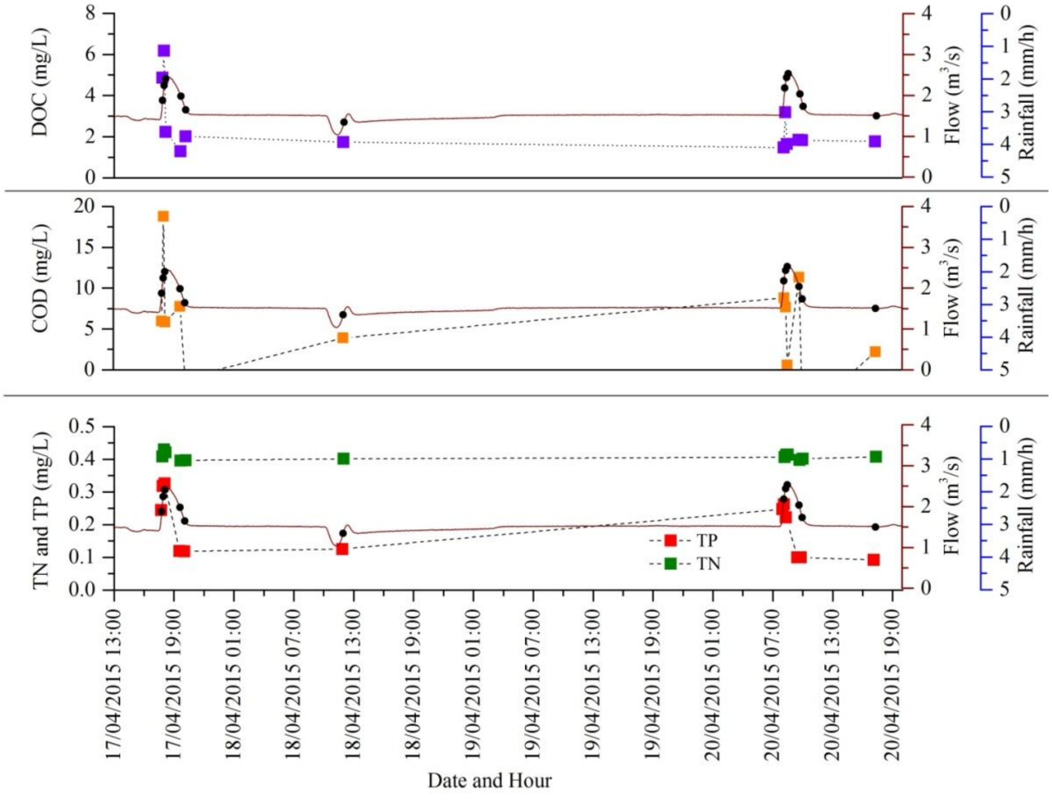


Figure 70 - Distribution of COD, TN and TP along event 8

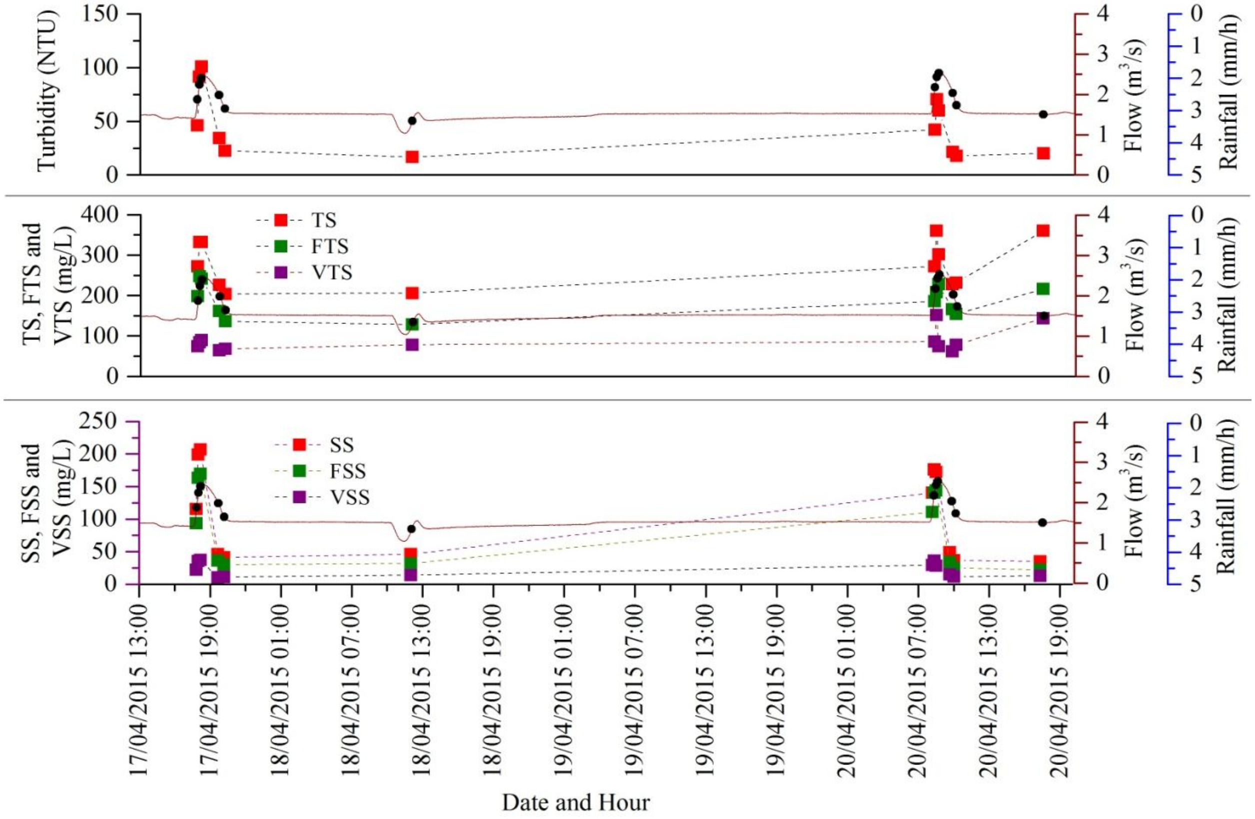


Figure 71 - Distribution of turbidity, TS (VTS and FTS), and SS (VSS and FSS) along event 8

Table 13, as follows, summarize the characteristics of special events and average of water quality parameters for each event performed. Event 5 had the biggest water discharge (5,36 m^3), but event 8 part 1 had the biggest flow variation, about 1,06 m^3 s^{-1} (1,40 – 2,46 m^3 s^{-1}). This happened because event 8 had a faster discharge than event 5 and, consequently the river response was fast and produce a peak discharge. The discharge in event 5 was longer during the time, not producing wide flow range instantly (about 0,75 m^3 s^{-1} [1,70 – 2,45 m^3 s^{-1}]). Additionally, event 8 had the biggest DOC concentrations (3,31 ± 2,09 mg C L^{-1}).

PH and DO values were bigger than 8 in all special events performed. The high pH values are due the site geochemical characteristics and DO can say that water removal and discharge can produce some aeration and it´s not produced significantly changes in oxygen dynamics into the river. N:P ratio indicates that nitrogen was limiting factor in all events. The physical parameters remained stables among events, and turbidity values were lower values than turbidity of rainfall events.

Table 13 - Summary of special events and range of water quality parameters

	Events					
	5	6	7		8	
Class	WS / WD	WS	WD	WS	WD1	WD2
NB	4	6	4	2	5	6
Vol	2,87 / 5,36	1,80	2,96	3,29	2,66	2,96
ΔQ	1,73 – 1,16/ 1,70 – 2,45	2,14 – 1,36	1,68 – 2.71	1,60 – 1,01	1,40 – 2,46	1,51 – 2,54
Cond	261,25 ± 2,06	237,67 ± 8,76	-	-	309,00 ± 3,67	312,00 ± 3,03
Alka	170,00 ± 2,59	157,49 ± 4,74	-	-	175,77 ± 5,35	179,57 ± 2,84
Temp	15,68 ± 0,26	15,22 ± 0,48	-	-	20,68 ± 0,59	20,15 ± 0,15
pH	8,16 ± 0,05	8,02 ± 0,13	-	-	8,26 ± 0,03	8,21 ± 0,04
DO	8,67 ± 0,02	8,48 ± 0,44	-	-	8,01 ± 0,14	8,05 ± 0,09
DOC	-	2,16 ± 1,05	2,29 ± 1,09	1,16 ± 0,23	3,31 ± 2,09	1,96 ± 0,62
COD	10,10 ± 1,63	14,53 ± 4,21	< DL	< DL	7,47 ± 7,15	4,15 ± 6,31
TN	0,46 ± 0,02	0,49 ± 0,03	0,39 ± 0,005	0,39 ± 0,004	0,41 ± 0,01	0,41 ± 0,01
NH_4^+	42,05 ± 37,98	123,78 ± 122,39	40,51 ± 10,25	55,35 ± 30,91	3,55 ± 4,54	13,76 ± 14,75
NO_2^-	-	-	4,61 ± 4,57	8,33 ± 7,63	2,96 ± 2,29	3,14 ± 2,59
NO_3^-	-	-	3,26 ± 4,85	< DL	6,51 ± 2,85	5,74 ± 2,95
TP	0,07 ± 0,03	0,11 ± 0,06	0,07 ± 0,02	0,07 ± 0,01	0,22 ± 0,10	0,17 ± 0,08
Turb	64,35 ± 17,44	63,62 ± 17,07	-	-	59,06 ± 35,06	38,68 ± 22,63
TS	255,50 ± 36,60	213,00 ± 20,66	249,50 ± 44,76	221,00 ± 9,90	273,20 ± 59,02	193,00 ± 29,25
FTS	210,50 ± 26,50	185,67 ± 23,64	184,00 ± 38,19	164,00 ± 2,83	197,20 ± 48,92	99,33 ± 38,57
VTS	45,00 ± 15,53	27,33 ± 16,28	65,50 ± 8,06	57,00 ± 12,73	76,00 ± 10,86	101,67 ± 68,69
SS	103,98 ± 93,10	63,00 ± 24,54	77,13 ± 49,50	43,25 ± 8,84	121,80 ± 79,78	79,42 ± 58,69
FSS	85,47 ± 81,76	47,58 ± 18,70	59,25 ± 40,45	27,50 ± 7,07	98,50 ± 66,88	22,25 ± 10,34
VSS	18,51 ± 11,42	15,42 ± 6,41	17,88 ± 9,10	15,75 ± 1,77	23,30 ± 12,92	38,68 ± 22,63

Class - classification; WS – water sink (removal); WD – water discharge; NB – number of bottles; Vol – volume transported (by removal or discharge) (10^4 m^3); ΔQ – flow range (m^3 s^{-1}); Cond – conductivity (µS cm^{-1}); Alka – alkalinity (mg $CaCO_3$ L^{-1}); Temp – temperature (°C); DO (mg L^{-1}); DOC (mg C L^{-1}); COD (mg O_2 L^{-1}); TN (mg N L^{-1}); $NH4^+$ - nitrogen ammonia (µg L^{-1}); NO_2^- - nitrite (µg L^{-1}); NO_3^- - nitrate (µg L^{-1}); TP (mg P L^{-1}); Turb – turbidity (NTU); TS (FTS and VTS) and SS (FSS and VSS) (mg L^{-1}); DL – detection limit.

4.7. Discussion

The potential of results determined in this research is overwhelmimg, considering similar experiences described in the literature. The strategy defines to consider two distinct parts, although their natural integration:

i) Pollutographs: conducted in pollutants behavior during rise and fall of the measured hydrographs;
ii) EMC: conducted in analyzes of EMC curves as proposed by Metádier and Bertrand-Krajewski (2012), and contrasting EMC values with event characteristics.

For each analysis, it is presented a general view of results (commented in detail in sections above) with similar studies and results found in literature review.

4.7.1. Pollutrograph analyses

Flow and concentrations in each event have different and complex dynamics (Métadier and Bertrand-Krajewski (2012) as influenced by the hydrograph characteristics and rainfall impacts. Besides, runoff volume produced during a rainfall event tends to increase risk of pollutant transport (Delpla et al 2011). In general, pollutographs measured during this research showed an interesting patterns for the rainfall events registered

Conductivity, alkalinity, pH, DO and temperature, in general, were stable for all events, except for event 2, with small decrease with a rising hydrograph. For event 10, pH, DO and conductivity had the same behavior. In similar conditions, Moraetis et al (2010) did not find variation during rainfall event for pH, DO and temperature, highlighting that these parameters are extremely correlated and significant differences occur for distinct episodes during the day in comparison with the night. Also, partial pressure of carbon dioxide can determine increase or decrease in pH, due calcite deposition (Moraetis et al, 2010).

Chemical parameters had different dynamics among each other and for distinct events. DOC shows low values in events 2, 10 and 11, curiously, did not follow the hydrograph influence. Delpla et al (2011) also found low values of DOC was exported during the heaviest event (maximum intensity of 38.4 mm h^{-1}), because of the very low runoff volume due to the short duration of the rainfall (2.2h). Additionally, Delpla et al (2011) showed DOC maximum measured values at the beginning of the rainfall event (about 10.3 mg L^{-1} and decrease to 4.8 mg L^{-1} in end of the event), because, after that, dilution slows during continuous stage of the rainfall. This condition was observed in event 9, (the biggest event that happened slowly during long time) concentrations follow hydrograph conditions.

In Gao et al (2014) DOC concentration varied rapidly during rainfall event, increased sharply, with average of 4.72 ± 3.0 mg L^{-1}. In event 1 concentration decreased with hydrograph rise and increase in end of event. DOC decreased with flow increase in Chittoor Viswanathan et al (2015) study, due to dilution effect.

COD had stable behavior in event 1 and 11, while followed hydrograph conditions in events 2, 9 and 10. TN stayed stable in all events, different pattern also been observed by Chen et al (2012). Firstly, Chen et al (2012) affirms N fluxes increase with elevated discharge, and vice-versa. Exchanges in N fluxes are determinate by nitrate and nitrogen ammonia dynamic, possible controlled by different biogeochemical processes couples with hydrological processes. Therefore, spatial variability on N sources into watershed represent an interactive effect together with hydrological processes in N dynamic in terms of concentration, flux and composition in rainfall runoff (Chen et al, 2012).

Gao et al (2014) also affirm that biogeochemical dynamics of nitrogen and phosphorus in base flow are quali-quantitatively different from dynamics occurring after and during rainfall events. TP concentrations were stable in event 1 and 11, but in the others TP concentrations followed rise and fall hydrograph. Chen et al (2015) showed larger variation in P concentrations and fluxes during strong events when compared less strong events; this suggest storm-induced extreme hydrological condition increase P fluctuations. During storms, P forms changed at different rates with transport, varying sources areas by the different pathways (Chen et al, 2015). P transport showed dependence with intensity and amplitude of storm events as higher loads corresponded to larger water yields (Ramos et al, 2015).

In all events TN concentrations were bigger than TP concentrations, except for singles bottles during peak or base flow. Accordingly, Gao et al (2014) changes in N concentrations are more pronounced than changes in P concentration in runoff, and because phosphorus can be absorbed by soil particulars and slowly desorbed during rainfall and runoff processes.

Considering physical parameters, the pattern were strong in all of them. Turbidity, TS, SS and fractions (volatile and fixes) followed rise and fall hydrograph during events. Some events had peak more pronounced, and consequently, causing values more significant in these parameters. Ramos et al (2015) observed maximum turbidity value (1520.3 NTU) during first flush flood, and Chittoor Viswanathan et al (2015) observed higher turbidity levels accentuated by storm event.

In general, the pollutant tends to follow hydrograph behavior, but such factors can induce variations. Chemical parameters are extremely related to environment chemical process, as biogeochemical reactions (organism activities), ionic exchanges, soil chemistry, organic matter presence, and others. Therefore each condition can influence different interactions between components in aquatic ecosystem, been more or less bioavailable for example. Physical parameters are more robust and visible, been influenced by land use and occupation, antecedent dry days, and pollutant build-up. The equilibrium between these parameters govern the responses required and necessary to understand the entire process is still challenging and can be the basis of a strong reflection about how water quality parameters has been monitored.

4.7.2. EMC analyses

This method consist on analyzes of EMC curve divided in three zones, as presented in Chapter 3. Table 14 summarize, for different water quality parameters, the EMC curve classification considering three colors zones, where square red, blue and green (🟥 🟦 🟩) represent zone A, B and C, respectively. Symbol in pairs (i.e. 🟩-🟦 or 🟥-🟦) represent concavity curves changed from one zone to other zone.

As can be observed in Table 1, most of EMC curves are classified in zone B, mainly for all curves of conductivity, alkalinity, temperature, pH and DO in all events. Event 1 was the shortest event, reflecting in EMC values, where expect DOC, nitrogen ammonia and nitrite were classified in zone C and TP had concavity changed from zone C to B. Event 2 and 10 had similar EMC curves distribution, TP, turbidity and solids series (expect VTS for event 10 that was classified in zone C) were classified in zone A. Event 2 also had nitrogen ammonia in zone A while the concavity changed from zone A to zone B in event 10. The same changes happened for nitrite. Event 9 had various concavity changes in turbidity and solids series (expect TS and FTS).

Event 11 had more parameters classified in zone B, turbidity, SS, FSS and VSS in zone A, while nitrogen ammonia and DOC had concavity changes from zone B to A and C to B, respectively.

Table 14 - Summary of EMC classification according method proposed by Metádier and B-Krajewski

Parameters	Events				
	1	2	9	10	11
Cond	🟦	🟦	🟦	🟦	🟦
Alka	🟦	🟦	🟦	🟦	🟦
Temp	🟦	🟦	🟦	🟦	🟦
pH	🟦	🟦	🟦	🟦	🟦
DO	🟦	🟦	🟦	🟦	🟦
DOC	🟩	🟦	🟦	🟦	🟩-🟦
COD	🟦	🟦	🟦	🟦	🟦
TN	🟦	🟦	🟦	🟦	🟦
NH_4^+	🟩	🟥	🟥	🟥-🟦	🟦-🟥
NO_2^-	🟩	🟦	🟦	🟥-🟦	🟦
NO_3^-	-	-	🟥	🟩	🟦
TP	🟩-🟦	🟥	🟥	🟥	🟦
Turb	🟦	🟥	🟩-🟦	🟥	🟥
TS	🟦	🟥	🟦	🟥	🟦
FTS	🟦	🟥	🟦	🟥	🟦
VTS	🟦	🟥	🟩-🟦	🟩	🟦
SS	🟦	🟥	🟩-🟦	🟥	🟥
FSS	🟦	🟥	🟩-🟦	🟥	🟥
VSS	🟦	🟥	🟩-🟦	🟥	🟥

🟥 – zone A; 🟦 – zone B; 🟩 – zone C, 🟩-🟦 concavity changed from zone C to zone B, 🟥-🟦 concavity changed from zone A to zone B; 🟦-🟥 concavity changed from zone B to zone A.

Considering 93 classifications, 55 parameters were classified in zone B (59%), 23 in zone A (25%), 5 in zone C (5%) and 10 had concavity change (11%). This means that the most water quality parameters, classified in zone B that a transport volume is not significantly different from load pollutant transported. In Métadier and Bertrand-Krajewski (2012) two experimental catchments were investigated and EMC was calculated. From 263 curves in first site (Chassieu) 13% were classified in zone B, and for second site (Ecully) from 239 curves performed 21% was classified in zone B. Most rain classified in zone B by Métadier and Bertrand-Krajewski (2012) present the lowest maximum rainfall intensity in 30 minutes within 4 hours before the storm event. These events show moderate maximum rainfall intensities, demonstrating that for low rainfall intensities, pollutant load dynamic are similar and proportional to flow dynamics. Despite these aspects the authors do not present more detailed analyses from rainfall events.

The second highest rating was zone A, indicating that 25% of parameters had transport volume lower than load pollutant transported. Some cases can indicate concentration pattern. In general, the curves may be observed considering the percentage of mass pollutant transported in a percentage of water volume. Métadier and Bertrand-Krajewski (2012) showed curves in zone A correspond to the smallest rainfall depths, suggesting available pollutant stocks in small storms event are not limiting factor.

Hereafter there is that parameters with concavity change, corresponding to 11%, can be explained as temporal delay of concentration compared to flow, where pollutant transference is significantly lower than flow propagation (Metádier and Bertrand-Krajewski, 2012). Lastly were 5% of parameters classified in zone C, representing the portion where transport volume is significantly bigger than load pollutant transported. For zone C, the curves interpretations may be to consider the amount of mass pollutant transported in determinate percentage of water volume. Some cases can be classified as pollutant dilution.

According EMC distribution in zones, the most part of the parameters did not produce significant pollution contribution into the river, reflecting the main characteristics of the upper portion of the watershed, without intense urban occupation, impervious, industries and wastewater treatment station. Due percentage in zone A, other hypothesis is first flush phenomenon had intermediate influence in this site. However, for physical parameters first flush phenomenon induce the transport and carrying of solids to the water body. Metádier and Bertrand- Krajewski (2012) had percentage distribution for Chassieu and Ecculy sites of 8-13-79 % and 7-21-72 %, respectively for zones A, B and C. So, according Metádier and Bertrand-Krajewski (2012), this distribution suggest that first flush phenomenon is far from universal, varying with particular circumstances. Figure 72 to Figure 76 show EMC curves for event 1, 2, 9, 10 and 11.

Results in this research and, based on Metádier and Bertrand-Krajewski (2012) approach, confirms that flow and time series concentrations had complex and different dynamic in each event observed. The same pattern was show in event performed. Each event has it is own characteristics, like a personality, and the river response “(gentle or rude)”, carrying, diluting or concentrating pollution depend on some factors. For most events, concentrations dynamics appear similar in terms of distribution and EMC curves, and not comparable in terms of absolute values (Metádier and Bertrand- Krajewski, 2012).

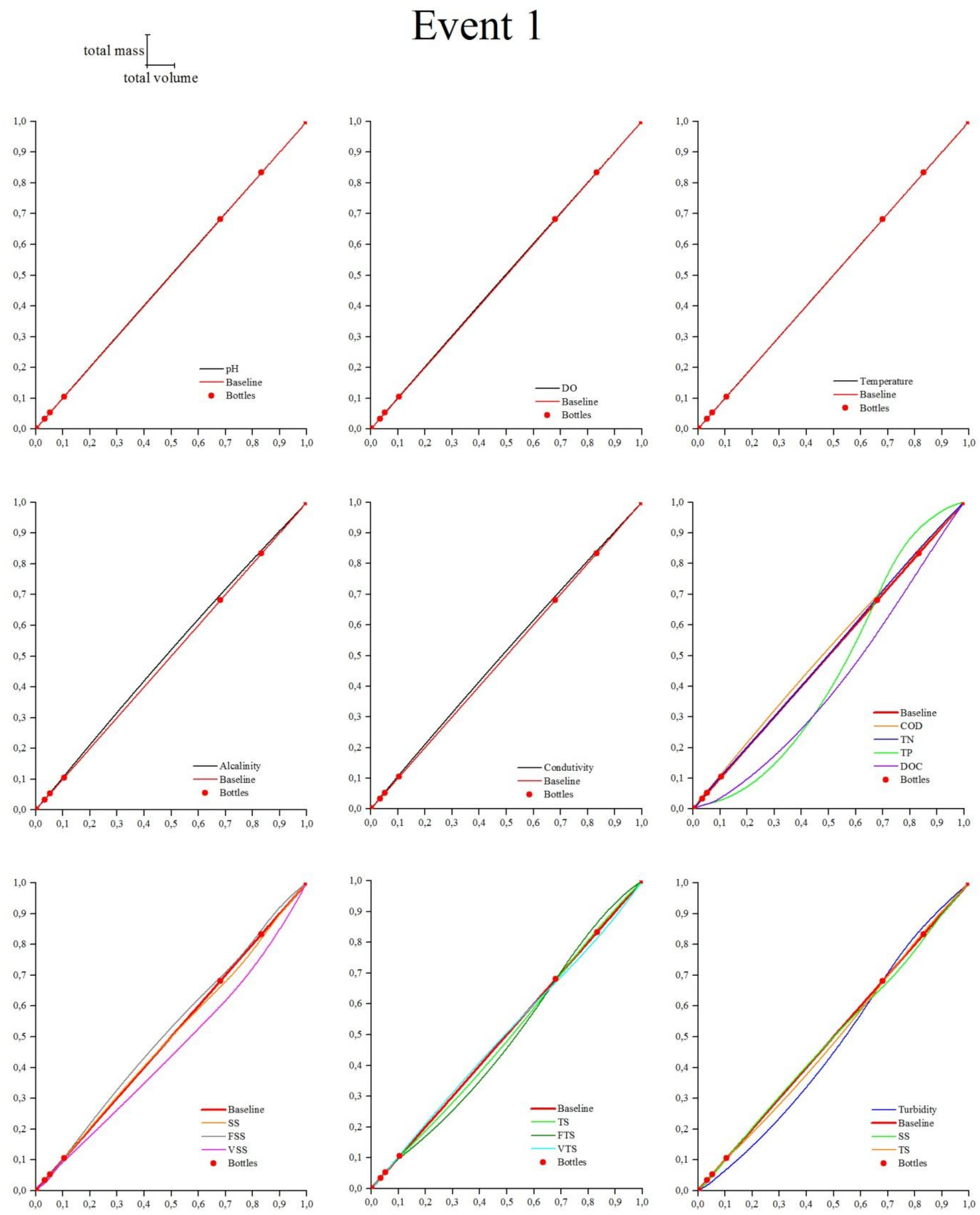


Figure 72 - EMC event 1

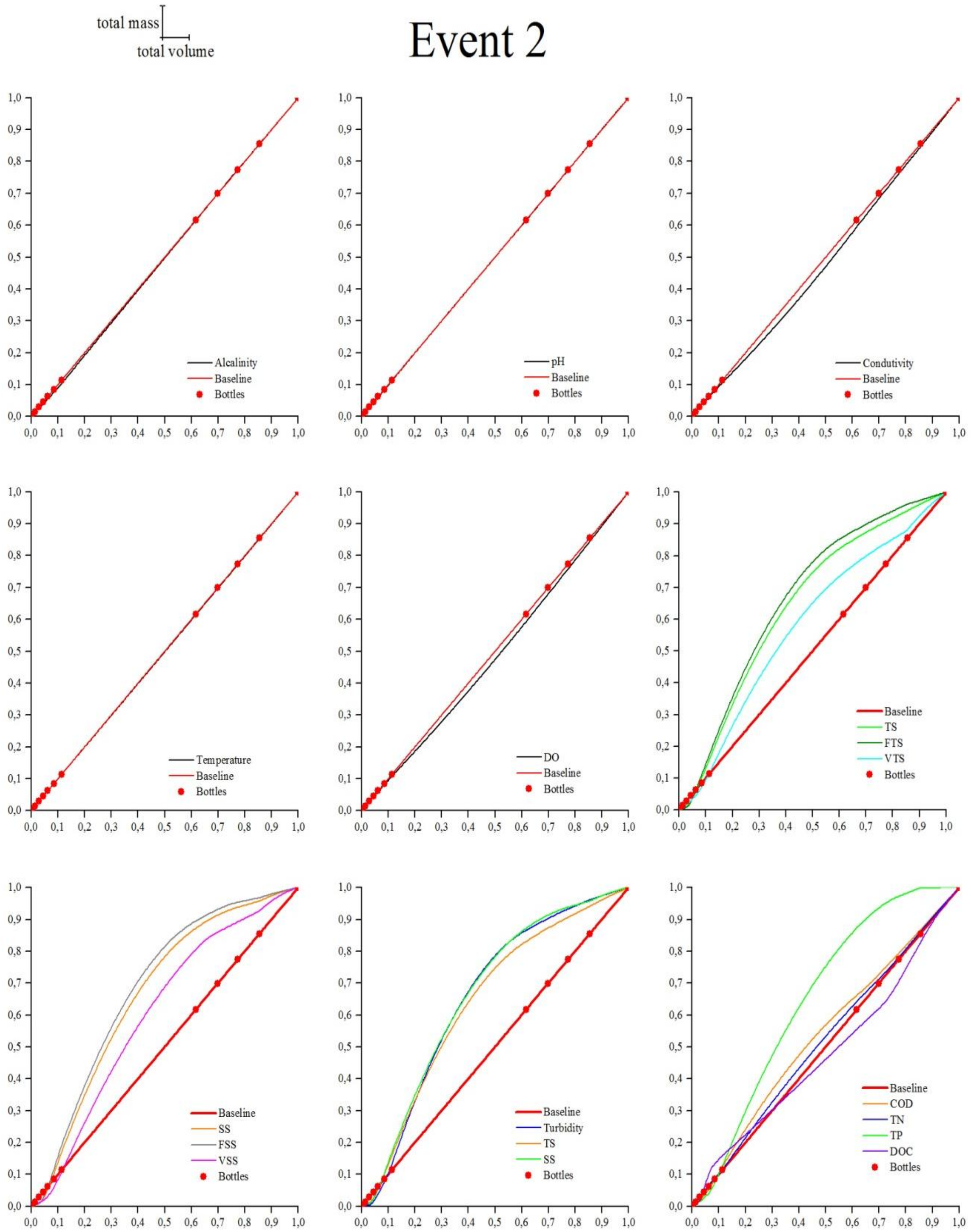


Figure 73 - EMC event 2

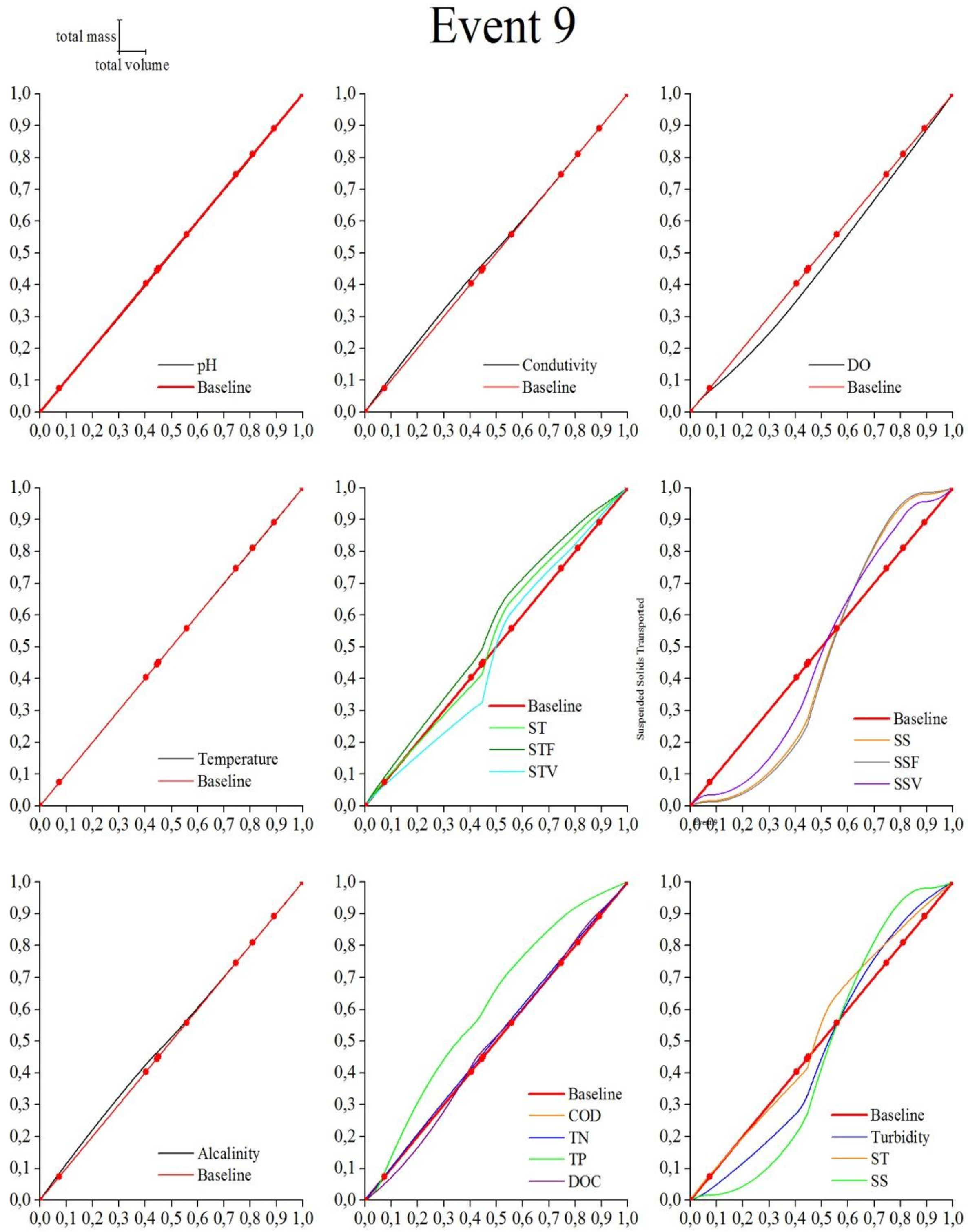


Figure 74 - EMC event 9

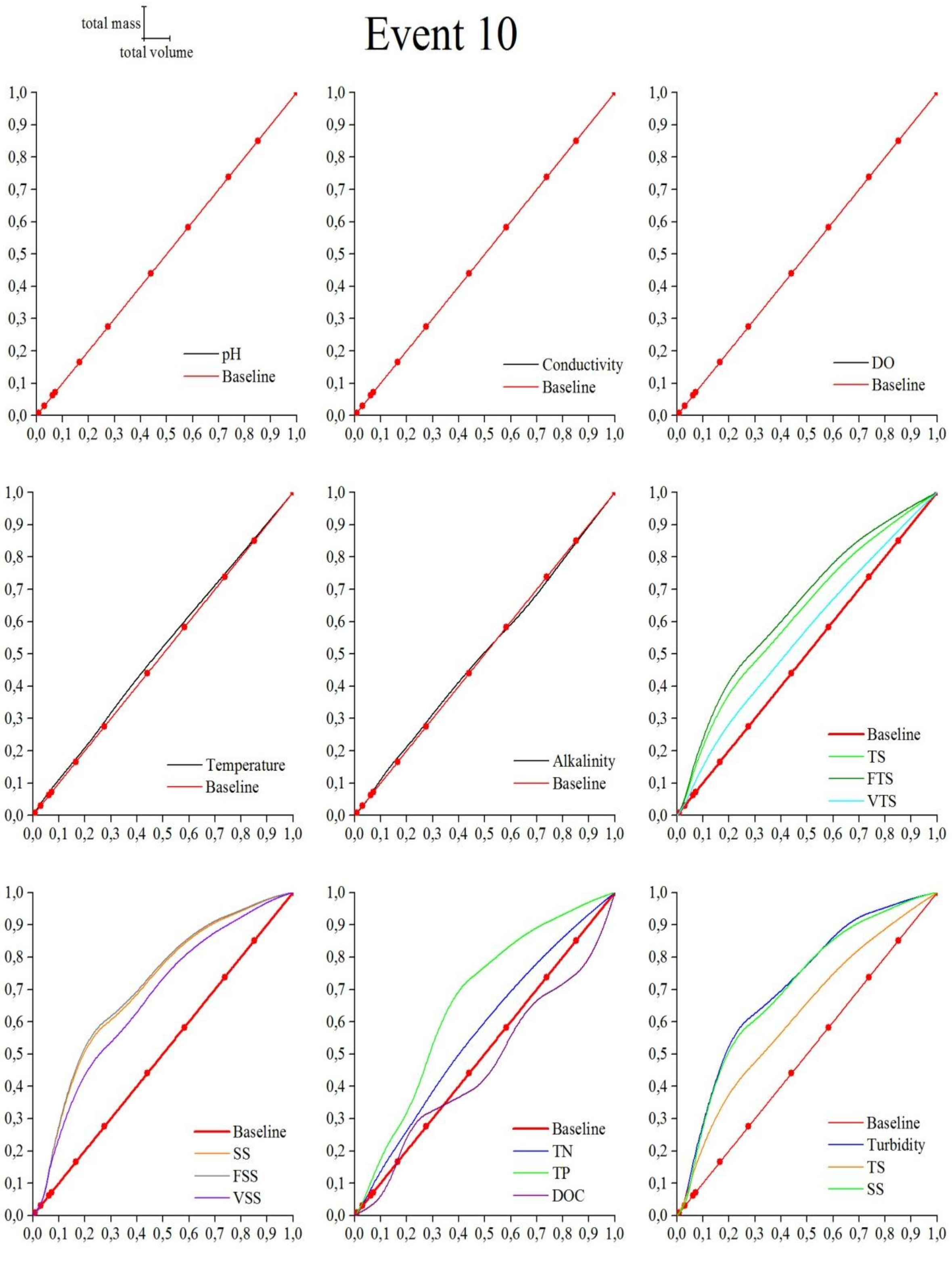


Figure 75 - EMC event 10

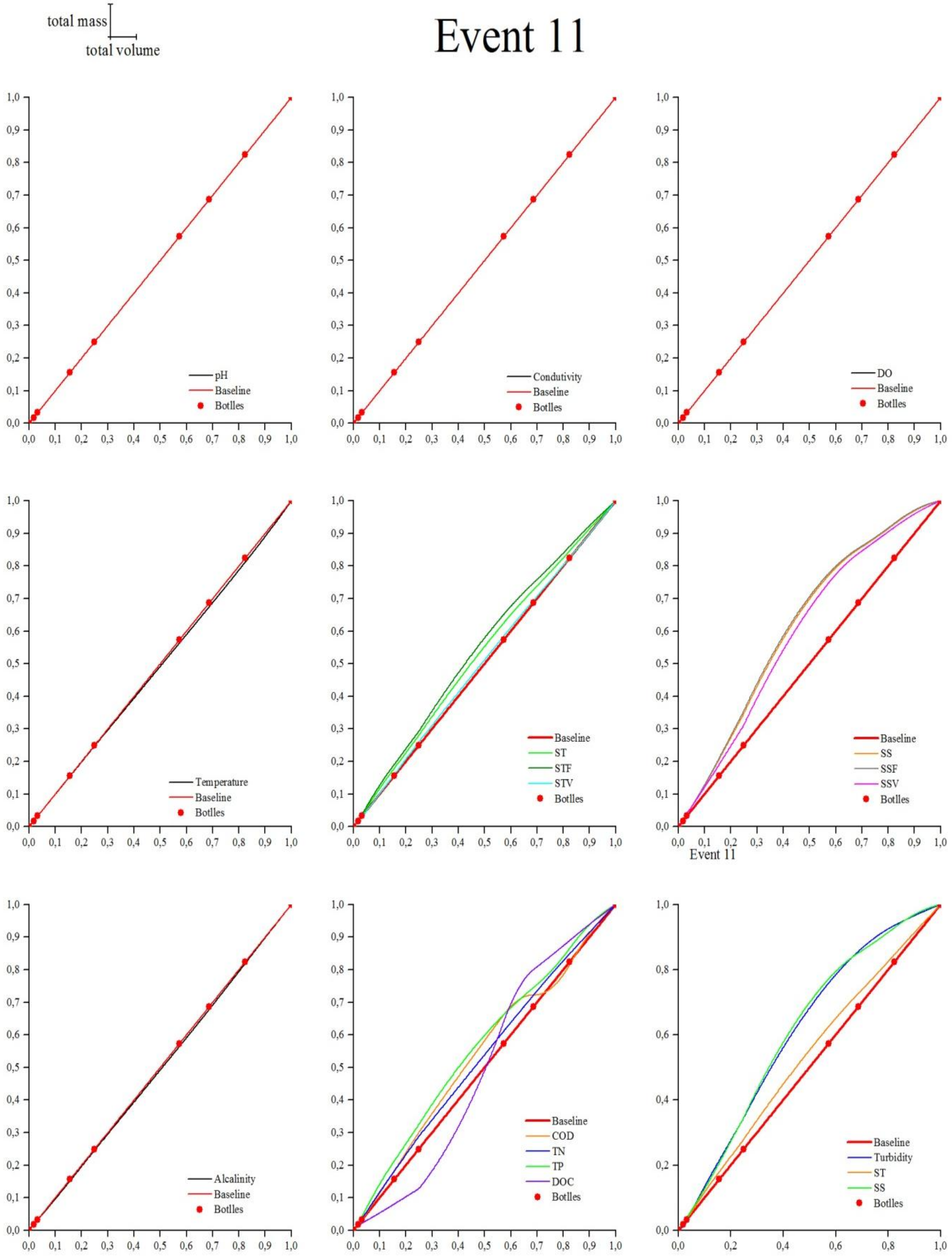


Figure 76 - EMC event 11

4.7.3. EMC x Event Characteristics

In many aspects, hydrological processes are the main influence over the EMC characteristics. Some events characteristics as, event duration, maximum flow (critical time), accumulated precipitation, and transported volume, were related to water quality parameter EMC to understand and explain pollutant behavior during rainfall events, as presented in table 2.

Table 15 - Characteristics of diffuse pollution events

Events characteristics					
Event	1	2	9	10	11
Duration	17,16	30,33	56,83	22,67	30,33
P_{acum}	2,29	14,73	38,61	31,50	28,70
V_{transp}	1,99	1,48	4,56	2,35	2,74
Q_{max}	3,66	4,48	3,30	3,85	3,28
ADD	32.42 / 1.35	23.66 / 0.98	22.13 / 0.92	98.42 / 4.1	147.58 / 6.15

Duration (h); P_{acum} – accumulated precipitation (mm); V_{transp} – water volume transported (10^5 m³); Q_{max} – maximum flow (m³/s); ADD – antecedent dry days (hour/day);

` The shorter event was event 1, classified as short-duration event. Event 2 and 11 had the same duration but the flow peak was greater in event 2 (4.48 m³/s) than event 11 (3.28 m³/s), while the water volume transported was bigger in event 11 (2.74 m³) than event 2 (1.48 m³). Also, event 11 had the bigger antecedent dry days before rainfall start. Event 9 was the longest one, with duration about 56.83 hours with 38.61 mm of accumulated precipitation. Besides, was the event that transported more water volume among all (4.56 x 10^4 m³). Event 10 was rainfall more intense, raining considerable in a short time. With this information, analyses of EMC values was divided in three water quality parameters groups: i) conductivity, alkalinity, pH, DO and temperature; ii) DOC, COD, TN and TP; iii) turbidity, TS, SS and fractions.

4.7.3.1. Conductivity, alkalinity, pH, DO and temperature

Table 16 shows EMC values for group 1 parameters. Interestingly, the EMC values show a interesting dynamics. The smaller event (1) produced similar values than the biggest event (9). pH was parameter more stable among all. EMC average was 233,25 ± 27,45 µS/cm to conductivity, 147,93 ± 10,80 mg $CaCO_3$/L for alkalinity, 8,00 ± 0,04 in pH, 7,68 ± 0,60 mg/L for DO and 18,99 ± 4,72 °C for temperature.

Table 16 - Summary of EMC group 1

	EMC					
Event	1	2	9	10	11	EMCm ± *sd*
Cond	259.31	204.53	265.20	213.09	224.12	233,25 ± 27,45
Alka	158.96	130.23	147.93	153.39	149.16	147,93 ± 10,80
pH	8.06	8.02	8.02	7.96	7.95	8,00 ± 0,04
OD	7.31	6.95	7.63	8.06	8.48	7,68 ± 0,60
Temp	23.54	23.17	20.20	14.20	13.83	18,99 ± 4,72

Alkalinity (mg $CaCO_3$/L); Conductivity (μS/cm); DO – dissolved oxygen (mg/L); Temperature (°C); EMCm – event mean concentration average; *sd* – standard deviation.

Figure 77 to Figure 80 shows correlation between EMC and event characteristics. Though this variation range did not caused significant impact, water quality parameters remained stable. It seems that different characteristics of each event did not have influence in transport of conductivity, alkalinity, pH, DO and temperature behavior. Relations between EMC and event characteristics can be evidence by estimate standard error (R²), show in Table 17.

Table 17 - Estimative standard error for group 1 of parameters

R²	Event Duration	Q max	P acum	V trans
Alkalinity	0,08	0,43	$2,10x10^{-3}$	0,05
Conductivity	0,15	0,43	$3,00\ x10^{-4}$	0,41
pH	$4,90x10^{-5}$	0,05	0,44	0,01
DO	$2,00x10^{-4}$	0,47	0,35	0,11
Temperature	$1,00x10^{-3}$	0,19	0,43	0,04

Numbers acknowledge what was observed in figures. Event duration had the worst estimative, with extremely low values. Maximum flow was the characteristic that had values more significant among all. Alkalinity, conductivity and DO had most correlation with maximum flow (0.43, 0.43 and 0.47, respectively), while pH and temperature had better correlation with accumulated precipitation (0.44 and 0.43, respectively).

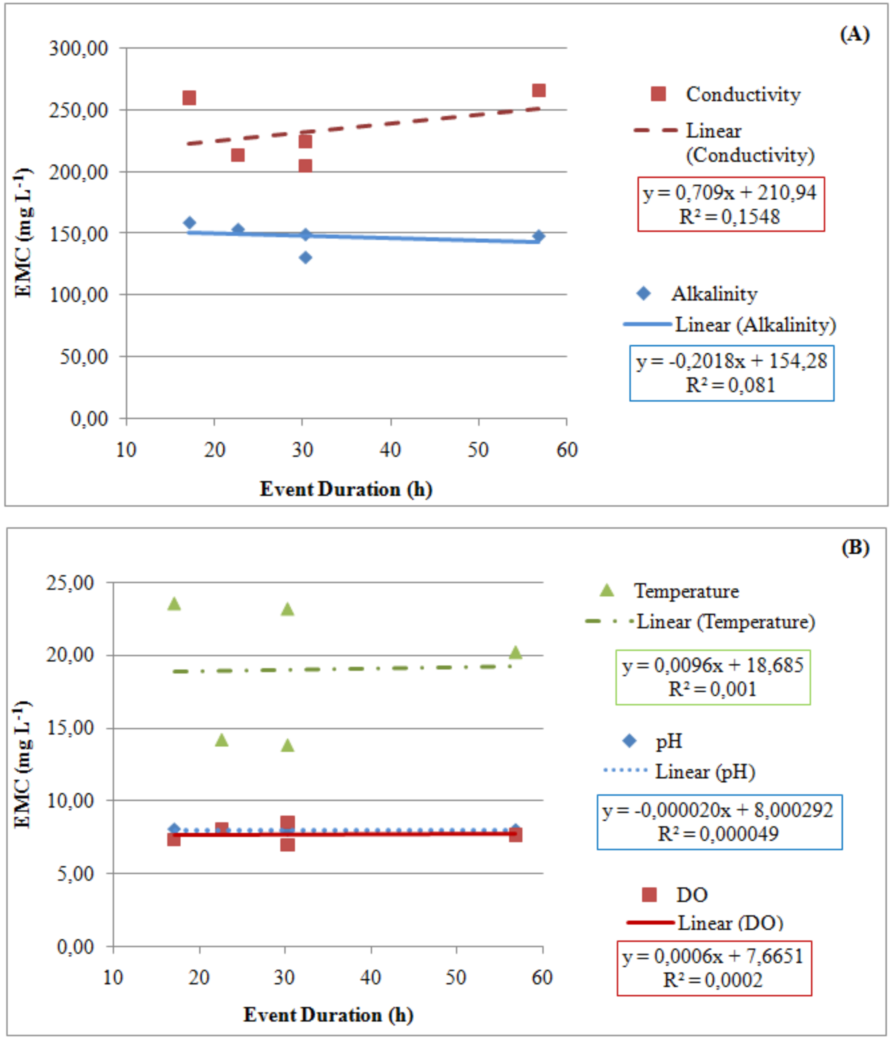


Figure 77 - EMC vs. Event Duration: (A) conductivity and alkalinity EMC values contrasting with event duration for each diffuse pollution event; (B) temperature, pH and DO EMC values contrasting with event duration for each diffuse pollution event

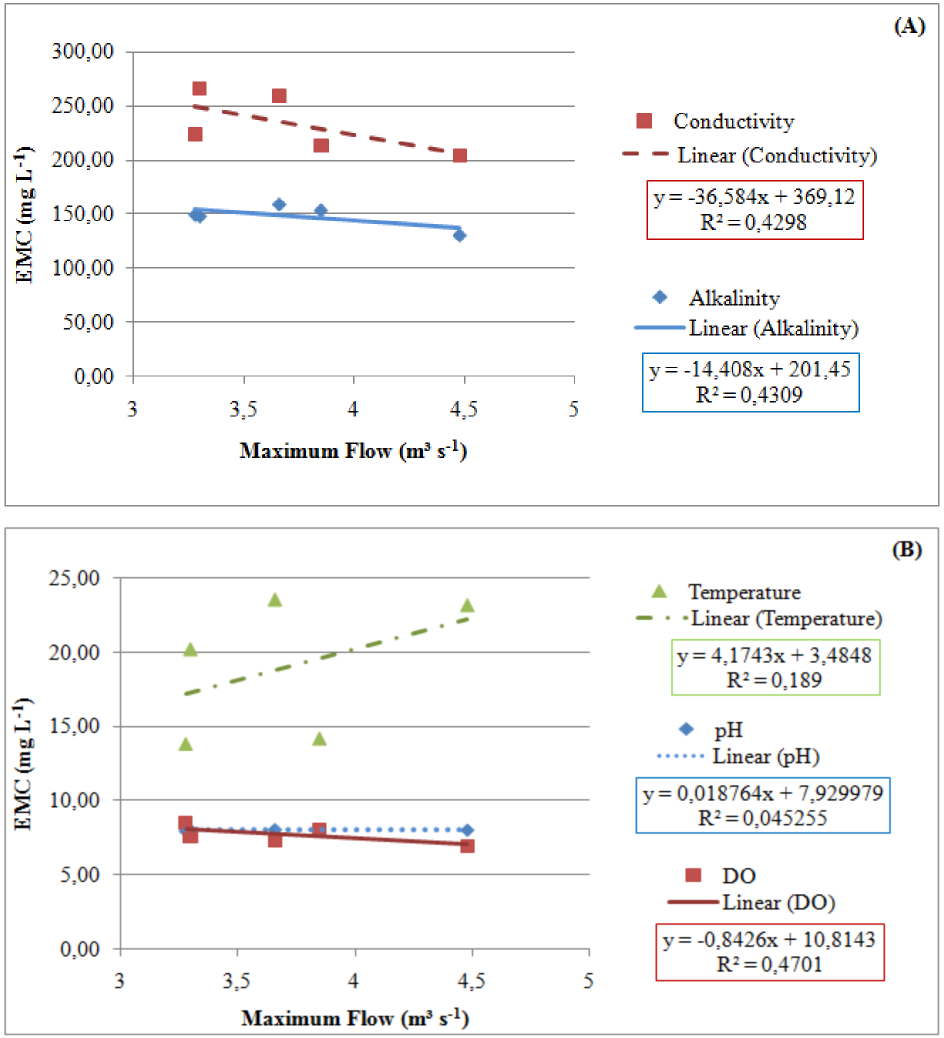


Figure 78 - EMC vs. Maximum Flow: (A) conductivity and alkalinity EMC values contrasting with maximum flow for each diffuse pollution event; (B) temperature, pH and DO EMC values contrasting with maximum flow for each diffuse pollution event

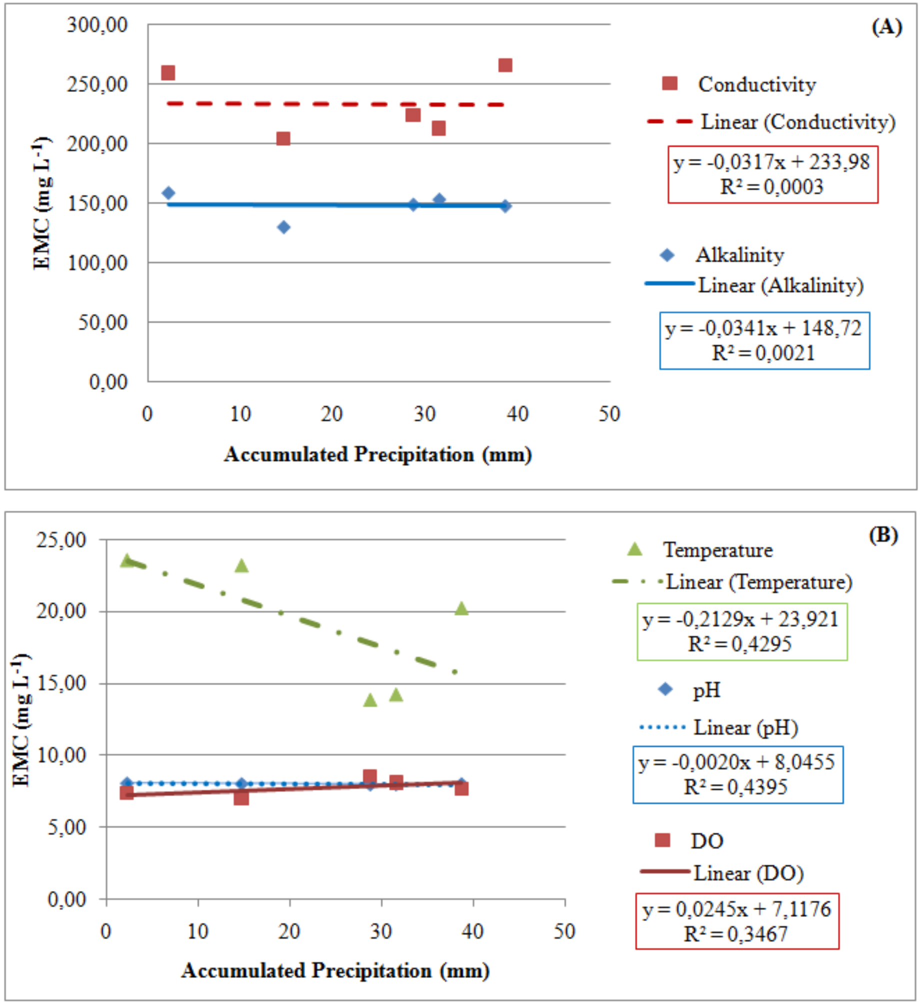


Figure 79 - EMC vs. Accumulated Precipitation: (A) conductivity and alkalinity EMC values contrasting with accumulated precipitation for each diffuse pollution event; (B) temperature, pH and DO EMC values contrasting with accumulated precipitation for each diffuse pollution event;

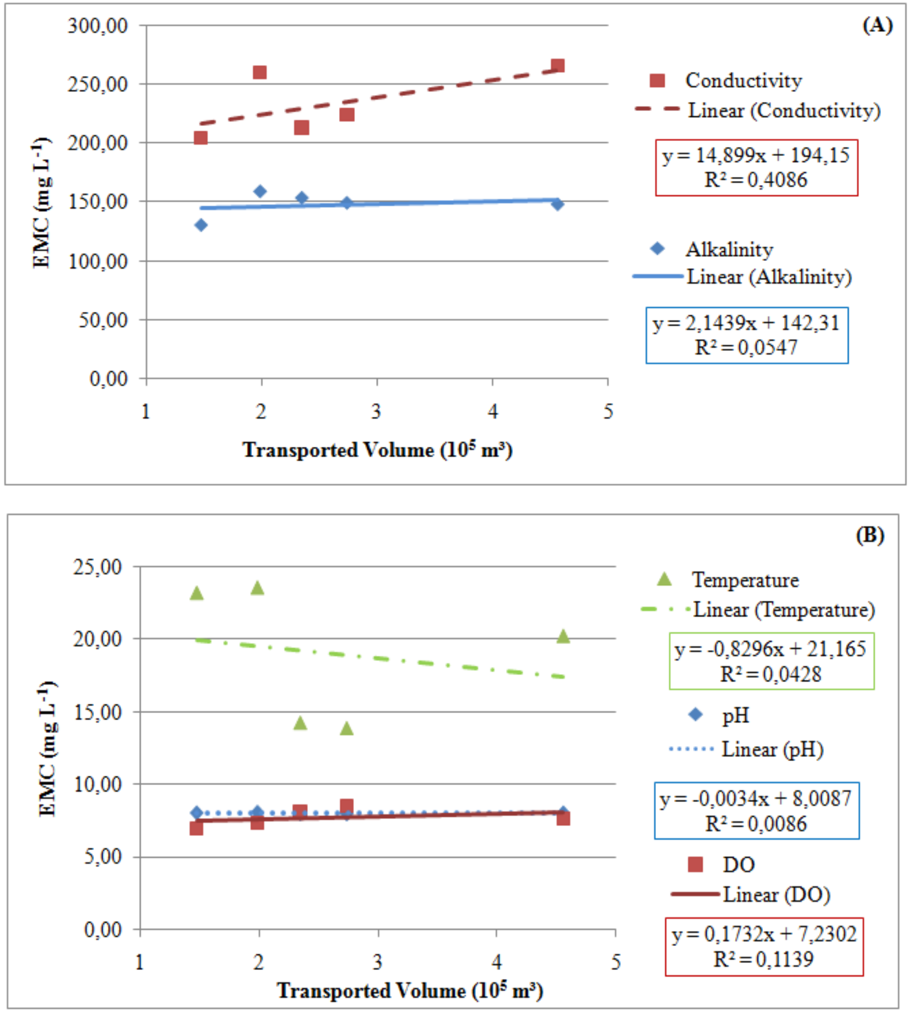


Figure 80 - EMC vs. Transported Volume: (A) conductivity and alkalinity EMC values contrasting with transported volume for each diffuse pollution event; (B) temperature, pH and DO EMC values contrasting with transported volume for each diffuse pollution event;

4.7.3.2. DOC, COD, TN and TP

EMC for group 2 shows more variability than group 1 (Table 18). DOC and COD had lower EMC in event 9 (biggest event) with 2,88 mg C/L and 10,35 mg O_2/L, respectively. This can indicate a dilution that these events characteristics induce. In smaller event (1) DOC and TN had biggest EMC values (5,64 mg C/L and 0,55 mg N/L), that can mean pollutant carrying and concentration during a small event. TP had the biggest concentration in event 2, an intense-event. The EMC average for DOC, COD, TN an TP was, respectively, 4.51 ± 1.23 mg C/L, 28.97 ± 21.68 mg O_2/L, 0.36 ± 0.20 mg N/L, 0.30 ± 0.22 mg P/L.

Table 18 - Summary of EMC group 2

	EMC					
Events	1	2	9	10	11	EMCm ± *sd*
DOC*	5.64	5.63	2.88	3.65	4.75	4.51±1.23
COD*	31.38	58.59	10.35	-	15.57	28.97 ±21.68
TN*	0.55	0.51	0.42	0.18	0.11	0.36±0.20
TP*	0.14	0.65	0.29	0.31	0.10	0.30±0.22

* all values were calculated in mg/L

Contrasting, EMC values with event characteristics were observed some patterns (Figure 81 to Figure 84). Total nitrogen did not have significant changes during the event and remained stable considering events characteristics. In the moment that event achieved maximum, flow pollutant transport was bigger, with higher pollutant concentrations. Intermediate-rainfall duration there were bigger concentrations. However, in big accumulated precipitations and water volume transported there were lower concentrations, this can be due dilution factor. A big rainfall with longer duration and high intensities produced more diluted runoff. (Métadier and Bertrand-Krajewski, 2012; Maniquiz et al., 2010).

Liu et al (2012) investigated some event characteristics (average rainfall intensity, initial rainfall intensity, maximum rainfall intensity, rainfall duration, rainfall depth and antecedent dry days) with EMC for TN and TP, and found greater values to TN EMC (6.85±5.99 mg/L) during a high-intensity short-duration rainfall while for TP EMC (3.29±3.06 mg/L) was for high-intensity long-duration rainfall. Antecedent dry days (ADD) did not have correlation to EMC and event characteristics, because ADD was similar in each event, so other characteristics trigger EMC range.

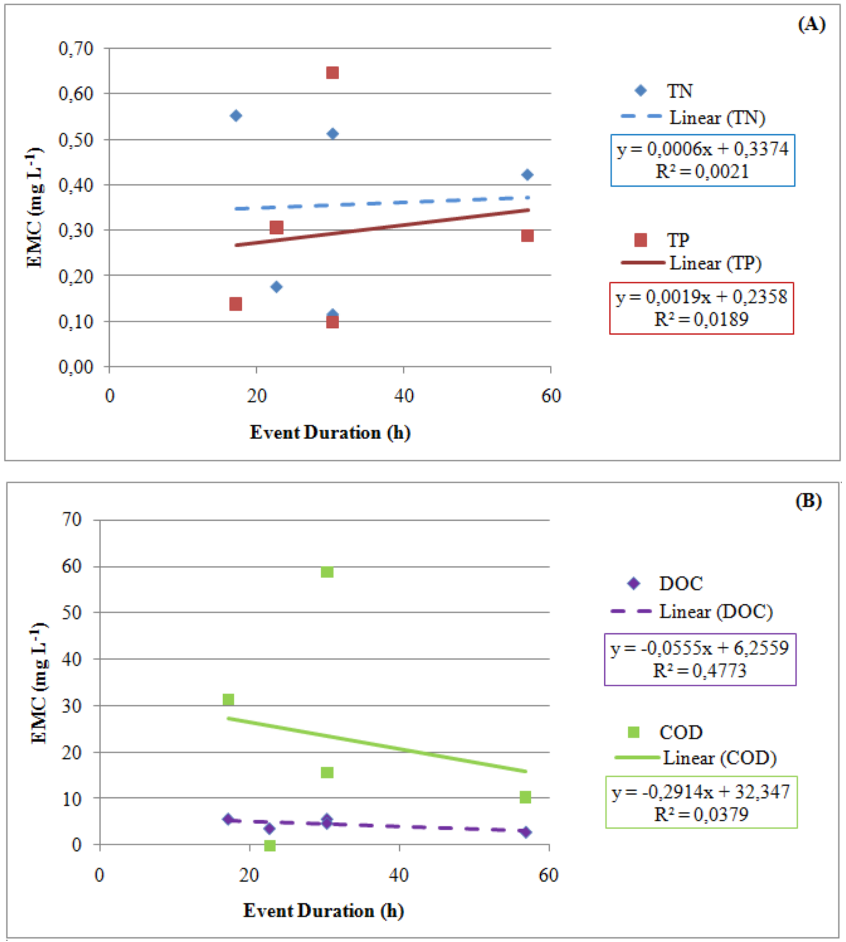


Figure 81 - EMC vs. Event Duration: (A) TN and TP EMC values contrasting with event duration for each diffuse pollution events; (B) COD and DOC EMC values contrasting with event duration for each diffuse pollution events

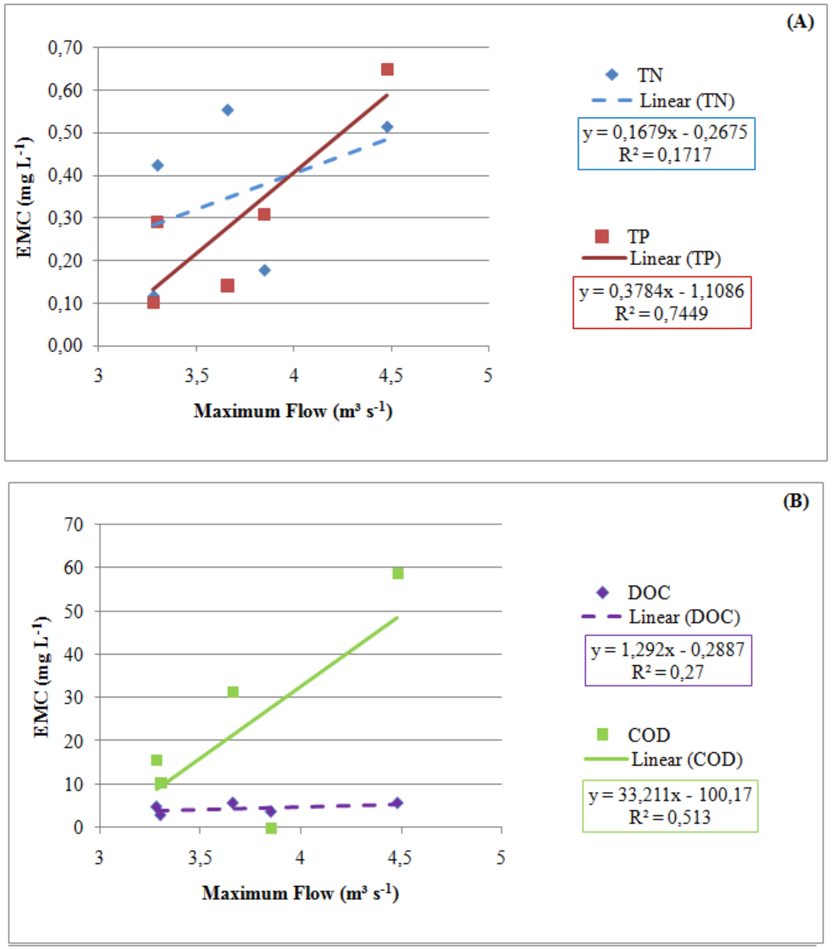


Figure 82 - EMC vs. Maximum Flow: (A) TN and TP EMC values contrasting with maximum flow for each diffuse pollution events; (B) COD and DOC EMC values contrasting with maximum flow for each diffuse pollution events

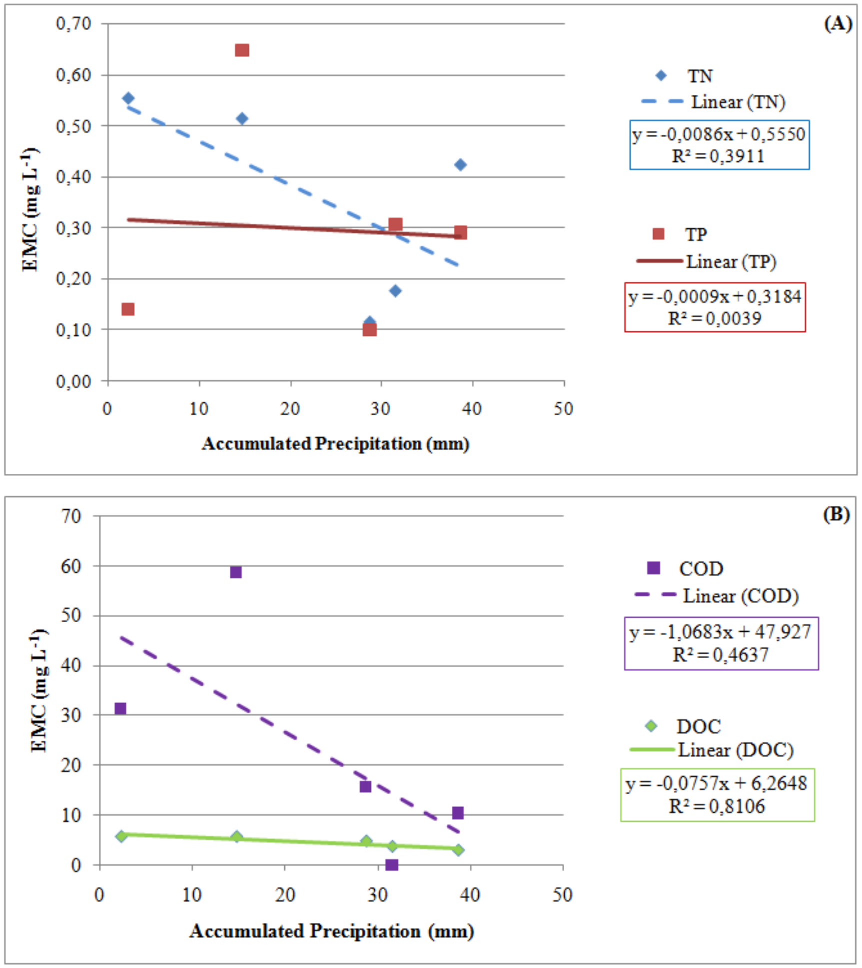


Figure 83 - EMC vs. Accumulated Precipitation: (A) TN and TP EMC values contrasting with accumulated precipitation for each diffuse pollution events; (B) COD and DOC EMC values contrasting with accumulated precipitation for each diffuse pollution events

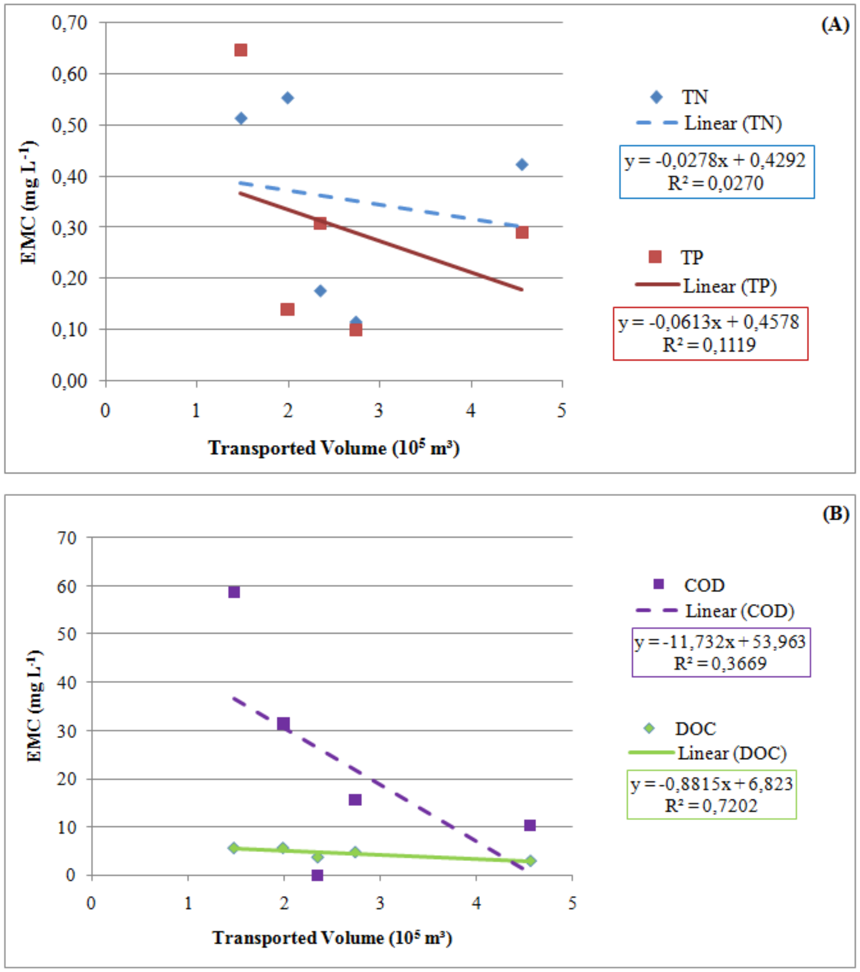


Figure 84 - EMC vs. Transported Volume : (A) TN and TP EMC values contrasting with transported volume for each diffuse pollution events; (B) COD and DOC EMC values contrasting with transported volume for each diffuse pollution events

In the same context, Maniquiz et al (2010) indentified that TN, TP and COD were better correlated to the average rainfall intensity, while DOC had better correlation with rainfall duration. The EMC values were 33.3 ± 17.2 mg/L of COD, 15.9 ± 10.6 mg/L of DOC, and 4.3 ± 2.8 mg/L, 0.8 ± 0.4 mg/L for TN and TP, respectively. The low values of TN an TP were correlated to longer duration rainfall that produce more dilute runoff. Authors defined ideals event characteristics to predict EMC as total rainfall, rainfall duration and average rainfall intensity; an antecedent dry day was not a good variable.

COD was a parameter with more variation among events (28.97 ±21.68) and had bigger value in event 2, intense precipitation in short duration that produced wide flow range (2.58 m^3/s). The wide distribution of EMC depends on the total rainfall and rainfall intensity because of the dilution effect during a rainfall (Kim et al 2007). In general, a pattern can be seem in figure 6, where maximum flow and water volume transported had similar response to parameters in group 2. Relations between EMC and event characteristics can be evidence by estimate standard error (R^2), show in Table 17.

Table 19 - Estimative standard error for group 2 of parameters

R^2	Event Duration	Q max	P acum	V trans
TN	2,10x10^{-3}	0,17	0,39	0,03
TP	0,02	0,74	3,90 x10^{-3}	0,11
COD	0,04	0,51	0,46	0,37
DOC	0,48	0,27	0,81	0,72

As found in group 1, event duration was the characteristic that presented the worst correlation in group 2. TN and TP present good relation with only characteristic, accumulated precipitation (0.39) in nitrogen case, and maximum flow (0.74) in phosphorus case. COD did not have significant relation just with event duration (0.04), and the best relation was maximum flow (0.51). DOC was parameter with significant relation in all event characteristics. The most representative was accumulated precipitation (0.81), followed by transported water volume (0.72), event duration (0.48), and maximum flow (0.27).

4.7.3.3. Turbidity, TS and SS.

Group 3 consist in physical parameter of water quality. EMC values are show in Table 20. Event 2 and 10 present, in general, the biggest EMC for these parameters. These events were more intense and produced wide flow range (2.58 m³/s in event 2, and 2.47 m³/s in event 10). Against, event 9 and 11 had the lower EMC. These events were longer with more water volume yield, so pollutant can be suffered dilution. EMC average for turbidity was 290.42 ± 267.55 NTU, for ST (STF:STV) was 497.61 ± 259.60 (338.97 ± 233.36:158.64 ± 33.64) mg/L, and for SS (SSF:SSV) was 308.58 ± 295.00 (246.48 ± 239.62: 62.10 ± 59.23) mg/L.

Table 20 – Summary of EMC group 3

	EMC					
Events	1	2	9	10	11	EMCm ± *sd*
Turb	124.06	686.16	90.46	451.24	100.17	290.42 ± 267.55
ST	307.98	877.38	349.59	659.01	294.06	497.61 ± 259.60
STF	165.10	675.91	178.13	493.07	182.61	338.97 ± 233.36
STV	142.88	201.47	171.47	165.93	111.45	158.64 ± 33.64
SS	192.59	789.50	102.74	384.50	73.59	308.58 ± 295.00
SSF	125.87	629.17	85.18	333.16	59.01	246.48 ± 239.62
SSV	66.73	160.34	17.55	51.33	14.57	62.10 ± 59.23

Contrasting EMC values with event characteristics was observed strong patterns for all physical parameters (Figure 85 to Figure 88). Event duration will be related with another characteristic, because rainfall with the same duration produce different flow and intensity, that consequently, produces different responses on solids carrying. Zhang et al (2008) found no significant correlations between pollutants concentrations and duration, suggesting different runoff mechanisms and duration control the event in different setting of land use. According Qin et al (2013) events with the same rainfall amount can have a rather different EMC and peak concentration because other event characteristic.

Intermediate-precipitation caused the bigger solids concentrations, however when precipitation increase the pollutant EMC decrease. This can be due dilution, as in volume transported: the bigger volume had lower concentration. Métadier and Bertrand-Krajewski, 2012) confirms that in intermediate-strong events rainfall intensity with several peak in discharge and clearly show a dilution effect. Considering maximum flow during an event, when peak flow happen, the river was receiving the most load possible, so solids carrying is bigger. This condition depends on when peak flow happened. In lower volume transported the amount solids EMC is bigger.

For this group, antecedent dry days can be more correlated to EMC concentrations. It happened because a relation about build-up pollutant during certain days and rainfall availability to wash-off these pollutant when rain start. More rainfall amount has capacity to flush off more pollutant buildup in the catchment and results in higher EMC (Qin et al, 2013). Also, Kayhanian et al (2007) affirms that longer antecedent dry periods tend to results in higher EMC in storm runoff, which is consistent with de build-up of pollutant during dry periods. However, when capacity of wash-off is more than buildup pollutant, more rainfall amount causes lower EMC (Qin et al 2013). Therefore, in some high rainfall or short antecedent dry days produce low EMC and high rainfall over long antecedent dry days reduce EMC due to dilution effect (Kim et al 2007).

Relations between EMC and event characteristics can be evidence by estimate standard error (R^2), show in Table 21. Event duration and accumulated precipitation were event characteristics with lower relation for physical parameters. However, maximum flow and volume transported showed significant values among all parameters analyzed. Maximum flow presents the biggest values for all parameters with, 0.90 for turbidity, 0.86 and 0.97 respectively for total solids and suspended solids.

Table 21 - Estimative standard error for group 3 of parameters

R^2	Event Duration	Q max	P acum	V trans
Turbidity	0.07	0,90	0,03	0,40
TS	0.03	0,86	0,01	0,30
FTS	0.05	0,85	0,01	0,35
VTS	0.06	0,57	$3,00x10^{-4}$	0,02
SS	0.06	0,97	0,10	0,44
FSS	0.05	0,95	0,06	0,41
VSS	0.10	0,93	0,33	0,54

The weak relation among EMC and accumulated precipitation can be function of rainfall intensity. Sometimes precipitation have same amount but in different intensities, producing different river assimilation and response. However, is in maximum flow that big solids transport happen, justifying strong relations. Volume transported has intermediate relations because this characteristic also depends of precipitation and event duration, but even so produces pollutant contribution.

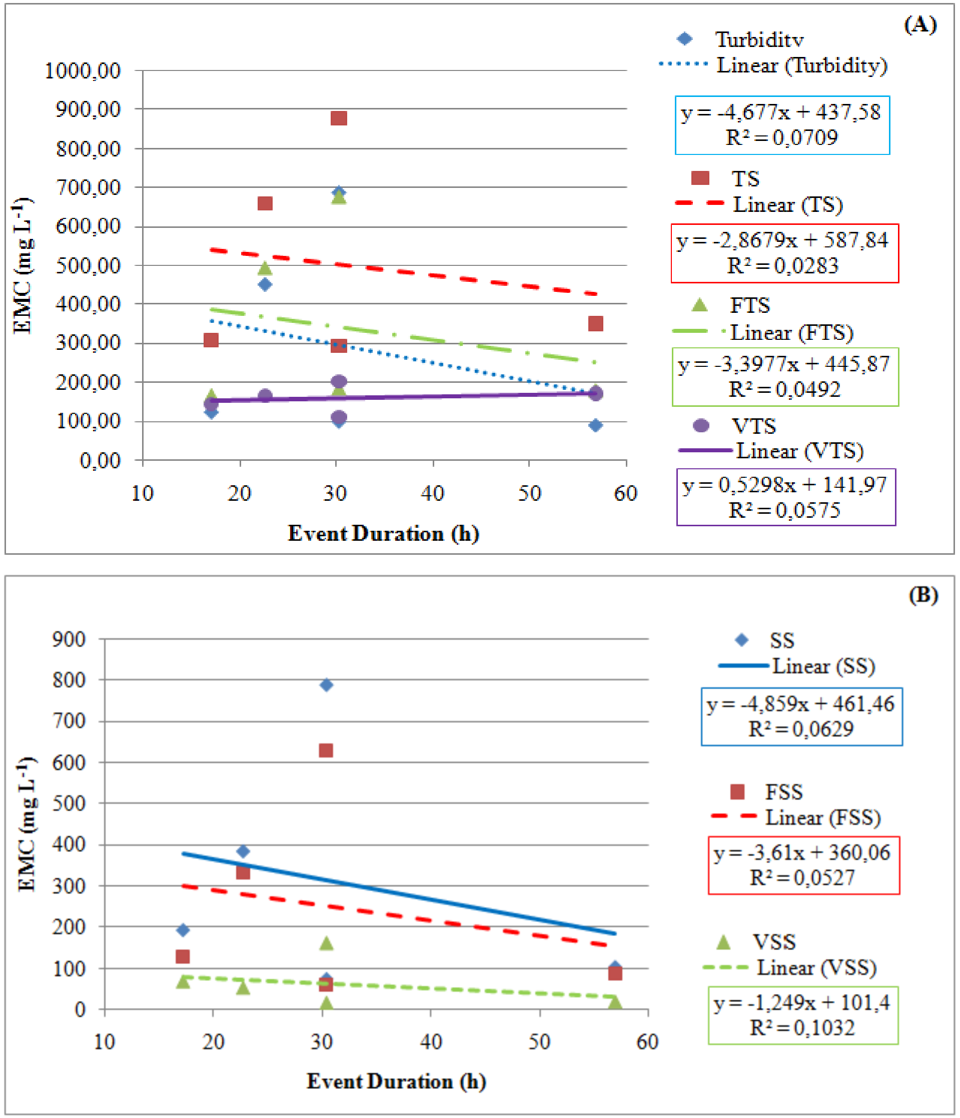


Figure 85 - EMC vs. Event Duration: (A) turbidity, TS (FTS and VTS) EMC values contrasting with event duration for each diffuse pollution event; (B) SS (FSS and VSS) EMC values contrasting with event duration for each diffuse pollution event

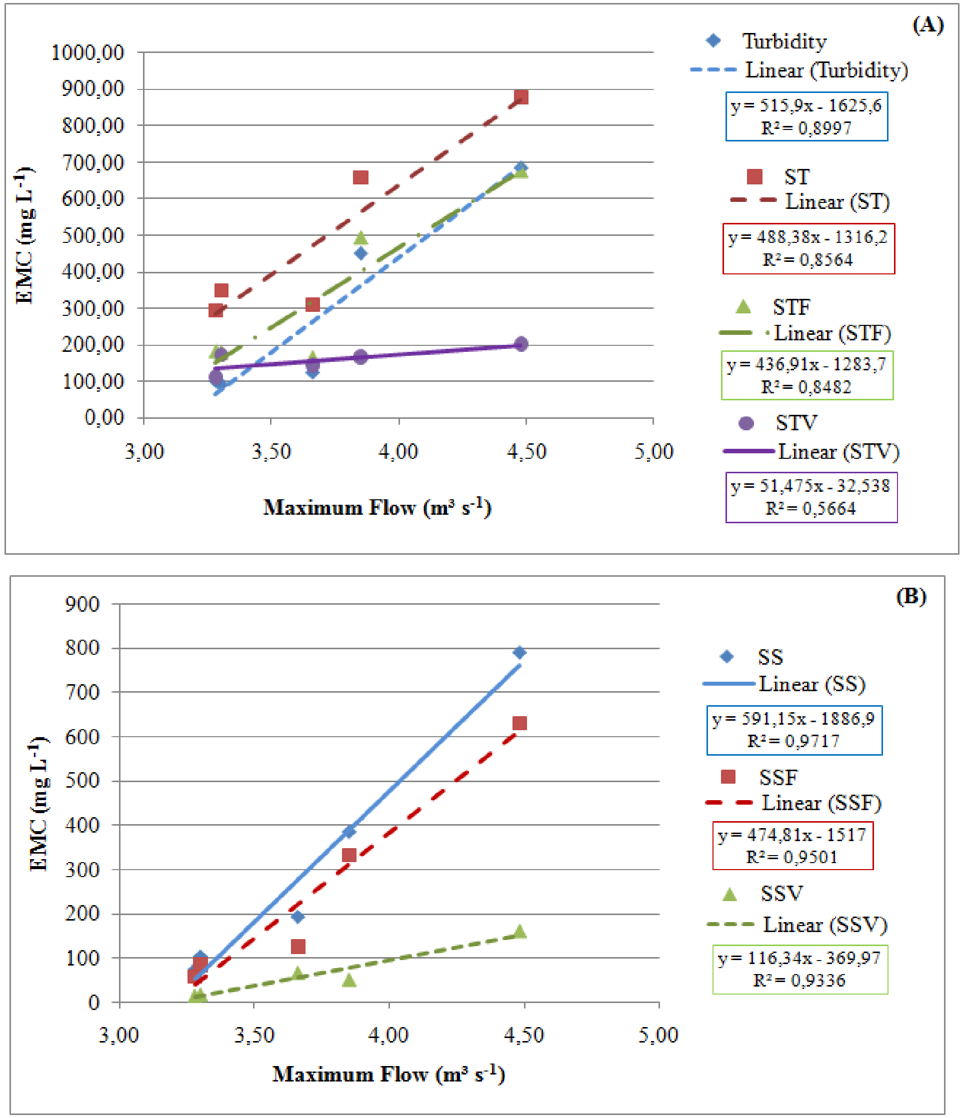


Figure 86 - EMC vs. Maximum Flow: (A) turbidity, TS (FTS and VTS) EMC values contrasting with maximum flow for each diffuse pollution event; (B) SS (FSS and VSS) EMC values contrasting with maximum flow for each diffuse pollution event

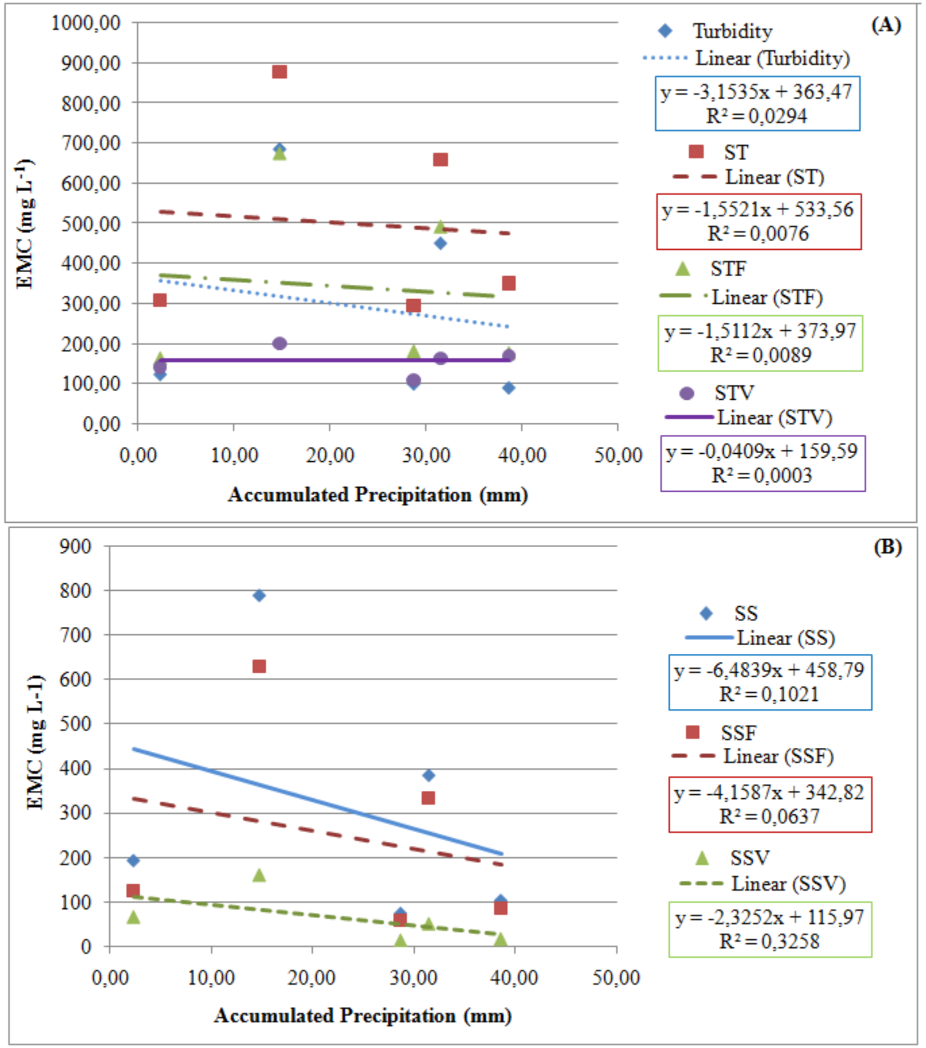


Figure 87 - EMC vs. Accumulated Precipitation: (A) turbidity, TS (FTS and VTS) EMC values contrasting with accumulated precipitation for each diffuse pollution event; (B) SS (FSS and VSS) EMC values contrasting with accumulated precipitation for each diffuse pollution event

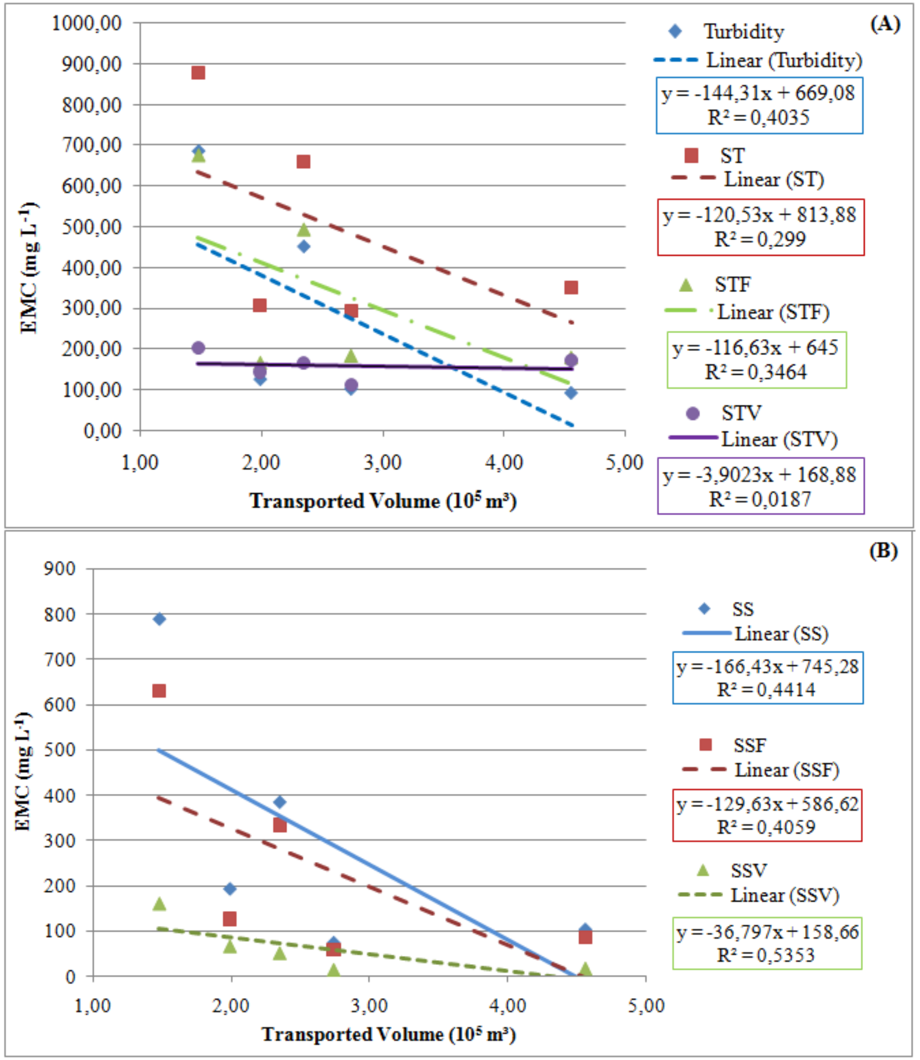


Figure 88 - EMC vs. Transported Volume: (A) turbidity, TS (FTS and VTS) EMC values contrasting with transported volume for each diffuse pollution event; (B) SS (FSS and VSS) EMC values contrasting with transported volume for each diffuse pollution event

4.8. Summary of the chapter

Chapter 4 showed rainfall events between February and May 2015. The aim to monitor this phenomenon was to feature quali-quantitatively diffuse pollution conditions using an intelligent automatic sampler during rainfall events. Water quality parameters were analyzed in laboratory to determine which kind of substances has been carried into the river and which effect is produced in river dynamics. In addition, SBN operated as water supervisor, identifying changes in water column level and, consequently, changes in flow. It was classified as water removal and water discharge.

The results for diffuse pollution events show a pattern behavior with the most water quality parameters, as COD, TN, TP, mainly, turbidity and solids series. Conductivity, alkalinity, pH, DO and temperature had a behavior more stable, while DOC was different behavior in comparison with other parameters. Results for special events show greater discharges and water removal that can be unknown a even situation. In reference to water quality parameters, the impact over the river dynamics was not evaluated and shall be investigated.

Also, in this chapter, analyses of pollutrographs and EMC are presented in order to understand and explain some of the diffuse pollution event characteristics. Some pattern were observed: i) similar rainfall can produce different results in EMC values due to different characteristics for each rainfall event and specific river response; ii) maximum flow, accumulated precipitation and transported water volume presented trends with water quality parameters; iii) pollutant dilution or concentration effects depend of antecedent dry days, rainfall intensity, volume transported, watershed kind (land use and occupation), and others. iv) physical parameters had trends more stable than chemical parameters; v) conductivity, pH, DO, temperature and alkalinity did not have any trends with events characteristics.

Chapter 5

Analytical Procedures Limitations Using an Automatic Sampler

"Speak softly and carry a big stick; you will go far."
— Theodore Roosevelt

The use automatic sampling has been used in distinct activities and, despite its contribution, in many aspects some water quality data limitations are unavoidable. Additional tests were made to ensure the best answers for the questions established in this research regarding the data reliability from SBN sampling, some potential analytical chemistry improvements and controls and which water quality parameters must be considered, in such a context, that has a better response to some standards limititations. This chapter presents the analysis performed and some reflections related to storage conditions, elapse time, analytical procedures and representativeness. The considerations made were made to a special monitoring point, Including: How sampler maintenance will be done? Which are the best sampler conditions to ensure the best sample preservation (both in field while in laboratory)? How elapsed time between collect and analyses interfere in the results quality?

The site chosen to make decay test is a point in Iguassu River, located in the most urbanized area of the Upper Iguassu Watershed, called IG02 (25°29'02" S and 49°11'23" O) (Figure 89). This site was considered relevant because had inputs of domestic and industrial effluents, and urban runoff. The occupation and land use of this site is urban (57,2 %) and agriculture (42,8 %). Also, IG02 is located a few meters downstream an important wastewater sewage treatment (Atuba Sul in Curitiba) (Knapik, 2014).

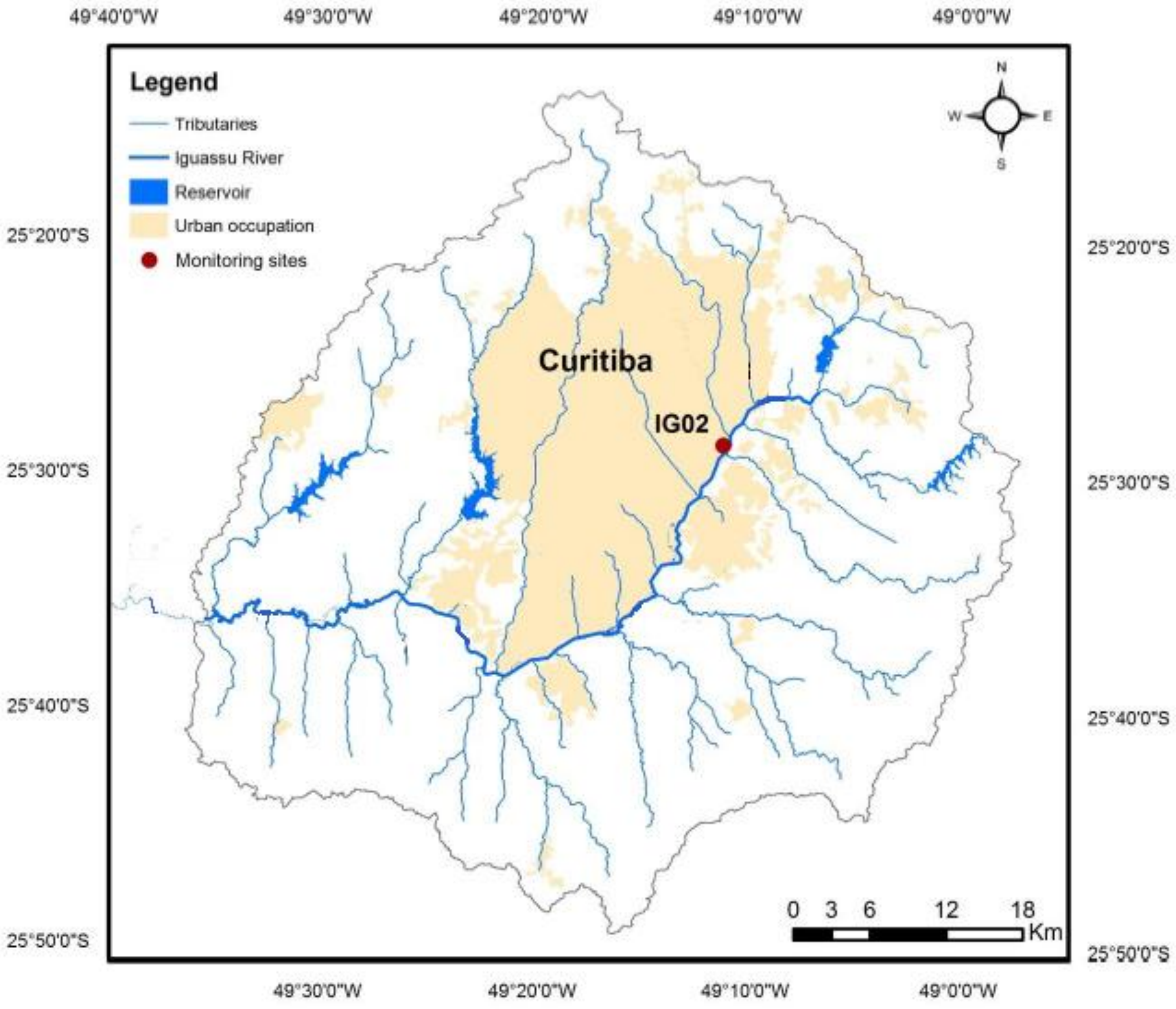


Figure 89 - Upper Iguassu Watershed and monitoring site IG02

Source: Knapik, 2014

5.1. Critical analysis for Water Quality parameters

The shorter elapsed time between sample collecting and lab processing is recommended by APHA (1998) to provide reliable results. Some water quality parameters can suffer changes according the time, storage conditions in situ or the proper sampling techniques. When the elapsed time will be long, it is recommended a preservation strategy which can be by cooling (4 °C) or addition of acid. The Standard Methods for the Examination of Water and Wastewater (APHA, 2000) summarizes some condition for sample storage and preservation and are show in Table 22.

Table 22 - Conditions for sample storage and preservation

Determination	Preservation	Maximum Storage Recommended
BOD	Refrigerate (stored at 4°C ± 2°C) in the dark	6 hours
COD	Analyze as soon as possible, or add H_2SO_4 to pH < 2; refrigerated	7 days
DOC	Analyze immediately; or refrigerate and add HCl, H_3PO_4, or H_2SO_4 to pH< 2.	7 days
Nitrogen Ammonia	Analyze as soon as possible, or add H_2SO_4 to pH < 2; refrigerated	7 days
Nitrite	Analyze as soon as possible; refrigerated	None
Nitrate	Analyze as soon as possible; refrigerated	48 hours
Total Phosphorus	Add $H_2SO_4$to pH <2 and refrigerate	28 days
Alkalinity	Refrigerate	24 hours
pH	Analyze immediately within 15 min of sample collection	0,25 hour
Temperature	Analyze immediately within 15 min of sample collection	0,25 hour
Dissolved Oxygen	Analyze immediately within 15 min of sample collection	0,25 hour

Source: adapted from APHA, 1998

In diffuse pollution studies, considering rainfall events as a determining factor, the unpredictability and duration of events provide much random about how and when the event will occur. SBN sampler needs to stay in the field for some days until event happens and samples automatically collected. The rainfall duration is a determining factor to larger or smaller time elapse, because long-event causes a large time elapse between first bottle collected to last bottle, and transfer to laboratory. Additionally, sometimes monitoring sites and laboratory are at distant location from each other. Hence, tests were made simulating the SBN condition on monitoring site considering time elapse of five days for water quality parameters. Also, as the version of SBN used in this study is an adaptation for automatic sampler yet (the adaptation consist in use SBN software adapted to datalloger). So, settings to preserve sample need to be investigated in detail, and consequently, to improve the infrastructure in the field.

5.2. Tests

The test were performed to investigate time influence on the water quality parameters. Tests were done to alkalinity, nitrogen series, TP, COD and BOD considering the following variables: (i) ambient sample (AS), (ii) 4°C refrigerated sample (RS), (iii) ambient acidified sample (AAS), and, (iv) 4°C refrigerated acidified sample (RAS).

Samples were collected in both sides of Iguassu River to insure the impact of water pollution and due the significant differences in hydrodynamic and color characteristics. The site IG2A correspond to left river side and site IG2B is right river side, with influence of Atuba and Palmital River (Figure 90).

The sampling was done in September 2015 and samples were carried to laboratory for the chemical analyses. Some samples were stored in refrigerator under 4°C, others were stored at room temperature, and, others were acidified and then stored in refrigerator and at room temperature. The chemical analyses started on 29th September and continued during five days in a row, reproducing all analyses every day considering each variable.

IG2A – Iguassu River IG2B – Iguassu River

Figure 90 - IG02 in both sides Iguassu River; IG2A - left side; IG2B - right side

5.2.1. BOD

According APHA (1998), BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. The initial DO may be measured shortly after collection, all oxygen uptakes occurring after is included in the BOD measurement. Therefore, when an analysis does not occur immediately after collecting, DO amount is consumed by biological process. Figure 91 represents BOD differences when analytical procedure had time variation.

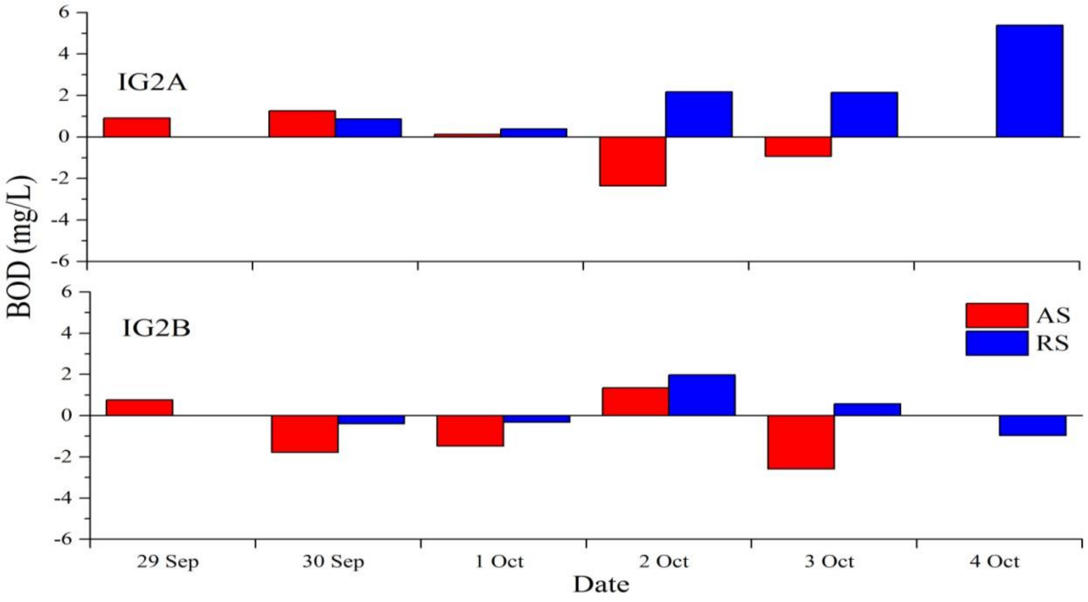


Figure 91 - BOD tests

Samples were incubated in first day and read fiver day later as proposed by Winkler method in APHA (1998). BOD concentration measured for IG2A was 9,14 mg L^{-1} and for IG2B was 7,60 mg L^{-1} and these values are considered baseline indices for comparison in subsequent days. In a second day, samples were stored for 24 hours and the test were performed at the same way, reproducing SBN conditions in a field. This routine was repeated during five tests days.

IG2A samples had not stable behavior during the test, with positive and negative values for BOD in ambient samples (fifth day was BOD -9,35 mg L^{-1}). Considering the refrigerated samples, the first day analyzes was the one closest to baseline value (BOD 8,75 mg L^{-1} in refrigerated samples stored refrigerated (4 °C) for 24 hours). After the values increased along the test, reaching 53,90 mg L^{-1} on fifth day. For IG2B, behavior was not stable and concentrations were decreased. The baseline value was not reproduced in any samples for both conditions. BOD in ambient sample ranged from 7,60 to -25,90 mg L^{-1}, and in refrigerated sample the range was of -4,00 to -9,56 mg L^{-1}, respectively for first and last day. The intermediate measures changed in positive and negative concentrations.

Percentage error was calculate and indicates wide variations between samples during tests days. The lower error was 4.27% for refrigerated sample in second day of the tests, representing the close value to baseline in IG2A. Other error ranging about 37 to 489 % in test for IG2A samples, and ranging to 25% until 440% in tests for IG2B samples. Table 23 summarizes BOD concentrations during tests and respective percentage error.

BOD decay test had expected results, with wide divergent values throughout analyses day. It means that BOD quantification cannot be reproduced with any time elapse. In samples of IG2B the variation was more expressive, decreasing to negative values just in second day of the tests. In IG2A happened significant errors, increasing along the tests days. Considering SBN use, this parameter will not be measure with precision because there are significant changes in concentrations values considering time elapse.

Table 23 - BOD concentrations during tests days and respective percentage error

BOD (mg L^{-1})				
	IG2A			
Tests Date	AS	Error (%)	RS	Error (%)
Sep 29	9,14	#	#	#
Sep 30	12,61	37,96	8,75	4,27
Oct 01	1,275	86,05	3,88	57,55
Oct 02	-23,63	358,53	21,68	137,20
Oct 03	-9,35	202,30	21,45	134,68
Oct 04	#	#	53,9	489,72

	IG2B			
Tests Date	AS	Error (%)	RS	Error (%)
Sep 29	7,60	#	#	#
Sep 30	-17,80	334,21	-4,00	152,63
Oct 01	-14,70	293,42	-3,23	142,50
Oct 02	13,40	76,32	19,76	160,00
Oct 03	-25,90	440,79	5,65	25,66
Oct 04	#	#	-9,56	225,79

- not measured; AS – ambient sample; RS – refrigerate sample

5.2.2. COD

For COD, samples are tested for four variables commented above. The measure did on first day was used as baseline values to compared with other days. COD concentrations in IG2A on first day was 27,00 mg L^{-1} and IG2B was 39,70 mg L^{-1}. Figure 92 show COD variations during tests day. However acidified samples also perform accept results, and this condition is recommend for APHA (1998), this delay before analysis is unavoidable, preserve samples by acidification to pH ≤ 2 using H_2SO_4 conc.

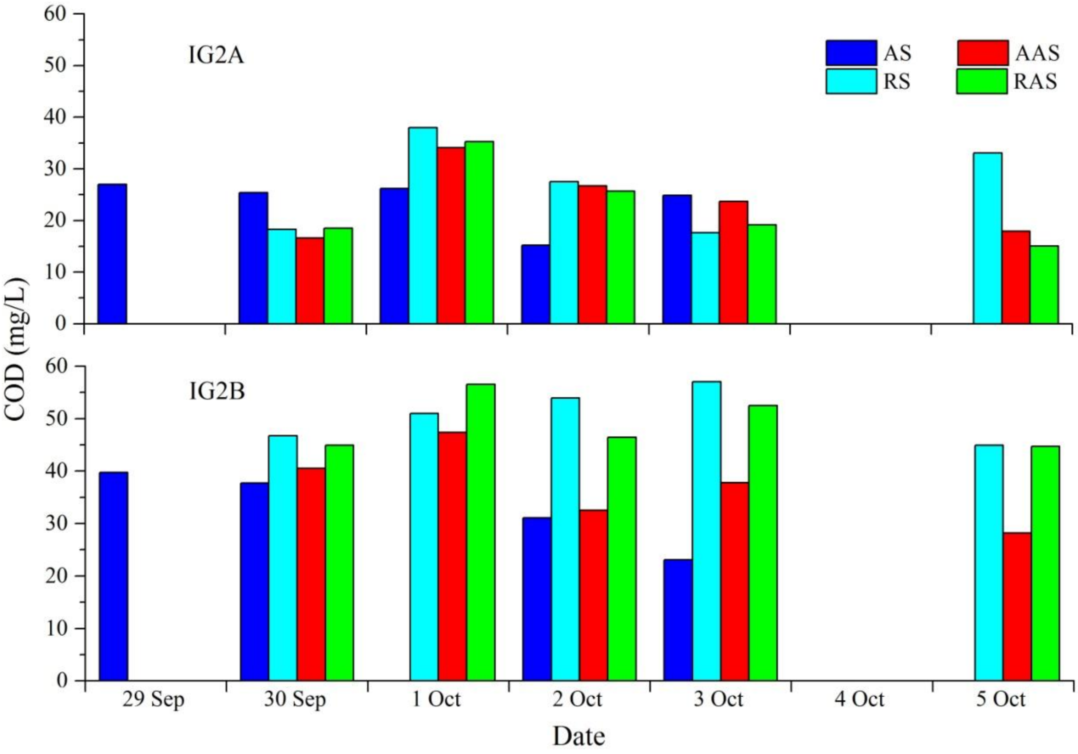


Figure 92 - COD tests

IG2A sample analyzed showed that any measurements replied exactly the values found on first day, for any variables and the subsequent values were lower than baseline. The differences between ambient sample in first day (27,00 mg L^{-1}) and other variables analyzes in second day was 1,60 mg L^{-1} (with 25,40 mg L^{-1} in ambient sample), 8,70 mg L^{-1} (with 18,30 mg L^{-1} in refrigerate sample), 10,40 mg L^{-1} (16,60 mg L^{-1} in ambient acidified sample) and 8,50 mg L^{-1} (18,50 mg L^{-1} in refrigerate acidified sample). Considering the second day analyzes, ambient sample had the lower percentage error, with about 6%, while for others variables the errors was bigger than 30%. COD concentrations and percentage error was shown in

Table 24.

The lowest errors was calculate for ambient sample test until third day analyzes, that indicates few variation on COD concentrations considering time elapse of three days for ambient sample. The values found for acidified samples (ambient and refrigerated) suggests preservation at the sample, because the values are close between them but different considering baseline value (error bigger than 30%).

The differences among baseline sample and other variables in second day samples were lower for IG2B, showing the lowest percentage errors (2% to ambient sample; 7% to refrigerated sample; 0,8% to ambient acidified sample; and 5% to refrigerated acidified sample). Ambient acidified samples in second day (40,50 mg L^{-1}) was only replied the baseline value (39,70 mg L^{-1}) with the lower error (0,80 %). The values measures in IG2B were not stable, increasing and decreasing concentrations along tests days.

Table 24 - COD concentrations during tests days and respective percentage error

COD (mg L^{-1})

Tests Date	IG2A							
	AS	Error (%)	RS	Error (%)	AAS	Error (%)	RAS	Error (%)
Sep 29	27,00	#	#	#	#	#	#	#
Sep 30	25,40	5,93	18,3	32,22	16,6	38,52	18,5	31,48
Oct 01	26,20	2,96	38	40,74	34,1	26,30	35,3	30,74
Oct 02	15,20	43,70	27,5	1,85	26,7	1,11	25,7	4,81
Oct 03	24,90	7,78	17,6	34,81	23,7	12,22	19,2	28,89
Oct 04	#	#	33,1	22,59	17,9	33,70	15,1	44,07

Tests Date	IG2B							
	AS	Error (%)	RS	Error (%)	AAS	Error (%)	RAS	Error (%)
Sep 29	39,7	#	#	#	#	#	#	#
Sep 30	37,7	2,00	46,70	7,00	40,50	0,80	44,90	5,20
Oct 01	-2,7	42,40	51,00	11,30	47,40	7,70	56,50	16,80
Oct 02	31,1	8,60	53,90	14,20	32,50	7,20	46,40	6,70
Oct 03	23,1	16,60	57,00	17,30	37,80	1,90	52,50	12,80
Oct 04	#	#	44,90	5,20	28,20	11,50	44,70	5,00

- not measured; AS – ambient sample; RS – refrigerate sample; AAS – ambient acidified sample; RAS – refrigerated acidified sample

COD analyzes had different behavior along test and among variables as expected. The variable more stable was ambient sample. This can be due analytical procedure used in COD determination (5220D: closed reflux proposed by APHA (1998), that is an energetic procedure (addition concentrated acid that produce strong chemical compounds consume). So, considering SBN use, nothing needs to be done because ambient sample (in time elapse about 3 days) can reproduce well the values, without significant differences.

5.2.3. DOC

Organic carbon in water is composed of a variety of organic compounds in various oxidation states, which can be measure by oxidation in BOD and COD methods. However, total organic carbon (TOC) is a direct expression of total organic content, but does not provide the same information than BOD or COD. DOC is a fraction of TOC, separate by filtering in membrane of 0,45µm (APHA, 1998). Fraction measured in this test was DOC.

Baseline values were measured in first day tests and had concentrations of 5,51 mg L^{-1} in IG2A and 4,21 mg L^{-1} in IG2B. Considering variables investigated, ambient and refrigerated samples, both acidified, were variables that can reproduce baseline values more close than others variables, for IG2A (6,78 mg L^{-1} and 6,68 mg L^{-1}, respectively). However, the percentage values for these variables was more than 20%. At the same time, for IG2B samples, any variables investigated can reproduce values with error below 10%. Table 25 shown DOC concentrations measured during tests days and respective percentage errors.

Some results had high DOC increase (refrigerated sample on September 30 (IG2B) and October 1 (IG2A)), which can be due some possible contamination during test, or some potential bacterial activity that can alter the DOC quantity and characteristics as mentioned by Knapik (2014). RAS sample in September 29 and AAS sample in October 02 cannot be measured due storage problems.

APHA (1998) recommend to preserve samples if cannot be examined immediately, holding at 4°C with minimal exposure to light and atmosphere. Acidification is indicated at the time of collection, to a $pH \leq 2$, especially for unstable samples. Acid preservation invalidates any inorganic carbon determination on the samples. As can be observed in Figure 93, acid samples were stable proportionally with baseline value in IG2A and less stable in IG2B, but with percentage error greater than 20%.

Table 25 - DOC concentrations during tests days and respective percentage error

DOC (mg L^{-1})								
Tests Date	IG2A							
	AS	Error (%)	RS	Error (%)	AAS	Error (%)	RAS	Error (%)
Sep 29	5,51	#	#	#	#	#	#	#
Sep 30	5,54	0,54	9,14	65,88	6,78	23,05	6,68	21,23
Oct 01	3,84	30,14	18,62	237,93	6,49	17,79	*	*
Oct 02	5,28	5,99	5,00	9,26	8,44	53,18	7,35	33,39
Oct 03	4,14	25,95	3,94	28,49	5,64	2,36	5,58	1,27
Oct 04	#	#	4,97	9,80	7,15	29,76	5,03	8,71

Tests Date	IG2B							
	AS	Error (%)	RS	Error (%)	AAS	Error (%)	RAS	Error (%)
Sep 29	4,21	#	#	#	#	#	#	#
Sep 30	7,77	84,56	11,63	176,25	7,67	82,19	5,72	35,87
Oct 01	11,51	173,40	6,73	59,86	12,03	185,75	16,68	296,20
Oct 02	10,80	156,53	5,89	39,90	*	*	8,90	111,40
Oct 03	4,24	0,71	6,05	43,71	8,14	93,35	8,15	93,59
Oct 04	#	#	2,84	32,54	5,15	22,33	5,85	38,95

- not measured; * - procedure error; AS – ambient sample; RS – refrigerate sample; AAS – ambient acidified sample; RAS – refrigerated acidified sample

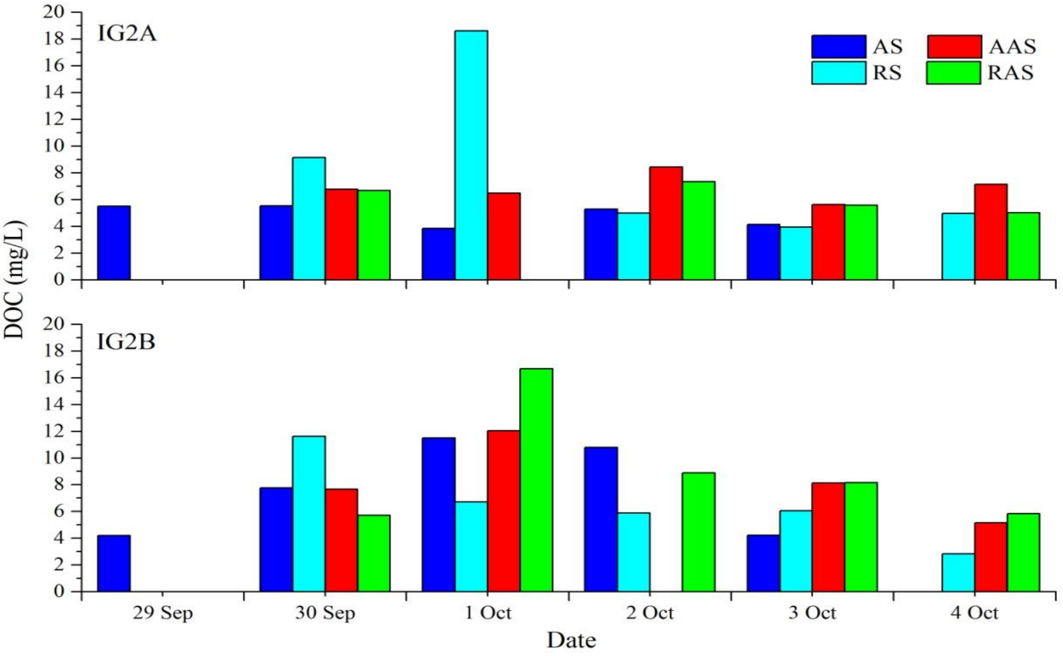


Figure 93 - DOC tests

Considering SBN use, in general terms, acidified samples shown a representative improvement, because the values measured for acidified samples were repeated each other, but error were more than 20%. However, to verify DOC stability is necessary more similarly tests in order to decrease percentage errors found in these tests. Additionally, glass bottles would be ensuring to collect and store samples to prevent any contamination. According APHA (1998), bottles must be washed with acid, sealed with aluminum foil and baked at 400°C for at least one hour.

5.2.4. Nitrogen Ammonia

Nitrogen ammonia was parameters more instable and could not be reproduced by any variables during the tests. Baseline values were 1631,34 µg L^{-1} for IG2A and 6364,85 µg L^{-1} for IG2B. Subsequent days concentrations changes, increasing and decreasing. For IG2A concentratios were lower than IG2B, and without much variation. However, for IG2B, concentratios are much bigger and, consequently, range in values too.

Refrigerated sample with 24 hours of time elapse for IG2A was the only sample that can reproduce the baseline value (1551,47 µg L^{-1}) with error in order to 4,90%, but for other variables the differences was in order to 500 µg L^{-1}. For IG2B the differences between baseline value to others variables was in order to 4000 µg L^{-1}. The concentrations values and respective percentage error can be showed in Table 26.

According APHA (1998), the most reliable nitrogen ammonia results are obtained on fresh samples. If analytical procedure will happen within 24h of collection, samples may be refrigerate unacidified at 4°C. For preservation for up 28 days, is necessary freeze samples at - 20°C unacidified. This condition also can be observe in Figure 94 that shows nitrogen ammonia during tests. For acidified samples, concentration was underestimated, while ambience and refrigerated sample maintained close values each other, but not reproducing baseline value.

Table 26 - Nitrogen ammonia concentration and respective percentage error during tests days

Ammonia Nitrogen (µg L^{-1})								
Tests Day	IG2A							
	AS	Error (%)	AAS	Error (%)	RS	Error (%)	RAS	Error (%)
29/set	1631,34		-		-		-	
30/set	1457,12	10,68	1062,02	34,90	1551,47	4,90	1156,69	29,10
01/out	1825,83	11,92	1110,45	31,93	1906,28	16,85	1147,45	29,66
02/out	1458,31	10,61	1133,51	30,52	1674,08	2,62	1156,56	29,10
03/out	1522,05	6,70	1323,73	18,86	1736,38	6,44	1219,65	25,24
05/out	-		1089,56	33,21	1465,98	10,14	1061,38	34,94

Test Day	IG2B							
	AS	Error (%)	AAS	Error (%)	RS	Error (%)	RAS	Error (%)
29/set	6364,85		-		-		-	
30/set	8804,67	38,33	10574,67	66,14	10315,54	62,07	11219,29	76,27
01/out	7741,75	21,63	9051,25	42,21	7783,13	22,28	9262,13	45,52
03/out	9348,75	46,88	10529,13	65,43	8396,38	31,92	10755,13	68,98
05/out	-		7211,33	13,30	8272,08	29,97	8310,58	30,57

- not measured; * - procedure error; AS – ambient sample; RS – refrigerate sample; AAS – ambient acidified sample; RAS – refrigerated acidified sample

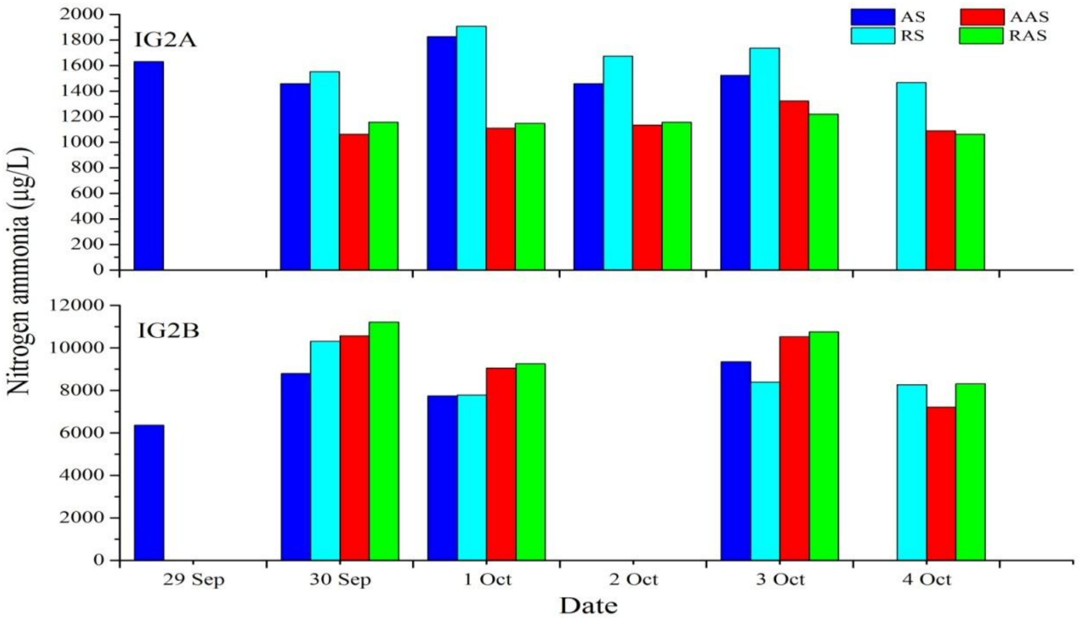


Figure 94 - Nitrogen ammonia tests

Considering SBN use, fresh samples are the best option for analysis this water quality parameters. If it is not possible, refrigerated samples can help to reproduce the values with time elapse (considering IG2A), but can not represent real concentration. To verify nitrogen ammonia stability is necessay more tests for these variables.

5.2.5. Nitrite

Considering nitrogen cycle, nitrite fraction is the most unstable compound. Therefore, is necessary the analytical procedure happen as soon as possible, to avoid bacterial conversion of NO_2^- to NO_3^-. Ambient sample measure in first day was baseline value to compare the other variables along tests. For IG2A the concentrations was 133,28 µg L^{-1} and in IG2B was 219,50 µg L^{-1}. During decay test, was observed that refrigerated sample can be replicate nitrite concentrations in first day without significant alterations for both sides, with percentage error below about 3.5% for IG2A and 13% for IG2B. The values measured and errors can be observed in Table 27. Besides that, refrigerated sample can to keep values along day analyzes (σ = 3,02 for IG2A and σ = 15,02 for IG2B) and ambient sample overestimated values (σ = 36,7 for IG2A and σ = 90,07 for IG2B).

Additionally, acidified samples underestimated nitrite concentrations (clearly observed in Figure 95), ranging about 133,28 µg L^{-1} for baseline value to 69,91 µg L^{-1} (47,55% error) for ambient acidified sample and 78,62 µg L^{-1} for refrigerated acidified sample measure in second day for IG2A, both with error more than 40%. Considering IG2B, the values measured were 219,50 µg L^{-1} for baseline value to 71,81 µg L^{-1} for ambient acidified sample and 73,69 µg L^{-1} for refrigerated acidified sample measure in second day, both with error more than 60%.. Therefore, acidified samples could not be used to determinate nitrite in water. This conclusion corroborate with APHA (1998) that affirms "never use acid preservation for samples to be analyzed for NO_2^- and make determination promptly on fresh samples; for short-term preservations (1 or 2 days), freeze at - 20°C or store at 4°C".

Table 27 - Nitrite concentrations during tests days

NO$_2^-$ (ug L^{-1})								
Tests Day	IG2A							
	AS	Error (%)	AAS	Error (%)	RS	Error (%)	RAS	Error (%)
29/set	133,28	#	#	#	#	#	#	#
30/set	143,05	7,33	69,91	47,55	137,12	2,88	78,62	41,01
01/out	174,37	30,84	69,50	47,85	133,79	0,38	86,75	34,91
02/out	214,71	61,10	64,25	51,79	132,30	0,73	83,72	37,18
03/out	348,69	161,63	58,24	56,30	134,39	0,84	81,50	38,85
05/out	#	#	50,51	62,10	128,90	3,28	77,46	41,88

Tests Day	IG2B							
	AS	Error (%)	AAS	Error (%)	RS	Error (%)	RAS	Error (%)
29/set	219,50	#	#	#	#	#	#	#
30/set	384,09	74,98	71,81	67,29	212,52	3,18	73,69	66,43
01/out	391,23	78,23	82,56	62,39	231,72	5,57	79,63	63,72
02/out	302,16	37,66	86,03	60,81	247,84	12,91	68,94	68,59
03/out	197,13	10,19	56,54	74,24	246,43	12,27	71,74	67,32
05/out	#	#	86,32	60,67	245,31	11,76	87,41	60,18

- not measured; * - analytical procedure error; AS – ambient sample; RS – refrigerate sample; AAS – ambient acidified sample; RAS – refrigerated acidified sample

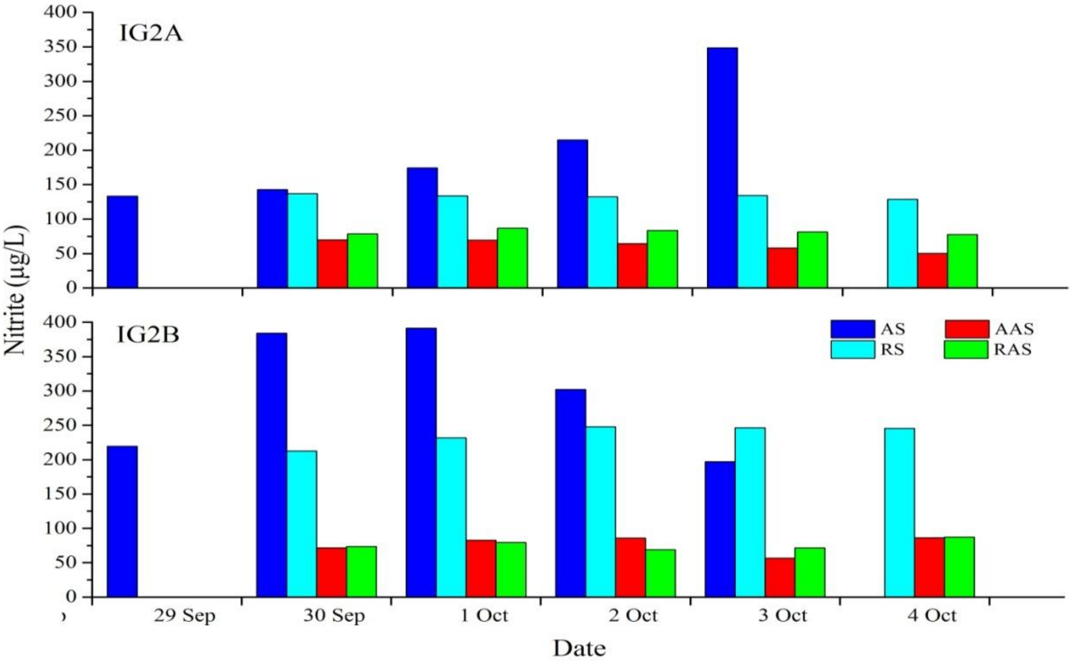


Figure 95 - Nitrite tests

In general, considering SBN use, a refrigerate system can help to keep nitrite concentration integrity in the samples during, at least, five days. An acidification sample is not recommended by overestimated nitrite concentrations.

5.2.6. Nitrate

Similarly to nitrite, APHA (1998) recommend that determinations may be promptly after sampling, and if storage is necessary, store for up to 2 days at 4 without acid preservation. Acidified samples overestimate nitrate values, ranging about 127,57 µg L^{-1} for baseline event to 217,90 µg L^{-1} for ambient acidified (70,80% of error) and 207,71 µg L^{-1} for refrigerate acidified (88,72% of error) in IG2A, and about 165,95 µg L^{-1} for baseline to 211,79 µg L^{-1} for ambient acidified (27,63% of error) and 214,38 µg L^{-1} refrigerate acidified (29,18% of error) in IG2B considering 24 hours elapse time. The differences and respective errors can be observed in Table 28.

Table 28 - Nitrate concentration during tests days and respective percentage errors

Nitrate (ug L^{-1})

Tests Day	IG2A							
	AS	Error (%)	AAS	Error (%)	RS	Error (%)	RAS	Error (%)
29/set	127,57		-		-		-	
30/set	232,31	82,10	217,90	70,80	240,75	88,72	207,71	62,82
01/out	230,38	80,58	222,10	74,10	223,71	75,36	207,50	62,65
02/out	254,31	99,35	121,89	4,46	223,06	74,85	139,69	9,50
03/out	280,90	120,18	181,25	42,08	209,44	64,17	179,33	40,57
05/out	-		174,96	37,14	202,60	58,81	132,06	3,52

Tests Day	IG2B							
	AS	Error (%)	AAS	Error (%)	RS	Error (%)	RAS	Error (%)
29/set	165,95		-		-		-	
30/set	243,50	46,73	211,79	27,63	225,44	35,85	214,38	29,18
01/out	360,33	117,14	209,21	26,07	82,19	50,47	209,77	26,41
02/out	138,88	16,31	203,75	22,78	257,58	55,22	216,02	30,17
03/out	110,19	33,60	186,75	12,54	232,02	39,82	190,29	14,67
05/out	-		202,94	22,29	221,00	33,17	180,25	8,62

- not measured; * - procedure error; AS – ambient sample; RS – refrigerate sample; AAS – ambient acidified sample; RAS – refrigerated acidified sample

Any variables could reproduce nitrate concentration close to baseline value. Refrigerated samples had the lowest variation between values along tests day (σ = 14,73 for IG2A, and σ = 16,35 for IG2B), considering all variables. Figure 96 shows nitrate concentration behavior during test days, where, in general, the values measured showed greater than baseline value. Considering SBN use, refrigerated samples is an improvement that can preserve this parameter, but if it is possible, the analytical procedure to determinate nitrate need to be made as soon as possible. The error ranged approximately between 30% and 200%, being necessary more tests to verify nitrate stability in order to minimize percentage errors during analytical procedures.

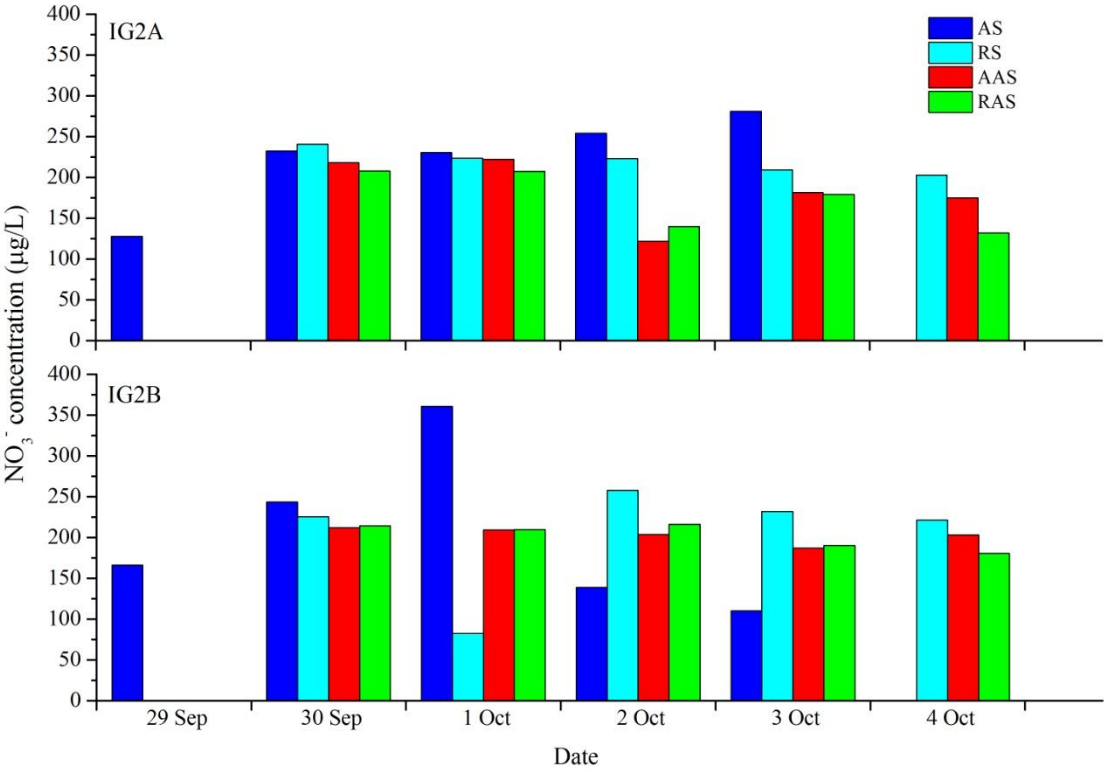


Figure 96 - Nitrate tests

5.2.7. Total Nitrogen

Total nitrogen is sum of nitrite, nitrate, nitrogen ammonia and organic nitrogen. According that, total nitrogen there was significantly underestimate condition for acidified samples, because acid affect nitrogen fractions available. Figure 97 shown test results for total nitrogen.

Total nitrogen had baseline value to IG2A of 1,22 mg L^{-1} and for IG2B of 1,71 mg L^{-1}. Refrigerated samples reproduced baseline values with 24 hours of time elapse, respectively 1,10 mg L^{-1} for IG2A (9,66% of error) and 1,72 mg L^{-1} (0,10% of error) for IG2B. Until third day the analytical procedure was able to maintain total nitrogen concentration for ambient sample and refrigerated sample, because these variables present the lowest percentage errors (below 10%), considering mainly IG2B. The values measured during test and respective percentage error can be shown in Table 29.

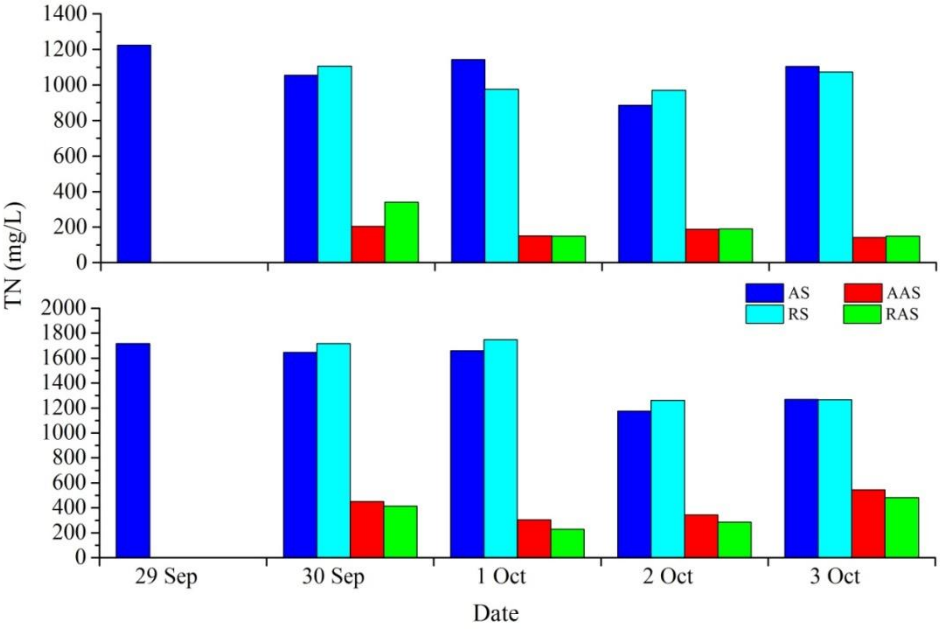


Figure 97 - TN tests

However, acidified samples (refrigerated or not) underestimate total nitrogen concentration. For IG2A ranging was from 1,22 mg L^{-1} for ambient sample measure in first day to 0,20 mg L^{-1} (83,37% of error) and 0,34 mg L^{-1} (72,29% of error) for ambient acidified and refrigerate acidified samples measure in second day, respectively. And for IG2B, the range was from 1,72 mg L^{-1} for ambient sample measure in first day to 0,45 mg L^{-1} and 0,41 mg L^{-1} for ambient acidified and refrigerate acidified samples measure in second day, respectively, both with percentage error greater than 70%.

Table 29 - TN concentration during tests days and respective percentage error

Total Nitrogen (µg L^{-1})

Tests Day	IG2A							
	AS	Error (%)	AAS	Error (%)	RS	Error (%)	RAS	Error (%)
29/set	1224,84		-		-		-	
30/set	1054,35	13,92	203,69	83,37	1106,48	9,66	339,44	72,29
01/out	1143,85	6,61	151,17	87,66	976,77	20,25	148,69	87,86
02/out	886,22	27,65	187,35	84,70	970,06	20,80	189,42	84,54
03/out	1104,21	9,85	141,46	88,45	1074,19	12,30	149,00	87,84
05/out	-		-		-		-	

Tests Day	IG2B							
	AS	Error (%)	AAS	Error (%)	RS	Error (%)	RAS	Error (%)
29/set	1717,70		-		-		-	
30/set	1647,27	4,10	451,17	73,73	1715,96	0,10	415,29	75,82
01/out	1658,06	3,47	303,27	82,34	1749,19	1,83	227,79	86,74
02/out	1175,94	31,54	343,15	80,02	1262,35	26,51	285,27	83,39
03/out	1269,10	26,12	544,17	68,32	1265,98	26,30	482,75	71,90
05/out	-		-		-		-	

- not measured; AS – ambient sample; RS – refrigerate sample; AAS – ambient acidified sample; RAS – refrigerated acidified sample

5.2.8. Total Phosphorus

For phosphorus analysis, ambience samples remained stable during all tests days, producing error less than 30% for IG2A and 13% for IG2B, as can be shown in Table 30. Acidified ambient and refrigerate samples slight overestimated phosphorus concentration in IG2A (0,24 mg L^{-1} for ambient acidified and 0,25 mg L^{-1} for refrigerated acidified samples) with error more than 17%. Therefore, refrigerated sample had decrease in concentration compared for baseline value (0,20 mg L^{-1} for baseline and 0,15 mg L^{-1} in refrigerated sample), with errors more than 10% considering five day tests.

Table 30 – TP concentrations during tests days and respective errors

Total Phosphorus (ug L^{-1})								
Tests Day	**IG2A**							
	AS	Error (%)	AAS	Error (%)	RS	Error (%)	RAS	Error (%)
29/set	202,06		-		-		-	
30/set	197,36	2,33	237,89	17,73	144,89	28,29	254,64	26,02
01/out	165,98	17,86	272,84	35,03	172,38	14,69	275,24	36,22
02/out	223,11	10,42	275,44	36,32	238,78	18,17	259,61	28,49
03/out	144,78	28,35	205,51	1,71	180,11	10,86	219,03	8,40
04/out	-		242,33	19,93	125,80	37,74	170,93	15,40

Tests Day	**IG2B**							
	AS	Error (%)	AAS	Error (%)	RS	Error (%)	RAS	Error (%)
29/set	585,69		-		-		-	
30/set	574,22	1,96	1005,97	71,76	833,89	42,38	965,56	73,81
01/out	622,11	6,34	985,31	68,23	870,04	48,55	1017,98	54,04
02/out	665,98	12,91	972,71	66,08	672,38	14,80	902,18	54,74
03/out	604,71	2,86	961,56	64,18	643,38	9,85	906,31	52,22
05/out	-		708,47	20,96	765,73	30,74	891,53	100,00

- not measured; AS – ambient sample; RS – refrigerate sample; AAS – ambient acidified sample; RAS – refrigerated acidified sample

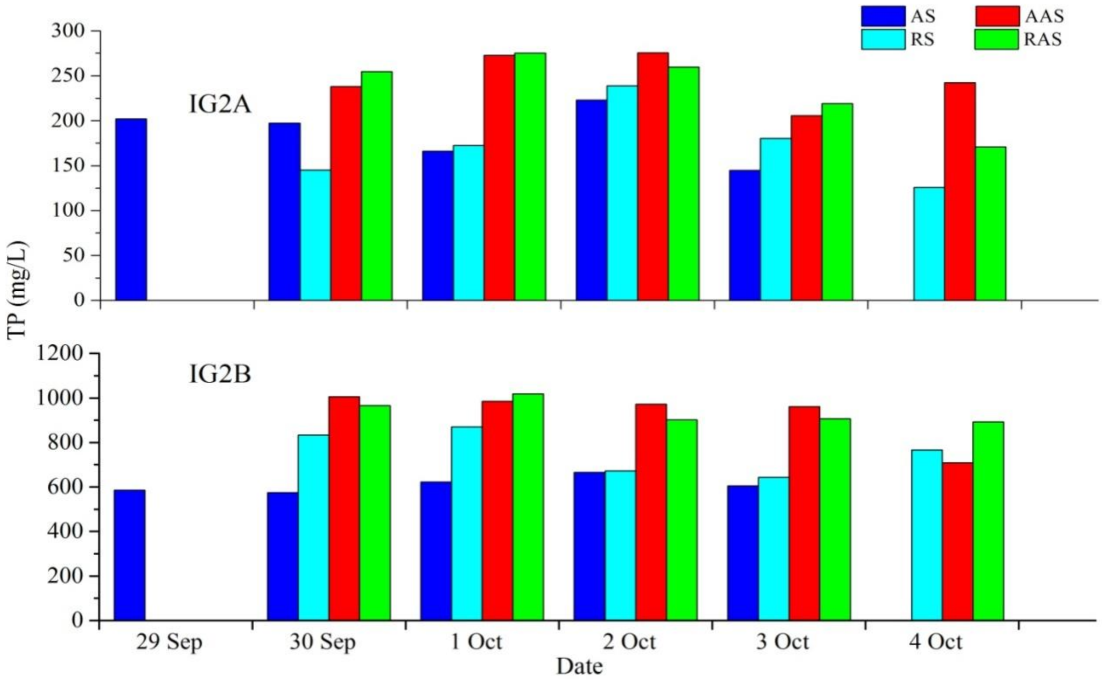


Figure 98 - TP decay tests

For IG2B all variables had increase in phosphorus concentration with 24 hour of time elapse, with errors more than 42%. The baseline value was 0,58 mg L^{-1}, while for refrigerated, ambient acidified and refrigerated acidified was, respectively, 0,84 mg L^{-1}, 1,00 mg L^{-1} and 0,96 mg L^{-1}. For IG2B, the second and third test days, the errors were less than 7% considering ambience sample. The TP concentration distribution can be observed in Figure 98.

However, acidified samples overrated phosphorus concentration during the tests more for IG2B than IG2A. This experience is not reported in APHA (1998) that suggest adding acid sulfuric to pH < 2, and cool to 4°C, or freeze sample without any acid additions if total phosphorus will be determined.

In general, ambient samples showed most stable variable to determine phosphorus with time elapse, because the errors were less than 10%. The values measured in ambient samples were close along the days. Considering SBN use, any improvement will be done for TP determinations.

5.2.9. Alkalinity

The variables investigated not produced significantly differences between ambience and refrigerated samples, as can be observed in Table 31. In IG2A difference between ambient sample (78,75 mg $CaCO_3$ L^{-1}) measure in first day analyzes and refrigerated samples (75,6 mg $CaCO_3$ L^{-1}) measure in second day was 3,15 (error of 4%), decreasing values between variables. For IG2B the difference was 5,25 (error of 4,13%), increasing values between variables, where was 127,05 mg $CaCO_3$ L^{-1} for ambient sample and 132,30 mg $CaCO_3$ L^{-1} for refrigerate sample. Average value of alkalinity along tests day for IG2A was 72,86 ± 6,16 mg $CaCO_3$ L^{-1} for ambient sample and 70,42 ± 4,19 mg $CaCO_3$ L^{-1} for refrigerated sample, and for IG2B was 127,13 ± 2,54 mg $CaCO_3$ L^{-1} for ambient sample and 127,25 ± 5,11 mg $CaCO_3$ L^{-1} for refrigerated sample.

Alkalinity shows stable during all analyses along the days (distribution along tests day can be shown in Figure 99). Although the results shows stability in measurements, according APHA (1998) is preferably the alkalinity measure within 1 day, due the microbial action and loss or gain of CO_2 or other gases when samples is exposed to air.

Table 31 - Alkalinity concentrations during tests day and respective percentage errors

Alkalinity (mg $CaCO_3$ L^{-1})								
Tests Date	IG2A				IG2B			
	AS	Error (%)	RS	Error (%)	AS	Error (%)	RS	Error (%)
Sep 29	78,75	#	#	#	127,05	#	#	#
Sep 30	78,75	0,00	75,6	4,00	128,10	0,83	132,3	4,13
Oct 01	66,66	15,35	66,66	15,35	124,23	2,22	121,2	4,60
Oct 02	73,85	6,22	73,85	6,22	130,82	2,97	124,49	2,01
Oct 03	66,3	15,81	66,3	15,81	125,46	1,25	127,5	0,35
Oct 04	#	#	69,7	11,49	#	#	133,25	4,88

- not measured; AS – ambient sample; RS – refrigerate sample

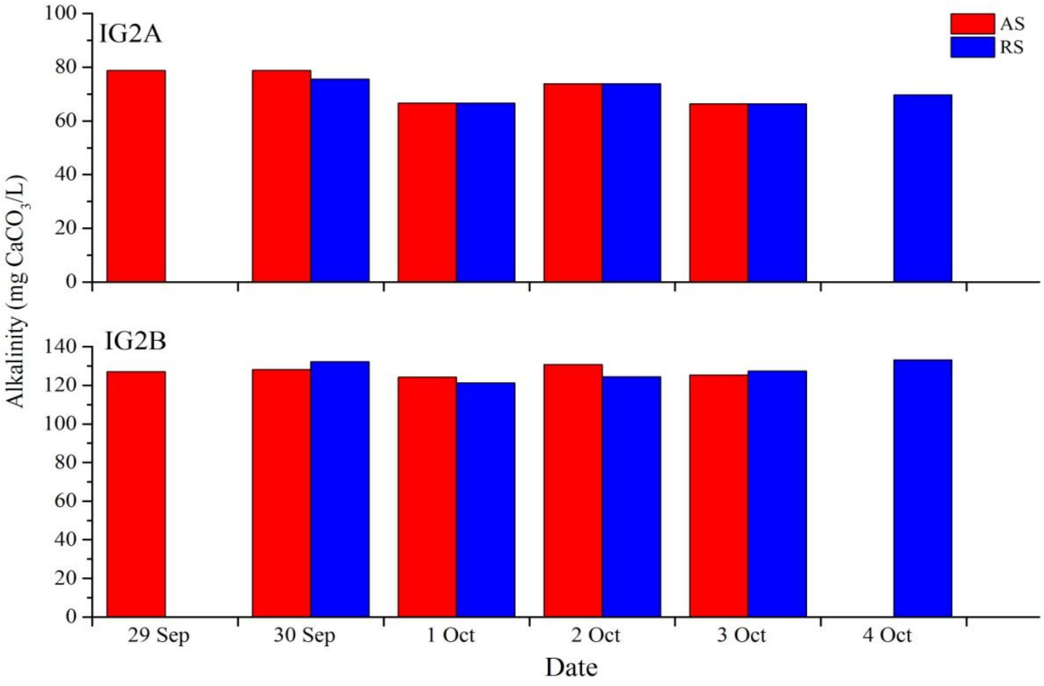


Figure 99 - Alkalinity tests

The biggest percentage errors found was in October 1st and 3rd, respectively about 15,35 and 15,81% for IG2A. Therefore, in these days the error were the same in ambience and refrigerated sample. Considering IG2B samples, the error were less than 5%, in both variables investigated. The stability found can be due simulation of SBN conditions in field, storage in the dark and with few air availability.

5.3. Reflections

Considering an error of 10%, the results indicate that ambient sample with time elapse about one or two days, the concentrations had few variations according baseline value for COD, DOC, NH_4^+, NO_2^-, TN, TP and alkalinity, considering ambience samples, and COD, NH_4^+, NO_2^-, TN and alkalinity considering refrigerated samples. The summary about error are show in Table 32, where B means baseline value, ✓ indicate the values with error less than 10%, and ✗ indicate the values with error more than 10%. Acidified samples were underestimating the real concentrations for nitrogen series. However, for TP, acidified samples overestimate the concentrations regarding first day analyses. For BOD parameter, the analytical procedure may be performed after collecting to ensure real values. DOC had positive stability in acidified samples. Finally, alkalinity and COD proved a water quality parameter more "stable" considering the impact over time.

Highlighting the kind of the sample is important in decision making. Samples represent a specific environment (in specific time and location) and after collect changes happen immediately. In laboratory, each sample is different and each characteristic, as best analytical procedure or influences of time elapse, will be produce different responses, according to the environment. In general, refrigerating samples can help slow down transformations.

The quality of the results was not overwhelming for the elapsed time. To ensure the representativeness and security of results, some improvements to SBN should be made, as: i) cooling system for samples; ii) telemetry system for transmit rainfall information and field conditions in real time. Others changes can be optimized in laboratory, in terms of routine in procedures, because preservation techniques just retard chemical and biochemical changes that inevitably continue after sample collection (APHA, 1998).

Table 32 - Summary of error during water quality parameters tests

Water quality parameters	Variables investigated – IG2A																							
	AS						RS						AAS						RAS					
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
BOD	B	✗	✗	✗	✗	#	#	✓	✗	✗	✗	✗	#	#	#	#	#	#	#	#	#	#	#	#
COD	B	✓	✓	✗	✓	#	#	✗	✗	✓	✗	✗	#	✗	✗	✓	✗	✗	#	✗	✗	✓	✗	✗
DOC	B	✓	✗	✓	✗	#	#	✗	✗	✓	✗	✓	#	✗	✗	✗	✓	✗	#	✗	*	✗	✓	✓
NH_4^+	B	✓	✗	✓	✓	#	#	✓	✗	✓	✓	✓	#	✗	✗	✗	✗	✗	#	✗	✗	✗	✗	✗
NO_2^-	B	✓	✗	✗	✗	#	#	✓	✓	✓	✓	✓	#	✗	✗	✗	✗	✗	#	✗	✗	✗	✗	✗
NO_3^-	B	✗	✗	✗	✗	#	#	✗	✗	✗	✗	✗	#	✗	✗	✓	✗	✗	#	✗	✗	✓	✗	✓
TN	B	✗	✓	✗	✓	#	#	✓	✗	✗	✗	-	#	✗	✗	✗	✗	-	#	✗	✗	✗	✗	-
TP	B	✓	✗	✗	✗	#	#	✗	✗	✗	✗	✗	#	✗	✗	✗	✓	✗	#	✗	✗	✗	✓	✗
Alka	B	✓	✗	✓	✗	#	#	✓	✗	✓	✗	✗	#	#	#	#	#	#	#	#	#	#	#	#

Water quality parameters	Variables investigated – IG2B																							
	AS						RS						AAS						RAS					
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
BOD	B	✗	✗	✗	✗	✗	B	✗	✗	✗	✗	✗	#	#	#	#	#	#	#	#	#	#	#	#
COD	B	✓	✗	✓	✗	#	#	✓	✗	✗	✗	✓	#	✓	✓	✓	✓	✗	#	✓	✗	✓	✗	✓
DOC	B	✗	✗	✗	✓	#	#	✗	✗	✗	✗	✗	#	✗	✗	*	✗	✗	#	✗	✗	✗	✗	✗
NH_4^+	B	✗	✗	✗	✗	#	#	✗	✗	✗	✗	✗	#	✗	✗	✗	✗	✗	#	✗	✗	✗	✗	✗
NO_2^-	B	✗	✗	✗	✗	#	#	✓	✓	✗	✗	✗	#	✗	✗	✗	✗	✗	#	✗	✗	✗	✗	✗
NO_3^-	B	✗	✗	✗	✗	#	#	✗	✗	✗	✗	✗	#	✗	✗	✗	✗	✗	#	✗	✗	✗	✗	✓
TN	B	✓	✓	✗	✗	#	#	✓	✓	✗	✗	#	#	✗	✗	✗	✗	-	#	✗	✗	✗	✗	#
TP	B	✓	✓	✗	✓	#	#	✗	✗	✗	✓	✗	#	✗	✗	✗	✗	✗	#	✗	✗	✗	✗	✗
Alka	B	✓	✓	✓	✓	#	#	✓	✓	✓	✓	✓	#	#	#	#	#	#	#	#	#	#	#	#

Chapter 6

Final Considerations

> “The important thing is not to stop questioning.
> Curiosity has its own reason for existing”
> — Albert Einstein

6.1. Main Contributions and Conclusions

The traditional water quality monitoring plan is based upon samples collected at specific day and time, subject to seasonal conditions, high-frequency, time between campaigns, hydrological processes influence such as rainfall, or eventually changes that could be produced by fast urban development. This monitoring model has been used and supposedly to be effective to evaluate rivers conditions along the days, months or years in specific moment, like a “photograph”, fundamentally influenced by the legislation nature of river classification and impact water pollution assessment.

When using automatic sampling, such as what is propose to be by the SBN equipment (Braga, 2013), the river behavior dynamic condition is explored through unsteady condition as consequence of rainfall events. More precisely, to allow, like a “movie” on unique monitoring site specifically, an opportunity to provide a better evaluation of the mass transport from the dynamics of the catchment. In this research, efforts to evaluate the SBN performance allowed to better assess water quality dynamics during rainfall events. All the strategy herein analyzed in depth, the water depth as the dynamic variable that “triggered” the sampling plan through SBN.

As in many other monitoring plan eventually, some difficulties were found. Different sites produce different answers. Land use and soil occupation is a decisive key factor in diffuse pollution events, what makes all this process challenging. The monitoring site at Barigui River in Almirante Tamandaré, the land use is influenced a combination of agricultural and some urban areas, with low urban density occupation and some commercial areas. The water quality base line is this monitoring point always remained low values, what required more care for analytical procedures, even though based upon the traditional standards.

Besides that, each rainfall produces different answers. An intense and short rainfall can eventually induce more mass transport, with wide ranging in the flow. In contrast, the same intense rainfall but with long time duration can induce pollutant dilution and low mass transport. Furthermore, quick rainfall can induce pollutant contribution as well as not to produce significantly transport, due antecedent dry days. This dynamic was captured through the events analyzed and confirmed the intrinsic relation between water volume, rainfall event and amount of pollutant transported.

Therefore, event characteristics are unique and extremely depending of the river dynamics and the watershed response. As mentioned previously, the SBN strategy is driven by water level. In such a context, each rainfall event is peculiar considering the mass transport perspective. Moraetis et al (2010) measured pH, nitrate, water temperature, dissolved oxygen and river stage in 5 minutes intervals, producing a significant amount of data through electronic sensors. In this research, emphasis was done to a broader water quality analysis following standard procedures.

Besides that, lack of in situ probes, telemetric gauging, or automatic stations is a encouraging strategy that we expect to add to our monitoring infrastructure. In order to evaluate the improvements that should be designed the tests performed indicates that the flexibility of the electronic control is more important than potential acclimatization,

Reflections

How this study can help future studies considering pollution diffuse, rainfall events and automatic sampler use?

Automatic sampling can be help to provide answer about diffuse pollution during rainfall events. The first one is based is the river response though the watershed influence. Rainfall spatial and temporal characteristics provide different river responses according to intensity, duration, land use and soil occupation, for example. In this research, other potential variables based upon urban characteristics, with strong water quality influence was not captured through the data provided such as the influence due to impervious area, solid deposition, solid waste, and industrial effluents and treatment systems

Despite all effort to produce water quality data in this research, it is necessary to improve the assessment considering different events, seasons, location or land use. In this research the infrastructure allowed only one monitoring site.

How precipitation events have influence on river water quality, considering an automatic sampler driven by dynamic external effects?

The dynamic of water quality parameter changes based upon the combination of the chemical or physical nature of the system being analyzed. For example, some dependent chemical parameters could not suffer the rainfall influence (as in total nitrogen case that remained stable during events) or to follow rising and falling hydrograph pattern (as in total phosphorus and COD case) or even can dilute due to amount of water volume transported during rainfall event (as DOC case, where were found low values and dilution tends during rainfall events). In contrast, physical parameters as turbidity and solids series presented clear pattern, always rising and falling hydrograph fluxes.

The SBN performance was stable through this research. All samples were performed following hydrograph nature of superficial flow. The trigger worked with precision and samples were collected always in the same sampler conditions. Regular maintenance is recommended, to ensure sensors quality (cleaning), calibrations, pluviometric station conservation and protection, equipment restart, and batteries exchanges.

How to evaluate the relevance in use automatic sampler? How to considered intelligent automatic sampler limitations?

In this research focus was done through the SBN, an intelligent automatic sampler that collected samples during rainfall events considering water level dynamics. Questions about storage time, time elapse, preservations, and samples quantity were discussed. Storage time, sample preservations, and time elapse were investigated in Chapter 5.

Storage conditions were reproduced (samples stored in the dark, open to air contact); time elapse (24-48-72-96-120 hours gap) and preservations (acidified, refrigerated and not acidified or refrigerated) were considered. Measurements showed little differences according to parameters. In general, (except BOD) all parameters provided a good response to tests, and refrigerated variables showed better results.

The unique variable that, definitely, is very sensitive through SBN operation is BOD. Due to biological process involved (dissolved oxygen consumption), this parameter needed to be measured as soon as sample is collected. In this research, this operational characteristic was not addressed. The simulation performed in laboratory scale, and presented in chapter 5 reveals the limitations. Improvements recommended, based upon the data and literature review are still related to water quality sensors and telemetry to provide high frequency data.

Is it possible to evaluate potential impacts of water quality dynamics considering rainfall events?

To assess potential impacts thorough the river system from precipitation events, more data is necessary. In this thesis, through EMC values we can only assess the amount of mass that has been added to the system, but is not representative to evaluate the overall river system, suggesting the need to add a second automatic sampler to better understand the true impact.

In contrast, the data amount performed in this thesis can be use in mathematical models calibration. According to Ferreira (2015), monitoring data was required, mainly as temporal series that consider seasonal and diurnal ranges. These data can provide enough information to water quality model calibration, as well as, information about diffuse load contributions, even is no more information is produced.

Is feasible to use event mean concentration (EMC) analyses for rainfall events characterization?

EMC analyzes (values and curves) showed good response to evaluate pollutant loads in rainfall events. The responses were based in dilution or concentration conditions. However, it was necessary high analytical procedures in laboratory that were converted in a single value. This kind of monitoring require large time to process data and, considering a water resources management strategies, can become unfeasible, due to time and responses provided.

Reflections about water quality and quantity integration and diffuse pollution

Water quality is a set of parameters which provide specifics responses. However, each parameter, in their essence, also represents environment condition, in terms of bioavailability or mass transport. Water quality parameters represent a combination of distinct information that point out to different interpretation, depending upon the reference to answer main questions. The integrated analysis of distinct parameters can provide a better understanding of the dynamics of mass added to the river system.. Additionally, this information must be associated to events characteristics and environment conditions.

Considering rainfall event, maybe physical parameters can provide a better response; which in turn can be more adequate to what is happening. Chemical parameters suffer much influence of chemistry in their essence. However, we could not let chemical issues set aside. Therefore, the sum of parameters (physical and chemicals) can provide answers about how environment is assimilating the “perturbations” produced during rainfall.

Final remarks

Each water quality parameter is very important in their essence and have its own particularity, like people´s personality, especially if the real understanding of watershed/river system is addressed Hydrological processes interfere significantly and is in general, not truly considered when the strategies for water resources planning and management is required. Brazilian legislation does not encourage a wider and broader perspective for this analysis.

In a more chemical perspective, distinct water quality parameters has to be considered as part of integrated groups to complement information from other groups. Here, we can visualize why automatic sampling is relevant.

The opportunity to understand rate responses, the real water quality impacts, the balance for chemical equilibrium, and integration for the real watershed/river response is really encouraging and can be considered the main contribution of this research. The literature review indicates more surrogate results than real environmental chemistry response.

Essentially, all world look for equilibrium, including and mainly aquatic systems such as rivers. Water quality parameters in equilibrium provide, at the same time, two answers: i) which one we want as: river is in good quality, clean and stable; ii) which one we need, as: what is going on, in fact? Which is the problem? What is need to do?

These are final questions that is always the motivation quote for monitoring. Engineers persist in their eternal fight to real reproduce physical response of environmental systems.

Chapter 7

References

ANDRADE, E.M. de; ARAÚJO, L. de F.P.; ROSA, M.F.; DISNEY, W.; ALVES, A.B. (2007) Seleção dos indicadore da qualidade das águas superificiais pelo emprego da análise multivariada. **Eng. Agríc.** v. 27, n. 3, p. 683-690.

ÁGUAS PARANÁ. Instituto de Águas do Paraná. Disponível em: <http://www.aguasparana.pr.gov.br/>. .

APHA (1998) **Standard Methods for the Examination of Water and Wastewater.** 20. ed. ed.Washington: APHA.

BALLO, S.; LIU, M.; HOU, L.; CHANG, J. (2009) Pollutants in stormwater runoff in Shanghai (China): Implications for management of urban runoff pollution. **Progress in Natural Science**, v. 19, n. 7, p. 873–880.

BARRELLA, W.; PETRETE JR, M.; SMITH, W. S.; MONTAG, L. F. DE A. As relações entre as matas ciliares, os rios e os peixes. (2001) In: R. R. Rodrigues; H. de F. L. Filho (Orgs.); **Matas ciliares: conservação e recuperação.** 2 edição, 320p. São Paulo: EDUSP.

BEM, C. C. (2009) **Determinação do estado de eutrofização de um lago raso: Estudo de caso do Lago Barigui – Curitiba.** 129p. Dissertação (Mestrado em Engenharia de Recursos Hídricos e Ambiental) - Universidade Federal do Paraná.

BRADY, N.; WEIL, R. (2010) **Elements of the nature and properties of soil**. 3rd Edition. Pearson Education Inc., Prentice Hall Copyright ©. ISBN: 9780135014332.

BRAGA, B.; HESPANHOL, I.; CONEJO, J. G. L.; MIERZWA J.C.; BARROS, M.T.L de.; SPENCER, M.; PORTO, M.; NUCCI, N,; JULIANO, N.; EIGER, S. (2005) **Introdução à Engenharia Ambiental**. 332p. Escola Politécnica da Universidade de São Paulo. 2ª Edição. Pearson Prentice Hall.

BRAGA, S. M. (2013) **Uma nova aborgagem para integração entre quantidade e qualidade da água para a avaliação da poluição difusa**. 188p. Tese (Doutorado em Engenharia de Recursos Hídricos e Ambiental) - Universidade Federal do Paraná.

BRASIL (1981) **Lei Federal n° 6.938, de 31 de agosto de 1981**. Dispõe sobre a Política Nacional do Meio Ambiente, seus fins e mecanismos de formulação e aplicação, e dá outras providências. Presidência da República - Casa Civil: Subchefia de Assuntos Jurídicos.

BRASIL (1997) **Lei Federal n° 9433, de 8 de janeiro de 1997**. Institui a Política Nacional de Recursos Hídricos, cria o Sistema Nacional de Gerenciamento de Recursos Hídricos. (Presidência da República - Casa Civil: Subchefia De Assuntos Jurídicos).

BRIDGEMAN, J.; BAKER, A.; BROWN, D.; BOXALL, J. B. (2015) Portable LED fluorescence instrumentation for the rapid assessment of potable water quality. **Science of The Total Environment**. v. 524-525, p. 338–346.

BU, H.; MENG, W.; ZHANG, Y.; WAN, J. (2014) Relationships between land use patterns and water quality in the Taizi River basin, China. **Ecological Indicators**, v. 41, p. 187–197.

BUCK, O.; NIYOGI, D. K.; TOWNSEND, C. R. (2004) Scale-dependence of land use effects on water quality of streams in agricultural catchments. **Environmental Pollution.** v. 130, n. 2, p. 287–299.

BUTTURINI, A.; FRANCESC, G.; JÉRÔME, L.; EUSEBI, V.; FRANCESC, S. (2006) Cross-site comparison of variability of DOC and nitrate c-q hysteresis during the autumn-winter period in three Mediterranean headwater streams: A synthetic approach. **Biogeochemistry**, v. 77, n. 3, p. 327–349.

BUTTURINI, A.; ALVAREZ, M.; BERNAL, S.; VAZQUEZ, E.; SABATER, F. (2008) Diversity and temporal sequences of forms of DOC and NO_3^- discharge responses in an intermittent stream: Predictable or random succession? **Journal of Geophysical Research: Biogeosciences**, v. 113, n. 3, p. 1–10.

CHANGWONY, K.; ALVAREZ, M.; LANYASUNYA, T. P.; DOLD, C.; BECKER, M.; SÜDEKUM, K.-H. (2015) Biomass and quality changes of forages along land use and soil type gradients in the riparian zone of Lake Naivasha, Kenya. **Ecological Indicators**. v. 49, p. 169–177.

CHAPIN, T. P. (2015) High-frequency, long-duration water sampling in acid mine drainage studies: A short review of current methods and recent advances in automated water samplers. **Applied Geochemistry**. v. 59, p. 118–124.

CHAPRA, S. C. (1997) **Surface Water Quality Modeling**. New York: McGraw-Hill Companies, Inc. 844 p.

CHEN, N.; WU, J.; HONG, H. (2012) Effect of storm events on riverine nitrogen dynamics in a subtropical watershed, southeastern China. **The Science of the total environment**. v. 431, p. 357–65.

CHEN, N.; WU, Y.; CHEN, Z. AND HONG, H. (2015) Phosphorus export during storm events from a human perturbed watershed, southeast China: Implications for coastal ecology. **Estuarine, Coastal and Shelf Science**. v. 166, p. 178-188.

CHITTOOR VISWANATHAN, V.; MOLSON, J.; SCHIRMER, M. (2015) Does river restoration affect diurnal and seasonal changes to surface water quality? A study along the Thur River, Switzerland. **Science of The Total Environment**. v. 532, p. 91–102.

COELHO, M. (2013) **Estratégia de monitoramento da qualidade da água para a gestão de recursos hídricos em bacias urbanas**. 163f. Dissertação (Mestrado em Engenharia de Recursos Hídricos e Ambiental) - Universidade Federal do Paraná.

CONSELHO NACIONAL DO MEIO AMBIENTE - CONAMA. (2005) **Resolução n 357, 18 de março de 2005**. Dispões sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluente, e dá outras providências. DOU n° 053, de 18/03/2005, páginas 58-63.

DARWICHE-CRIADO, N.; COMÍN, F. A.; SORANDO, R.; SÁNCHEZ-PÉREZ, J. M. (2015) Seasonal variability of NO3- mobilization during flood events in a

Mediterranean catchment: The influence of intensive agricultural irrigation. **Agriculture, Ecosystems and Environment**. v. 200, p. 208–218.

DEC, L. P. (2016) **Biofilm utilization for trace metal monitoring in aquatic ecosystem.** 100p. Dissertação (Mestrado em Engenharia de Recursos Hídricos e Ambiental) - Universidade Federal do Paraná.

DELPLA, I.; BAURÈS, E.; JUNG, A. V.; THOMAS, O. (2011) Impacts of rainfall events on runoff water quality in an agricultural environment in temperate areas. **Science of the Total Environment**. v. 409, n. 9, p. 1683–1688.

ETHERIDGE, J.R.; BIRGAND, F.; BURCHELL II, M.R. (2015) Quantifying nutrient and suspended solids fluxes in a constructed tidal marsh following rainfall: The value of capturing the rapid changes in flow and concentrations. **Ecological Enggineering.** v. 78, p. 41-52.

FACCHI, A.; GANDOLFI, C.; WHELAN, M. J. (2007) A comparison of river water quality sampling methodologies under highly variable load conditions. **Chemosphere**. v. 66, n. 4, p. 746–756.

FELLMAN, J.B.; HOOD, E.; EDWARDS, R.T.; D'AMORE, D.V. (2009) Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. **Journal of Geophysical Research**. v. 114, p. 1-14.

FERNANDES, C. V. S.; AZEVEDO, J. C. R. DE; PORTO, M. F. DO A. (2014) **INTEGRA 2: Bases Técnicas para a Integração de Instrumentos de Gestão de Recursos Hídricos -** Estudo de Caso da Bacia do Alto Iguaçu e Bacia do Alto Tietê. Curitiba: UFPR, UTFPR e USP. (CNPq/CT-Hidro). Partial Report 01.

FERREIRA, D.M. **Simulação hidrodinâmica e de qualidade da água em rios: Impacto para os Instrumentos de Gestão de Recursos Hídricos.** 126f. Dissertação (Mestrado em Engenharia de Recursos Hídricos e Ambiental) - Universidade Federal do Paraná.

FILELLA, M. (2009) Freshwaters: Which NOM matters? **Environmental Chemistry Letters**. v. 7, n. 1, p. 21–35.

FILL, H.D.; SANTOS, I. dos; FERNANDES, C.V.S. (2002) Balanço Hídrico da Bacia do Rio Barigui, PR. **Revista Brasileira de Recursos Hídricos.**

GAO, Y.; ZHU, B.; YU, G.; CHEN,W.; HE, N.; WANG, T.; MIAO, C. (2014) Coupled effects of biogeochemical and hydrological processes on C, N, and P export during extreme rainfall events in a purple soil watershed in southwestern China. **Journal of Hydrology.** v. 511, p. 692–702.

GKRITZALIS-PAPADOPOULOS, A.; PALMER, M. R.; MOWLEM, M. C. (2012) Combined use of spot samples and continuous integrated sampling in a study of storm runoff from a lowland catchment in the south of England. **Hydrological Processes**. v. 26, n. 2, p. 297–307.

GONÇALVES, M. F. (2008) **Variação temporal e espacial da presença dos metais pesados Cd, Cr, Ni, pB, Zn na bacia do Rio Barigui e identificação de suas fontes ponteciais.PhD Proposal**. 151p. Dissertação (Mestrado em Engenharia de Recursos Hídricos e Ambiental) - Universidade Federal do Paraná.

HARMEL, R. D.; KING, K. W.; SLADE, R. M. (2003) Automated Storm Water Sampling on Small Watersheds. **Applied Engineering in Agriculture**. v. 19, n. 6, p. 667–674.

INSTITUTO NACIONAL DE METROLOGIA, QUALIDADE E TECNOLOGIA - INMETRO (2010) **Orientação sobre validação de métodos analíticos: DOQ-CGCRE-008**

JANNASCH, H. W.; WHEAT, C. G.; PLANT, J.; KASTNER, M.; STAKES, D. (2004) Continuous chemical monitoring with osmotically pumped water samplers: OsmoSampler design and applications. **Limnology and Oceanography: Methods**. v. 2, p. 102–113.

KAYHANIAN, M.; SUVERKROPP, C.; RUBY, A.; TSAY, K. (2007) Characterization and prediction of highway runoff constituent event mean concentration. **Journal of Environmental Management.** v. 85, n. 2, p. 279–295.

KIM, L. H.; KAYHANIAN, M.; STENSTROM, M. K. (2004) Event mean concentration and loading of litter from highways during storms. **Science of the Total Environment.** v. 330, n. 1-3, p. 101–113.

KIM, L. H.; KO, S. O.; JEONG, S.; YOON, J. (2007) Characteristics of washed-off pollutants and dynamic EMCs in parking lots and bridges during a storm. **Science of the Total Environment.** v. 376, n. 1-3, p. 178–184.

KNAPIK, H. G. (2014) **Organic matter characterization and modeling in polluted rivers for water quality planning and management**. 281f. Thesis (Doctor in Water Resources and Environmental Engineering) - Federal University of Paraná.

KOZAK, C.; FERNANDES, C. V. S.; BRAGA, S. M.; PRADO, L. L. do; KNAPIK, H. G. (2015) **Quantifying diffuse pollution from rainfall events using automatic and manual sampling**. XXI Simpósio Brasileiro de Recursos Hídricos. Brasília - DF.

LALIKA, M. C. S.; MEIRE, P.; NGAGA, Y. M.; CHANG'A, L. (2015) Understanding watershed dynamics and impacts of climate change and variability in the Pangani River Basin, Tanzania. **Ecohydrology & Hydrobiology**. v. 15, n. 1, p. 26–38.

LEE, E.; SEONG, C.; KIM, H.; PARK, S.; KANG, M. (2010) Predicting the impacts of climate change on nonpoint source pollutant loads from agricultural small watershed using artificial neural network. **Journal of Environmental Sciences**. v. 22, n. 6, p. 840–845.

LEE, J. H.; BANG, K. W.; KETCHUM, L. H.; CHOE, J. S.; YU, M. J. (2002) First flush analysis of urban storm runoff. **The Science of the total environment**. v. 293, n. 1-3, p. 163–175.

LEE, J. Y.; KIM, H.; KIM, Y.; HAN, M. Y. (2011) Characteristics of the event mean concentration (EMC) from rainfall runoff on an urban highway. **Environmental Pollution**. v. 159, n. 4, p. 884–888.

LI, S.; GU, S.; LIU, W.; HAN, H.; ZHANG, Q. (2008) Water quality in relation to land use and land cover in the upper Han River Basin, China. **Catena**. v. 75, n. 2, p. 216–222.

LIU, A.; GOONETILLEKE, A.; EGODAWATTA, P. (2012) Taxonomy for rainfall events based on pollutant wash-off potential in urban areas. **Ecological Engineering.** v. 47, p. 110-114.

MADRID, Y.; ZAYAS, Z. P. (2007) Water sampling: Traditional methods and new approaches in water sampling strategy. **TrAC - Trends in Analytical Chemistry.** v. 26, n. 4, p. 293–299.

MAIE, N.; SEKIGUCHI, S.; WATANABE, A.; TSUTSUKI, K.; YAMASHITA, Y.; MELLING, L.; CAWLEY, K.M.; SHIMA, E.; JAFFÉ, R. (2014) Dissolved organic matter dynamics in the oligo/meso-haline zone of wetland-influenced coastal rivers. **Journal of Sea Research**. v. 91, p. 58–69.

MANIQUIZ, M. C.; LEE, S.; KIM, L. H. (2010) Multiple linear regression models of urban runoff pollutant load and event mean concentration considering rainfall variables. **Journal of Environmental Sciences**. v. 22, n. 6, p. 946–952.

MÉTADIER, M.; BERTRAND-KRAJEWSKI, J. L. (2012) The use of long-term on-line turbidity measurements for the calculation of urban stormwater pollutant concentrations, loads, pollutographs and intra-event fluxes. **Water Research**. v. 46, n. 20, p. 6836–6856.

MINELLA, J.P.G.; MERTEN, G.H.; MAGNAGO, P.F. (2011) Análise qualitativa e quantitativa da histerese entre vazão e concentração de sedimentos durante eventos hidrológicos. **Revista Brasileira de Engenharia Agrícola e Ambiental.** v. 15, n. 12, p. 1306-1313.

MORAETIS, D.; EFSTATHIOU, D.; STAMATI, F.; TZORAKI, O.; NIKOLAIDIS, N.P.; SCHNOOR, J.L.; VOZINAKIS, K. (2010) High-frequency monitoring for the identification of hydrological and bio-geochemical processes in a Mediterranean river basin. **Journal of Hydrology**. v. 389, n. 1-2, p. 127–136.

NOVOTNY, V. (2002) **Water quality - Diffuse pollution and watershed management**. 2nd Edition. New York: John Wiley & Sons. ISBN 0-471-39633-8.

OH, N.-H.; PELLERIN, B. A.; BACHAND, P. A. M.; HERNES, P.J.; BACHAND, S.M.; OHARA, N.; KAVVAS, M.L.; BERGAMASCHI, B.A.; HORWATH, W.R. (2013) The role of irrigation runoff and winter rainfall on dissolved organic carbon loads in an agricultural watershed. **Agriculture, Ecosystems & Environment**, v. 179, p. 1–10.

OKAMURA, K.; NOGUCHI, T.; HATTA, M.; SUNAMURA, M.; SUZUE, T.; KIMOTO, H.; FUKUBA, T.; FUJII, T. (2013). Development of a 128-channel multi-water-sampling system for underwater platforms and its application to chemical and biological monitoring. **Methods in Oceanography**. v. 8, p. 75–90.

OLIVEIRA, B. S. S. de; CUNHA, A. C. da. (2014) Correlação entre qualidade da água e variabilidade da precipitação no sul do Estado do Amapá. **Revista Ambiente e Agua.** v. 9, n. 2, p. 261–275.

PARK, M. H.; SWAMIKANNU, X.; STENSTROM, M. K. (2009) Accuracy and precision of the volume-concentration method for urban stormwater modeling. **Water Research**. v. 43, n. 11, p. 2773–2786.

PEREIRA, M. C. B.; SCROCCARO, J. L. (2010) **Bacias Hidrográficas do Paraná - Série Histórica**. 140p. Secretaria do Estado do Meio Ambiente e Recursos Hídricos. Governo do Estado do Paraná e Agência Nactional de Águas. Disponível em: <www.meioambiente.pr.gov.br>.

PORTO, M. F. A.; PORTO, R. L. L. (2008) Gestão de bacias hidrográficas. **Estudos Avançados**, v. 22, n. 63, p. 43–60.

PRADHAN, U. K.; WU, Y.; SHIRODKAR, P. V.; ZHANG, J.; ZHANG, G. (2014) Multi-proxy evidence for compositional change of organic matter in the largest tropical (peninsular) river basin of India. **Journal of Hydrology**. v. 519, p. 999–1009.

PRADO, L. L. do. **Phosphorus Analytical Procedure - Acid Digestion**. Personal conversation, 2015.

PRODANOFF, A. J. H. (2005) **Avaliação da Poluição Difusa Gerada por Enxurradas em Meio Urbano**. 266p. Tese (Doutorado em Ciências em Engenharia Civil) - Universidade Federal do Rio de Janeiro.

QIN, H.; TAN, X.; FU, G.; ZHANG, Y.; HUANG, Y. (2013) Frequency analysis of urban runoff quality in an urbanizing catchment of Shenzhen, China. **Journal of Hydrology.** v. 496, p. 79-88.

RAMOS, T. B.; GONÇALVES, M. C.; BRANCO, M. A.; BRITO, D.; RODRIGUES, S.; SÁNCHEZ-PÉREZ, J.-M.; SAUVAGE, S.; PRAZERES, A.; MARTINS, J.C.; FERNANDES, M.L.; PIRES, F.P. (2015) Sediment and nutrient dynamics during storm events in the Enxoé temporary river, southern Portugal. **Catena.** v. 127, p. 177–190.

SILVA, A. E. P.; ANGELIS, C. F.; MACHADO, L. A. T.; WAICHAMAN, A. V. (2008) Influência da precipitação na qualidade da água do Rio Purus. **Acta Amazonica**. v. 38, n. 4, p. 733–742.

SINGH, K. P.; MALIK, A.; SINHA, S. (2005) Water quality assessment and apportionment of pollution sources of Gomti river (India) using multivariate statistical techniques - A case study. **Analytica Chimica Acta.** v. 538, n. 1-2, p. 355–374.

SMITH, A. P.; WESTERN, A. W.; HANNAH, M. C. (2013) Linking water quality trends with land use intensification in dairy farming catchments. **Journal of Hydrology**. v. 476, p. 1–12.

VON SPERLING, M. (2005) **Introdução à qualidade das águas e ao tratamento de esgotos**. 2^{a} Edição ed.Belo Horizonte, MG: UFMG.

SUPERINTENDÊNCIA DO DESENVOLVIMENTO DE RECURSOS HÍDRICOS E SANEAMENTO AMBIENTAL - SUDERHSA (2002) **Plano Diretor de Drenagem para a Bacia do Rio Iguaçu na Região Metropolitana de Curitiba**. Relatório Final: Capacidade do sistema atual e medidas de controle de cheias. Edição Final, CH2M Hill do Brasil Serviços de Engenharia Ltda.

TERRADO, M.; BORRELL, E.; CAMPOS, S. de; BARCELÓ, D.; TAULER, R.; (2010) Surface-water-quality indices for the analysis of data generated by automated sampling networks. **TrAC - Trends in Analytical Chemistry**. v. 29, n. 1, p. 40–52.

THOMANN, R. .; MUELLER, J. A. (1987) **Principles of surface water quality modeling and control**. New York, USA: Happer Collins Publishers INC.

TUCCI, C. E. M. (1997) **Hidrologia: ciência e aplicação**. Porto Alegre: UFRGS.

TUCCI, C. E. M. (2008) Águas Urbanas. **Estudos Avançados**. v. 22, n. 63, p. 97–112.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA) (1984) Report to Congress: Nonpoint Source Pollution in the U.S. 160p. Washington D.C.

WATER ENVIRONMENT FEDERATION (WEF) (1995) **Odor Control in Wastewater treatment Plants**: Manual of practice n. 2. New York: ASCE Manuals and Reports on Engineering Practice n. 82, p. 282.

WESTERHOFF, P.; ANNING, D. (2000) Concentrations and characteristics of organic carbon in surface water in Arizona: influence of urbanization. **Journal of Hydrology.** v. 236, p. 202-222.

WU, L.; LONG, T. Y.; LIU, X.; GUO, J. S. (2012) Impacts of climate and land-use changes on the migration of non-point source nitrogen and phosphorus during rainfall-runoff in the Jialing River Watershed, China. **Journal of Hydrology**. v. 475, p. 26–41.

YE, Y.; HE, X.; CHEN, W.; YAO, J.; YU, S.; JIA, L.; (2014) Seasonal Water Quality Upstream of Dahuofang Reservoir, China - the Effects of Land Use Type at Various Spatial Scales. **CLEAN - Soil, Air, Water**. v. 42, n. 10, p. 1423–1432.

YU, S.; XU, Z.; WU, W.; ZUO, D. (2016) Effect of land use types on stream water quality under seasonal variation and topographic characteristics in the Wei River basin, China. **Ecological Indicators**. v. 60, p. 202–212.

ZHANG, Z.; FUKUSHIMA, T.; ONDA, Y.; MIZUGAKI, S.; GOMI, T.; KOSUGI, K.; HIRAMATSU, S.; KITAHARA, H.; KURAJI, K.; TERAJIMA, T.; MATSUSHIGE, K.; TAO, F. (2008) Characterisation of diffuse pollutions from forested watersheds in Japan during storm events - its association with rainfall and watershed features. **The Science of the Total Environment**. v. 390, n. 1, p. 215–26.

Chapter 8

Appendix

This chapter shows all data development in this thesis. The order of data presentation is.

1) Phosphorus Analytical Procedure – Acid Digestion, proposed by Prado (2015)
2) Data developed into laboratory for each campaign performed considering diffuse pollution and special events: summary data, calibrations curves, absorbance values determined.
3) Data developed during test of automatic sampler limitations, considering each variables investigated: summary data, calibrations curves, absorbance values determined.

In calibrations curves and absorbance triplicate, some values were removed to the calculation due wide different between samples. These values were considered analytical procedure error and are show in red color. In follow tables, “Aver” means average of values and “Aver-Blank” means average of values less standard sample.

Phosphorus Analytical Procedure – Acid Digestion

Method proposed by Prado (2015)

This method to measure phosphorus (P) in water samples were proposed due the difficulty of measure a lower P concentration in samples had high pH (around 8). In talk personal with the Environmental Chemistry Technique Luciane Lemos do Prado, employer of LABEAM, were this method were adapted from a analytical procedure for sediments to phosphorus determination.

In 25 mL of samples (may be collect under agitation due the particulate materials in the water sample and to ensure the best representativeness) add 5 mL of chloride acid (HCl) 1 mol/L and 0,8 mL of perssulfate solution. This solution must be prepared add 2,5 mL of sulfiric acid (H_2SO_4 p.a.) and 2,5 g of potassium perssulfate into a volumetric flaks of 50 mL.

After the samples preparation come the acid digestion. The samples prepared must be placed in warming plate for 2 hours or until evaporate to 5 mL approximately. following the digestion step, the transfer remaining volume into a volumetric flaks of 25 mL. Washing with distillate water the glass where occurred the digestion and transfer to the volumetric flaks too.

Correct the pH of the samples: add phenolphthalein and then sodium hydroxide (NaCl 1N) until the pink color completely develop in sample. After add sulfuric acid (H_2SO_4 5N) until the pink color disappear. Filled the volumetric flaks (25 mL) until meniscus. Always homogenize the sample.

Remove a 5mL aliquot and add mix reactive. Wait for 10 minutes (but no more than 30 minutes) and procedure the reading in spectroscopy (λ = 880nm)

Campaign data performed

Baseline Campaign

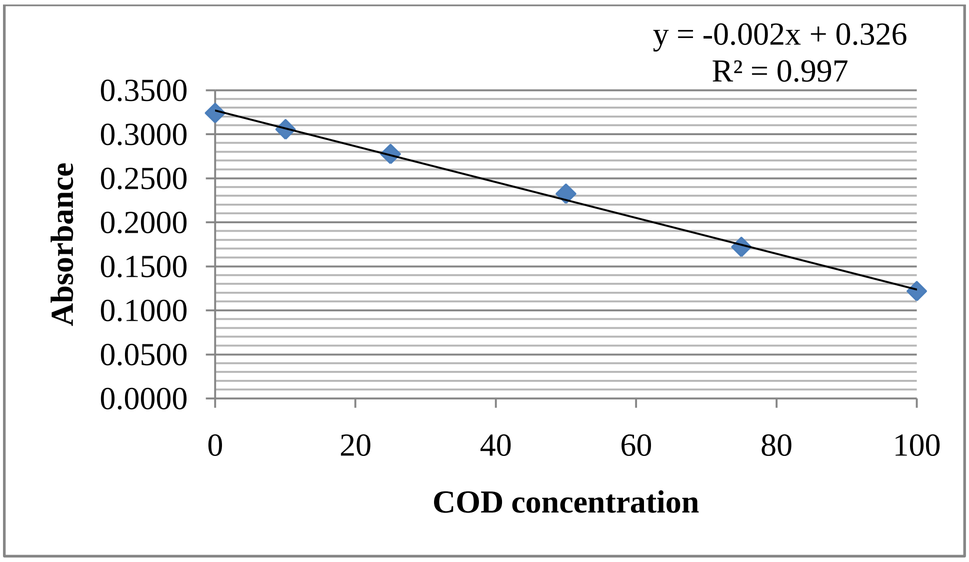
Hour	Water level (m)	Turb	Horiba Probe					BOD	COD	DOC	Nitrogen Serie			TP	Solids Serie					
			Turb	pH	DO	Cond	Temp				$N\text{-}NO_2^-$	$N\text{-}NH_3$	TN		TS	FTS	VTS	SS	FSS	VSS
9h30	0,94	47,1	74,1	7,74	7,47	0,267	19,89	5	12.15	3.51	12,60	37,83	0,42	0,08	156	130	26	38	28	10
10h30	0,92	38,6	65,2	7,75	7,37	0,267	19,93	4	5.75	3.14	11,56	41,33	0,51	0,08	144	118	26	36	30	6
11h30	0,92	42,2	64,3	7,78	7,36	0,268	20,08	7	6,30	3,79	11,20	57,92	0,54	0,09	166	130	36	49	35	14
12h30	0,91	28,7	59,8	7,69	7,15	0,270	20,33	6	1,80	3,15	11,26	57,72	0,53	0,09	168	156	12	42	30	11
13h30	0,90	32,8	59,0	7,79	7,16	0,271	20,62	3	12,03	2,80	11,51	190,08	0,46	0,07	150	150	0	70	32	38
14h30	0,89	34,8	59,4	7,84	6,97	0,271	20,95	0	8,48	2,67	12,06	66,75	0,39	0,07	186	150	36	38	28	10
15h30	0,88	27,3	57,5	7,84	6,96	0,273	21,25	7	6,33	1,05	11,63	34,42	0,40	0,07	182	164	18	41	33	8
16h30	0,86	33,2	52,8	7,85	7,01	0,272	21,40	9	2,38	5,72	11,60	158,75	0,38	0,09	158	148	10	35	26	9

BOD measured by Oxitop method

BOD (mg/L)								
Day	9h30	10h30	11h30	12h30	13h30	14h30	15h30	16h30
1°	2	2	1	2	1	2	3	2
2°	3	3	2	3	1	3	3	4
3°	3	3	4	4	2	1	4	5
4°	4	3	5	4	2	1	5	7
5°	5	4	7	6	3	0	7	9

Chemical Oxygen Demand (mg/L)

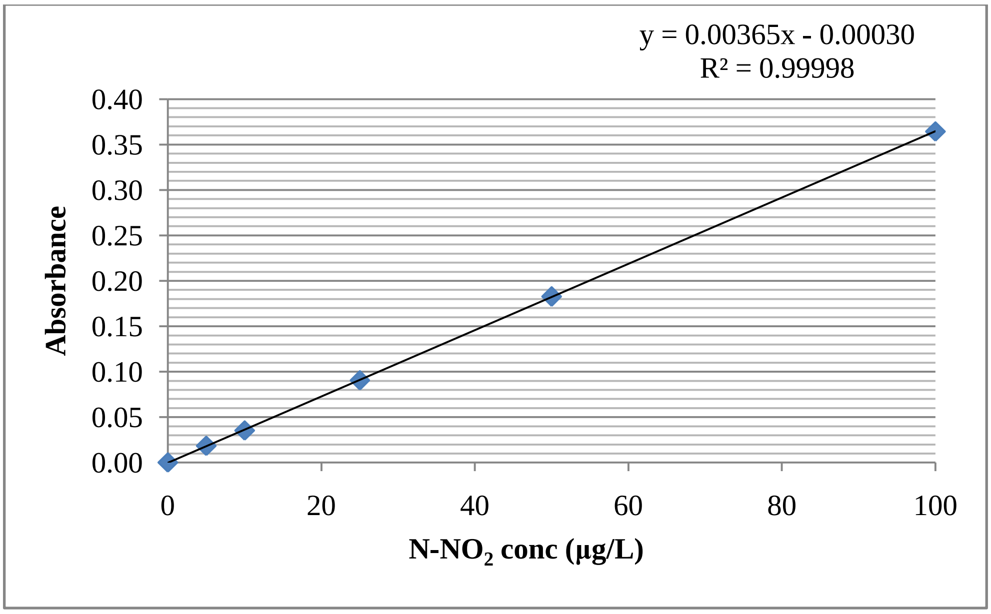
Calibration Curve				
COD know	A	B	C	Average
0	0,3438	0,3228	0,3251	0,3240
10	0,3242	0,3093	0,3013	0,3053
25	0,2803	0,2808	0,2714	0,2775
50	0,2285	0,2354	0,2335	0,2325
75	0,1703	0,1737	0,1906	0,1720
100	0,1205	0,1229	0,1111	0,1217



Samples					
Hour	A	B	C	Average	COD conc
9h30	0,3242	0,3081	0,2971	0,3026	12,15
10h30	0,3152	0,3137	0,3173	0,3154	5,75
11h30	0,3066	0,3116	0,3170	0,3143	6,30
12h30	0,3149	0,3242	0,3224	0,3233	1,80
13h30	0,3164	0,300	0,3057	0,3029	12,03
14h30	0,2947	0,3101	0,3098	0,3100	8,48
15h30	0,3247	0,3035	0,3145	0,3142	6,33
16h30	0,3188	0,3237	0,3206	0,3222	2,38

Nitrite: N-NO_2^- (µg/L)

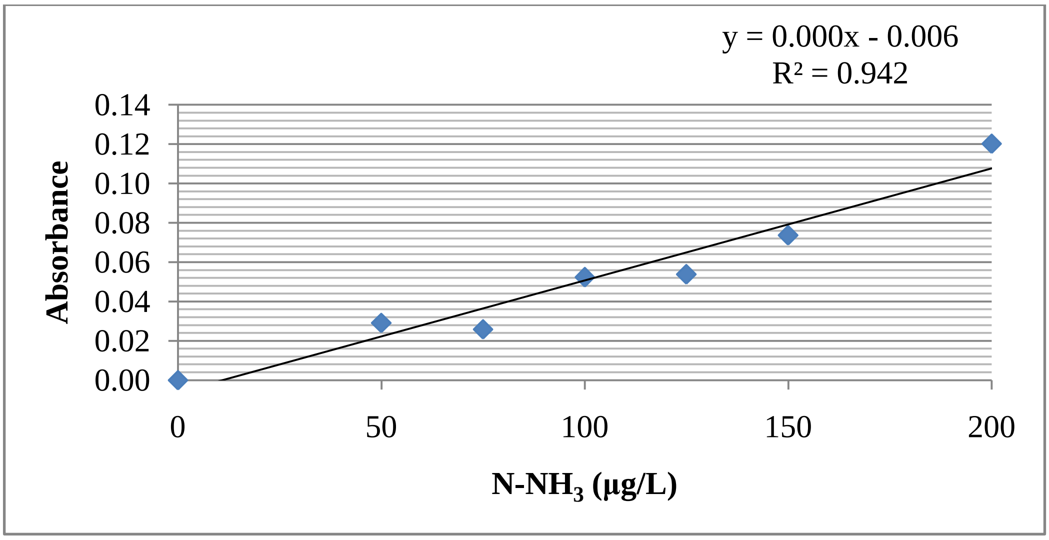
Calibration Curve					
N-NO_2^-	A	B	C	Average	Aver-Blank
0	0,0023	0,0033	0,0031	0,0032	0,0000
5	0,0227	0,0215	0,0209	0,0217	0,0185
10	0,0378	0,0388	0,0388	0,0385	0,0353
25	0,0945	0,0939	0,0931	0,0938	0,0906
50	0,1848	0,1893	0,1835	0,1859	0,1827
100	0,3689	0,3672	0,3672	0,3678	0,3646



Samples						
Hour	A	B	C	Average	Aver-Blank	Conc
9h30	0,0481	0,0492	0,0494	0,0489	0,0457	12,60
10h30	0,0441	0,0444	0,0468	0,0451	0,0419	11,56
11h30	0,0435	0,0442	0,0436	0,0438	0,0406	11,20
12h30	0,0435	0,0433	0,0452	0,0440	0,0408	11,26
13h30	0,0452	0,0457	0,0438	0,0449	0,0417	11,51
14h30	0,0464	0,0465	0,0479	0,0469	0,0437	12,06
15h30	0,0446	0,0458	0,0457	0,0454	0,0422	11,63
16h30	0,0450	0,0455	0,0452	0,0452	0,0420	11,60

Ammoniacal Nitrogen: N-NH3 (µg/L)

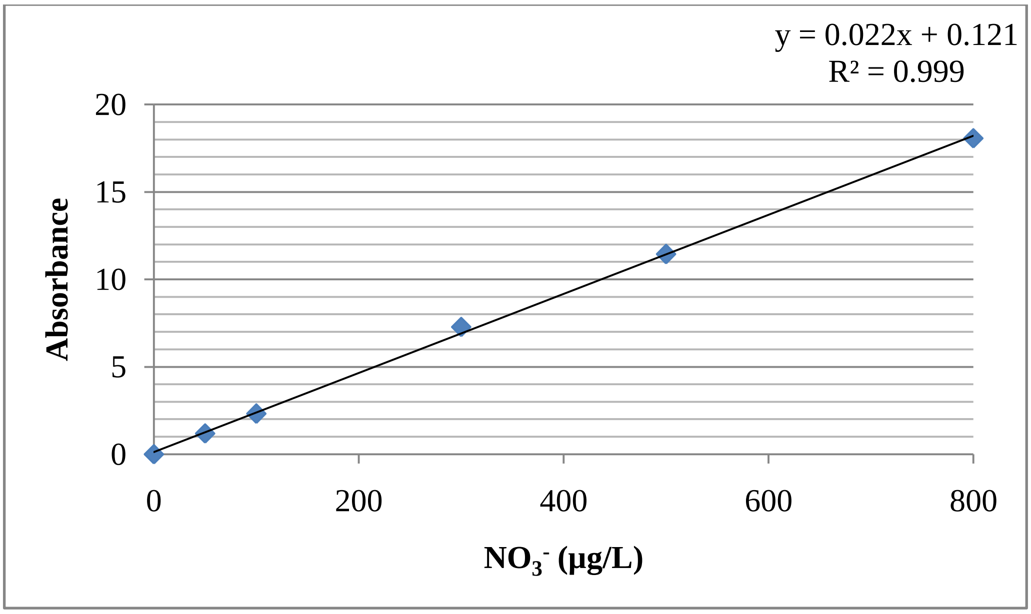
Calibration Curve					
$N\text{-}NH_3$	A	B	C	Average	Aver-Blank
0	0,1404	0,1328	0,1609	0,1366	0,0000
50	0,1675	0,1639	0,2020	0,1657	0,0291
75	0,1626	0,1615	0,1631	0,1624	0,0258
100	0,1713	0,2234	0,2064	0,1889	0,0523
125	0,1958	0,1918	0,1833	0,1903	0,0537
150	0,2091	0,2062	0,2152	0,2102	0,0736
200	0,2373	0,2792	0,2538	0,2568	0,1202



Samples						
Hour	A	B	C	Average	Aver-Blank	Conc
9h30	0,1378	0,1503	0,1559	0,1531	0,0165	37,83
10h30	0,1543	0,1515	0,1598	0,1552	0,0186	41,33
11h30	0,1698	0,1605	0,1497	0,1652	0,0286	57,92
12h30	0,1635	0,1677	0,1639	0,1650	0,0284	57,72
13h30	0,1737	0,2554	0,2335	0,2445	0,1079	190,08
14h30	0,1639	0,1770	0,3179	0,1705	0,0339	66,75
15h30	0,1506	0,1515	0,2289	0,1511	0,0145	34,42
16h30	0,2291	0,2222	0,1490	0,2257	0,0891	158,75

Total nitrogen – TN (mg/L)

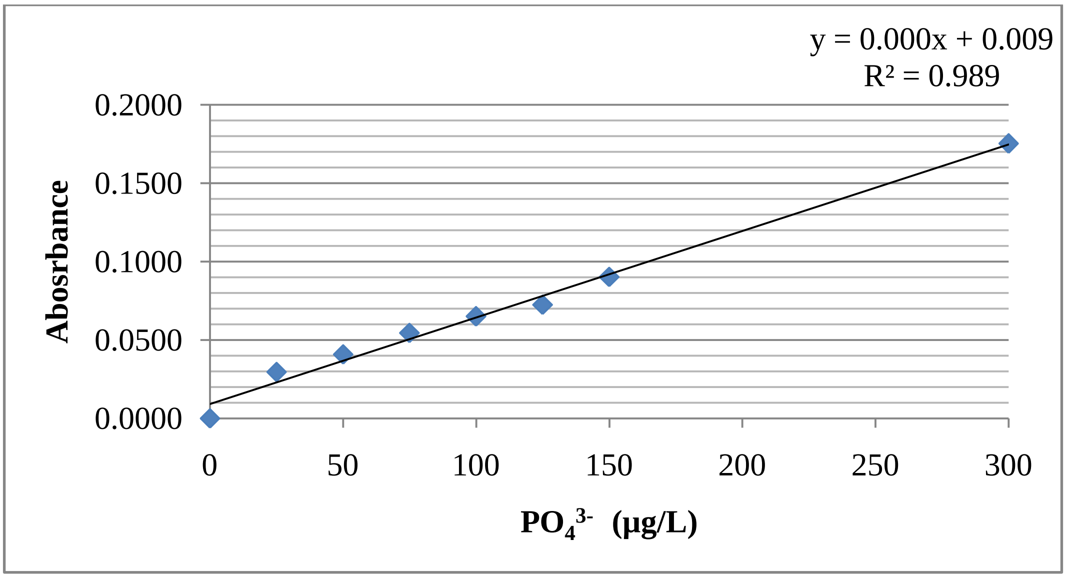
Calibration Curve						
NO_3^- (µg/L)	A	B	C	Aver	Aver-Blank	x10
0	0,0270	0,0276	0,0294	0,0280	0,0000	0
50	0,1510	0,1427	0,1467	0,1468	0,1188	1,188
100	0,2609	0,2601	0,2574	0,2595	0,2315	2,31467
300	0,7548	0,7639	0,7479	0,7555	0,7275	7,27533
500	1,1735	1,1798	1,1626	1,1720	1,1440	11,4397
800	1,8450	1,8130	1,8450	1,8343	1,8063	18,0633



Samples								
Hour	A	B	C	Aver	Aver-Blank	x10	Conc (µg/L)	Conc (mg/L)
9h30	0,9862	0,9956	1,0057	0,9958	0,9678	9,6783	422,86	0,42
10h30	1,1958	1,1790	1,1813	1,1854	1,1574	11,5737	506,72	0,51
11h30	1,2836	1,2607	1,2598	1,2680	1,2400	12,4003	543,30	0,54
12h30	1,2418	1,2301	1,2274	1,2331	1,2051	12,0510	527,84	0,53
13h30	1,0929	1,0818	1,0671	1,0874	1,0594	10,5935	463,35	0,46
14h30	0,9299	0,9164	0,8654	0,9232	0,8952	8,9515	390,70	0,39
15h30	0,9374	0,9371	0,9150	0,9373	0,9093	9,0925	396,94	0,40
16h30	0,9117	0,9036	0,8701	0,9077	0,8797	8,7965	383,84	0,38

Total Phosphorus – TP (mg/L)

Curva de Calibração						
$P\text{-}PO_4^{3-}$	A	B	C	Aver	Aver-Blank	x5
0	0,0110	0,0076	0,0049	0,0063	0,0000	0,0000
25	0,0125	0,0115	0,0125	0,0122	0,0059	0,0296
50	0,0165	0,0143	0,0145	0,0144	0,0082	0,0408
75	0,0161	0,0172	0,0171	0,0172	0,0109	0,0545
100	0,0256	0,0187	0,0198	0,0193	0,0130	0,0650
125	0,0222	0,0192	0,0208	0,0207	0,0145	0,0724
150	0,0365	0,0237	0,0249	0,0243	0,0181	0,0903
300	0,0470	0,0410	0,0416	0,0413	0,0351	0,1753



Amostras								
Hour	A	B	C	Aver	Aver-Blank	x5	Conc (µg/L)	Conc (mg/L)
9h30	0,0201	0,0187	0,0176	0,0182	0,0119	0,0595	84,00	0,08
10h30	0,0150	0,0171	0,0192	0,0182	0,0119	0,0595	84,00	0,08
11h30	0,0199	0,0176	0,0183	0,0186	0,0124	0,0618	87,75	0,09
12h30	0,0167	0,0186	0,0184	0,0185	0,0123	0,0613	86,92	0,09
13h30	0,0167	0,0162	0,0161	0,0163	0,0101	0,0504	68,86	0,07
14h30	0,0157	0,0162	0,0168	0,0165	0,0103	0,0513	70,25	0,07
15h30	0,0156	0,0161	0,0160	0,0161	0,0098	0,0490	66,50	0,07
16h30	0,0177	0,0192	0,0187	0,0190	0,0127	0,0635	90,67	0,09

Solids Series – mg/L

Total Solids							
Hour	Sample (mL)	P0 (g)	P1 (g)	TS	P2 (g)	FTS	VTS
9h30	50	43,7738	43,7816	156	43,7803	130	26
10h30	50	49,2362	49,2434	144	49,2421	118	26
11h30	50	37,6050	37,6133	166	37,6115	130	36
12h30	50	53,8834	53,8918	168	53,8912	156	12
13h30	50	42,0103	42,0178	150	42,0178	150	0
14h30	50	49,7474	49,7567	186	49,7549	150	36
15h30	50	50,8026	50,8117	182	50,8108	164	18
16h30	50	44,7896	44,7975	158	44,7970	148	10

Suspended Solids							
Hour	Sample (mL)	P0 (g)	P1 (g)	SS	P2 (g)	FSS	VSS
9h30	130	26,9110	26,9159	38	26,9146	28	10
10h30	130	31,1761	31,1808	36	31,1800	30	6
11h30	100	31,8141	31,8190	49	31,8176	35	14
12h30	125	27,5308	27,5360	42	27,5346	30	11
13h30	140	26,9550	26,9648	70	26,9595	32	38
14h30	160	32,9597	32,9657	38	32,9641	28	10
15h30	170	28,3657	28,3727	41	28,3713	33	8
16h30	170	27,1293	27,1353	35	27,1338	26	9

Dissolved Organic Carbon – mg/L

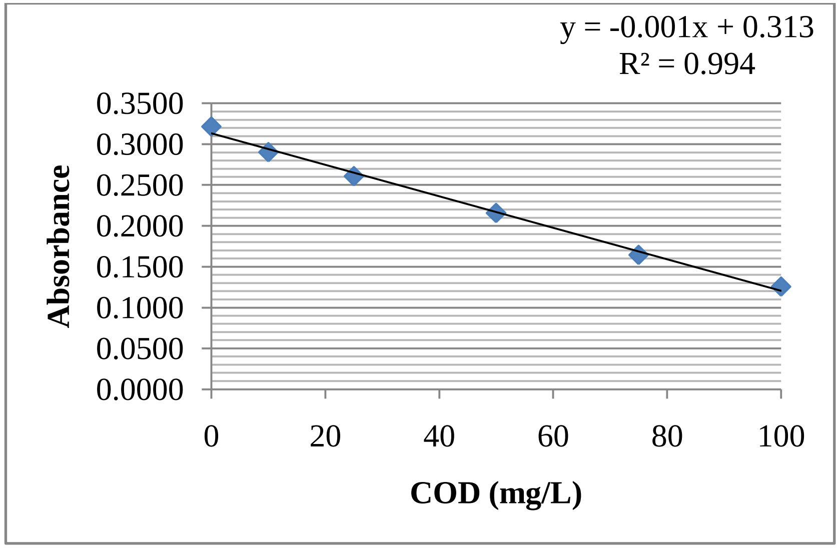
Sample	TC	IC	DOC
9h30	12,43	8,922	3,51
10h30	11,08	7,938	3,14
11h30	27,09	23,3	3,79
12h30	4,722	1,569	3,15
13h30	4,074	1,278	2,80
14h30	16,29	13,62	2,67
15h30	14,94	13,89	1,05
16h30	26,26	20,54	5,72

Temporized Campaign

Bottles	Hour	Date	Turb	pH	Cond	DO	Temp	COD	Nitrogen Serie			TP	Solids Series					
									$N\text{-}NO_2^-$	$N\text{-}NH_3$	TN		TS	FTS	VTS	SS	FSS	VSS
1	12h30	19/02/2015	69,2	8,8	231	7,4	25	21,18	21,42	72,05	0,50	0,08	240	148	92	53	49	4
2	16h30		39,1	8,12	228	7,53	23,8	10,00	72,28	21,41	0,50	0,07	196	164	32	51	39	12
3	20h30		36,3	8,05	229	7,68	23,3	13,32	46,35	36,91	0,46	0,03	206	120	86	49	41	8
4	00h30	20/02/2015	36,5	8,02	230	7,83	22,8	4,32	39,45	23,55	0,47	0,04	198	132	66	30	23	6
5	04h30		30,7	8,07	230	7,73	23,3	8,65	35,54	18,45	0,48	0,04	336	124	212	7	0	0
6	08h30		28,8	8,09	229	7,77	23,2	4,32	29,68	31,95	0,42	0,04	260	42	218	222	152	70
7	12h30		33,2	8,07	230	7,79	22,8	3,80	31,64	33,77	0,44	0,03	196	98	98	33	0	0
8	16h30		32,1	8,05	230	7,85	22,6	7,82	26,78	24,68	0,45	0,02	216	140	76	14	0	0
9	20h30		26,2	8,07	230	7,8	22,7	12,50	28,24	15,55	0,45	0,05	384	162	222	16	12	4
10	00h30	21/02/2015	1730,0	7,97	194,1	7,45	23	65,50	37,94	44,55	0,58	0,63	2124	1852	272	2180	1880	300
11	04h30		413,0	7,93	207,9	7,74	23,1	25,02	17,80	26,36	0,51	0,36	454	346	108	340	288	52
12	08h30		268,0	7,93	190,7	7,74	23,5	19,98	33,54	26,36	0,51	0,30	150	102	48	216	190	26
13	12h30		98,0	7,99	210,5	7,76	23,8	15,60	37,76	24,18	0,48	0,09	212	108	104	39	20	19
14	16h30		98,4	8	216,3	7,78	23,8	9,58	30,36	35,45	0,45	0,03	172	78	94	46	43	3
15	20h30		61,0	7,99	218	7,51	24,6	5,85	32,45	74,82	0,46	0,05	226	164	62	63	59	4
16	00h30	22/02/2015	47,7	8,01	217,7	7,76	23,8	2,97	23,42	31,55	0,45	0,02	152	70	82	24	21	3
17	04h30		41,9	8,04	218,1	7,77	23,3	25,90	22,43	15,09	0,43	0,04	188	124	64	11	8	3
18	08h30		39,4	8,05	219,2	7,79	23,4	15,88	21,49	44,45	0,45	0,03	122	110	12	27	21	7
19	12h30		34,5	8,2	220	7,81	23,4	13,88	21,08	22,45	0,45	0,01	190	128	62	13	6	7
20	16h30		38,4	8,1	222	7,74	23,6	12,35	21,69	57,55	0,45	0,01	158	132	26	24	5	19
21	20h30		34,1	8,07	222	7,74	23,5	15,23	25,30	70,73	0,42	0,02	188	106	82	44	34	10
22	00h30	23/02/2015	28,0	8,09	226	7,81	23,3	14,75	21,54	81,27	0,43	0,02	174	116	58	23	23	0
23	04h30		25,9	8,06	228	7,95	23,3	10,70	19,17	42,64	0,42	0,02	174	108	66	53	42	11
24	08h30		30,0	8,09	230	7,84	25,8	11,75	18,39	31,00	0,42	0,02	206	136	70	33	24	9

COD (mg/L)

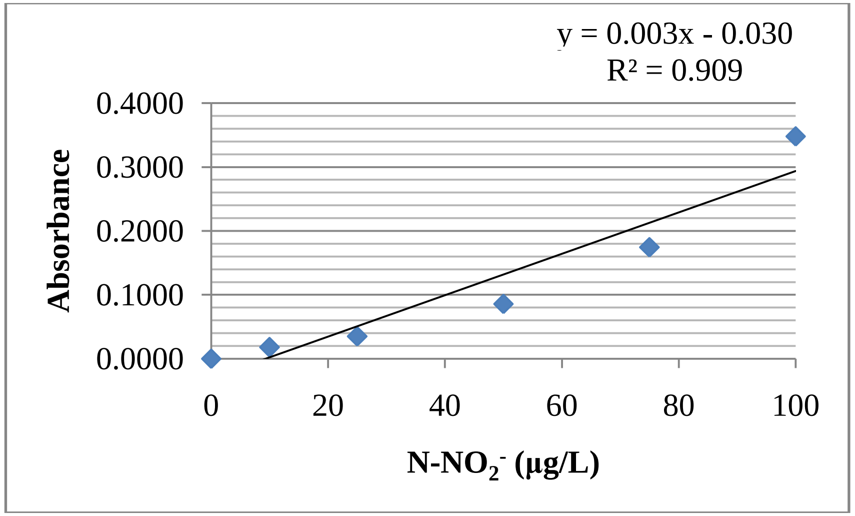
Calibration Curve				
COD	A	B	C	Média
0	0,3148	0,3279	0,3217	0,3215
10	0,3036	0,2955	0,2850	0,2903
25	0,5032	0,2683	0,2533	0,2608
50	0,2203	0,2163	0,2151	0,2157
75	0,1613	0,1650	0,1674	0,1646
100	0,1194	0,1263	0,1252	0,1258



Samples					
Bottles	A	B	C	Aver	Conc (mg/L)
1	0,2670	0,2726	0,2792	0,2729	21,19
2	0,2930	0,2921	0,3008	0,2953	9,42
3	0,2699	0,2954	0,3007	0,2981	7,97
4	0,3145	0,3033	0,3022	0,3028	5,50
5	0,2974	0,3030	0,2936	0,2980	8,00
6	0,3116	0,3064	0,3020	0,3042	4,74
7	0,3138	0,3088	0,3005	0,3047	4,50
8	0,2949	0,3037	0,3004	0,3021	5,87
9	0,2639	0,3083	0,2987	0,3035	5,11
10	0,2134	0,1641	0,1754	0,1698	75,50
11	0,2626	0,2749	0,2583	0,2653	25,23
12	0,2711	0,2688	0,2861	0,2753	19,93
13	0,2805	0,2826	0,2892	0,2841	15,32
14	0,2999	0,2941	0,2944	0,2961	8,98
15	0,3036	0,8121	0,3748	0,3036	5,05
16	0,3110	0,3092	0,3079	0,3094	2,02
17	0,2394	0,2876	0,7699	0,2635	26,16
18	0,2882	0,2897	0,2727	0,2835	15,61
19	0,5248	0,2891	0,2860	0,2876	13,50
20	0,2911	0,2943	0,2864	0,2906	11,89
21	0,2891	0,2806	0,8643	0,2849	14,92
22	0,2844	0,2872	1,0962	0,2858	14,42
23	0,2883	0,2985	0,2949	0,2939	10,16
24	0,2886	0,2955	0,2913	0,2918	11,26

Nitrite (µg/L)

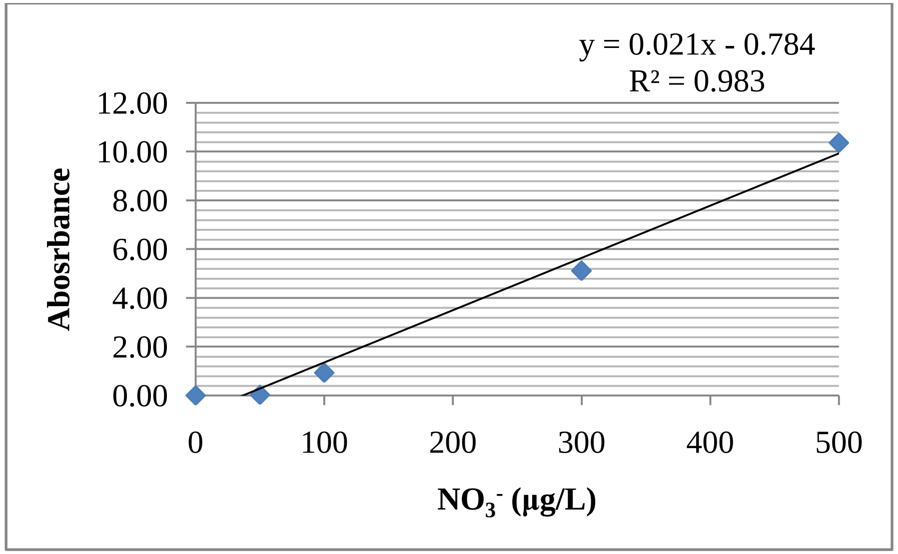
Calibration Curve					
$N\text{-}NO_2^-$	A	B	C	Aver	Aver-Blank
0	0,0004	0,0012	0,0000	0,0008	0,0000
10	0,0183	0,0186	0,0178	0,0185	0,0177
25	0,0359	0,0359	0,0356	0,0358	0,0350
50	0,0868	0,0883	0,0840	0,0864	0,0856
75	0,1779	0,1735	0,1747	0,1754	0,1746
100	0,3468	0,3506	0,3494	0,3489	0,3481



Samples						
Bottles	A	B	C	Média	Aver-Blank	Conc (ug/L)
1	0,0380	0,0387	0,0398	0,0388	0,0380	21,39
2	0,1998	0,2021	0,2029	0,2025	0,2017	72,53
3	0,1205	0,1183	0,1171	0,1177	0,1169	46,03
4	0,0963	0,0963	0,0970	0,0965	0,0957	39,42
5	0,0830	0,0839	0,0852	0,0840	0,0832	35,51
6	0,0642	0,0654	0,0662	0,0653	0,0645	29,65
7	0,0714	0,0708	0,0724	0,0715	0,0707	31,60
8	0,0552	0,0568	0,0560	0,0560	0,0552	26,75
9	0,0612	0,0607	0,0601	0,0607	0,0599	28,21
10	0,0917	0,0917	0,0917	0,0917	0,0909	37,91
11	0,0273	0,0272	0,0273	0,0273	0,0265	17,77
12	0,0778	0,0770	0,0781	0,0776	0,0768	33,51
13	0,0909	0,0918	0,0907	0,0911	0,0903	37,73
14	0,0674	0,0676	0,0674	0,0675	0,0667	30,33
15	0,0746	0,0737	0,0741	0,0741	0,0733	32,42
16	0,0446	0,0446	0,0465	0,0452	0,0444	23,39
17	0,0413	0,0414	0,0435	0,0421	0,0413	22,40
18	0,0391	0,0396	0,0385	0,0391	0,0383	21,46
19	0,0372	0,0381	0,0380	0,0378	0,0370	21,05
20	0,0398	0,0400	0,0393	0,0397	0,0389	21,66
21	0,0403	0,0393	0,0742	0,0398	0,0390	21,69
22	0,0388	0,0387	0,0402	0,0388	0,0380	21,36
23	0,0314	0,0314	0,0321	0,0316	0,0308	19,14
24	0,0292	0,0289	0,0293	0,0291	0,0283	18,35

Total Nitrogen (mg/L)

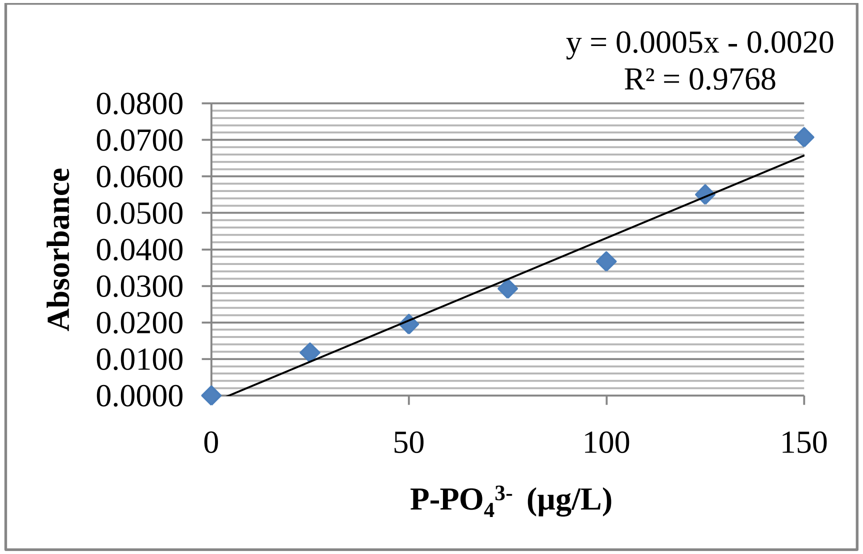
Calibration Curve						
$N\text{-}NO_3^-$	A	B	C	Aver	Aver-Blank	x10
0	0,0017	0,0026	0,0000	0,0022	0,0000	0,000
50	0,0056	0,0048	0,0050	0,0051	0,0030	0,030
100	0,0962	0,0959	0,0946	0,0956	0,0934	0,934
300	0,5162	0,5088	0,5155	0,5135	0,5114	5,114
500	1,0408	1,0366	1,0653	1,0387	1,0366	10,366



Samples								
Bottles	A	B	C	Aver	Aver-Blank	x10	Conc (ug/L)	Conc (mg/L)
1	0,9766	0,9950	0,9852	0,9856	0,9835	9,835	496,23	0,50
2	0,9740	0,9846	0,9924	0,9837	0,9815	9,815	495,33	0,50
3	0,9087	0,9186	0,9169	0,9178	0,9156	9,156	464,52	0,46
4	0,9294	0,9381	0,9423	0,9366	0,9345	9,345	473,33	0,47
5	0,9459	0,9427	0,9474	0,9453	0,9432	9,432	477,41	0,48
6	0,8148	0,8153	0,8315	0,8151	0,8129	8,129	416,53	0,42
7	0,8719	0,8772	0,8651	0,8746	0,8724	8,724	444,34	0,44
8	0,8943	0,8936	0,8940	0,8940	0,8918	8,918	453,41	0,45
9	0,8802	0,8867	0,8916	0,8835	0,8813	8,813	448,50	0,45
10	1,1664	1,1649	1,1483	1,1657	1,1635	11,635	580,36	0,58
11	1,0262	1,0212	1,0408	1,0237	1,0216	10,216	514,03	0,51
12	1,0200	1,0150	1,0425	1,0175	1,0154	10,154	511,14	0,51
13	0,9690	0,9515	0,9464	0,9556	0,9535	9,535	482,23	0,48
14	0,8701	0,8862	0,8948	0,8837	0,8816	8,816	448,61	0,45
15	0,9177	0,8989	0,9030	0,9065	0,9044	9,044	459,28	0,46
16	0,8834	0,8708	0,8539	0,8771	0,8750	8,750	445,53	0,45
17	0,8566	0,8506	0,8442	0,8536	0,8515	8,515	434,55	0,43
18	0,8827	0,8739	0,8906	0,8824	0,8803	8,803	448,00	0,45
19	0,8705	0,8823	0,9022	0,8764	0,8743	8,743	445,20	0,45
20	0,8834	0,8867	0,8654	0,8851	0,8829	8,829	449,24	0,45
21	0,8395	0,8208	0,7988	0,8302	0,8280	8,280	423,59	0,42
22	0,8391	0,8517	0,8488	0,8465	0,8444	8,444	431,24	0,43
23	0,8243	0,8312	0,8153	0,8236	0,8215	8,215	420,53	0,42
24	0,7996	0,8236	0,8212	0,8224	0,8203	8,203	419,97	0,42

Total Phosphorus (mg/L)

Calibration Curve						
P-PO$_4^{3-}$	A	B	C	Aver	Aver-Blank	x 5
0	0,0088	0,0040	0,0043	0,0042	0,0000	0,0000
25	0,0067	0,0063	0,0052	0,0065	0,0024	0,0118
50	0,0078	0,0083	0,0068	0,0081	0,0039	0,0195
75	0,0100	0,0088	0,0071	0,0100	0,0059	0,0293
100	0,0088	0,0125	0,0105	0,0115	0,0074	0,0368
125	0,0127	0,0142	0,0161	0,0152	0,0110	0,0550
150	0,0251	0,0183	0,0128	0,0183	0,0142	0,0708



Samples								
Bottles	A	B	C	Aver	Aver-Blank	x 5	Conc (ug/L)	Conc (mg/L)
1	0,0085	0,0132	0,0105	0,0119	0,0077	0,0385	81,00	0,08
2	0,0172	0,0111	0,0106	0,0109	0,0067	0,0335	71,00	0,07
3	0,0187	0,0067	0,0068	0,0068	0,0026	0,0130	30,00	0,03
4	0,0074	0,0082	0,0082	0,0082	0,0041	0,0203	44,50	0,04
5	0,0098	0,0081	0,0082	0,0082	0,0040	0,0200	44,00	0,04
6	0,0071	0,0074	0,0078	0,0074	0,0033	0,0164	36,83	0,04
7	0,0067	0,0083	0,0054	0,0068	0,0027	0,0133	30,50	0,03
8	0,0055	0,0060	0,0070	0,0058	0,0016	0,0080	20,00	0,02
9	0,0099	0,0085	0,0070	0,0092	0,0051	0,0253	54,50	0,05
10	0,0681	0,0603	0,0729	0,0671	0,0630	0,3148	633,50	0,63
11	0,0398	0,0391	0,0422	0,0395	0,0353	0,1765	357,00	0,36
12	0,0355	0,0323	0,0330	0,0336	0,0295	0,1473	298,50	0,30
13	0,0117	0,0129	0,0133	0,0126	0,0085	0,0424	88,83	0,09
14	0,0071	0,0067	0,0100	0,0069	0,0028	0,0138	31,50	0,03
15	0,0082	0,0083	0,0092	0,0083	0,0041	0,0205	45,00	0,05
16	0,0067	0,0050	0,0093	0,0059	0,0017	0,0085	21,00	0,02
17	0,0076	0,0071	0,0062	0,0074	0,0032	0,0160	36,00	0,04
18	0,0049	0,0068	0,0099	0,0072	0,0031	0,0153	34,50	0,03
19	0,0055	0,0046	0,0074	0,0051	0,0009	0,0045	13,00	0,01
20	0,0046	0,0045	0,0046	0,0046	0,0004	0,0021	8,17	0,01
21	0,0055	0,0055	0,0067	0,0059	0,0018	0,0088	21,50	0,02
22	0,0071	0,0056	0,0050	0,0053	0,0012	0,0058	15,50	0,02
23	0,0081	0,0050	0,0062	0,0056	0,0015	0,0073	18,50	0,02
24	0,0074	0,0061	0,0050	0,0056	0,0014	0,0070	18,00	0,02

Total Solids							
Bottles	Sample (mL)	P0 (g)	P1 (g)	TS	P2 (g)	FTS	VTS
1	50	49,1688	49,1808	240	49,1762	148	92
2	50	56,4534	56,4632	196	56,4616	164	32
3	50	54,4809	54,4912	206	54,4869	120	86
4	50	43,8104	43,8203	198	43,8170	132	66
5	50	43,0218	43,0386	336	43,0280	124	212
6	50	44,3161	44,3291	260	44,3182	42	218
7	50	50,2172	50,2270	196	50,2221	98	98
8	50	48,4176	48,4284	216	48,4246	140	76
9	50	41,2023	41,2215	384	41,2104	162	222
10	50	35,8045	35,9107	2124	35,8971	1852	272
11	50	50,6425	50,6652	454	50,6598	346	108
12	50	53,3411	53,3486	150	53,3462	102	48
13	50	51,3362	51,3468	212	51,3416	108	104
14	50	49,1126	49,1212	172	49,1165	78	94
15	50	47,0243	47,0356	226	47,0325	164	62
16	50	38,0334	38,0410	152	38,0369	70	82
17	50	47,6058	47,6152	188	47,6120	124	64
18	50	35,8091	35,8152	122	35,8146	110	12
19	50	53,3369	53,3464	190	53,3433	128	62
20	50	41,3601	41,3680	158	41,3667	132	26
21	50	48,2568	48,2662	188	48,2621	106	82
22	50	40,1501	40,1588	174	40,1559	116	58
23	50	38,8656	38,8743	174	38,8710	108	66
24	50	48,5535	48,5638	206	48,5603	136	70

Suspended Solids							
Bottles	Sample (mL)	P0 (g)	P1 (g)	SS	P2 (g)	FSS	VSS
1	130	26,9628	26,9697	53	26,9692	49	4
2	140	26,4828	26,4900	51	26,4883	39	12
3	200	31,8130	31,8228	49	31,8212	41	8
4	200	32,6237	32,6296	30	32,6284	23	6
5	200	33,5034	33,5048	7	-	-	-
6	50	29,6824	29,6935	222	29,6900	152	70
7	100	33,4182	33,4215	33	-	-	-
8	145	23,5976	23,5997	14	-	-	-
9	160	30,2836	30,2862	16	30,2855	12	4
10	20	25,0682	25,1118	2180	25,1058	1880	300
11	40	29,7429	29,7565	340	29,7544	288	52
12	50	27,8284	27,8392	216	27,8379	190	26
13	200	27,883	27,8908	39	27,8869	20	19
14	200	34,4004	34,4095	46	34,4089	43	3
15	140	31,1761	31,1849	63	31,1843	59	4
16	200	32,5366	32,5414	24	32,5408	21	3
17	200	31,2579	31,2601	11	31,2596	8	3
18	200	30,6684	30,6738	27	30,6725	21	7
19	200	32,1292	32,1318	13	32,1304	6	7
20	200	26,8057	26,8106	24	26,8068	5	19
21	200	31,1618	31,1705	44	31,1685	33,5	10
22	200	28,1804	28,1851	23	28,185	23	0
23	200	26,9545	26,965	53	26,9628	41,5	11
24	200	28,3650	28,3715	33	28,3697	23,5	9

DOC (mg/L)

Bottles	TC	IC	DOC
1	24,04	22,6	1,44
2	21,02	20,33	0,69
3	Error		
4	39,12	36,42	2,70
5	25,77	19,99	5,78
6	6,132	2,453	3,68
7	25,09	22,39	2,70
8	24,06	20,50	3,56
9	21,28	16,97	4,31
10	22,26	16,36	5,90
11	14,52	11,94	2,58
12	30,63	27,08	3,55
13	26,56	19,78	6,78
14	10,95	7,484	3,47
15	18,88	16,83	2,05
16	15,74	14,37	1,37
17	23,51	19,84	3,67
18	15,61	11,61	4,00
19	14,14	11,23	2,91
20	9,36	5,28	4,10
21	17,92	15,19	2,73
22	14,92	12,96	1,96
23	13,94	12,26	1,68
24	15,90	14,06	1,84

Campaign SBN 2: This campaign was composed by 19 bottles, where two diffuse pollution events was identified (event 1 and 2). Event 1 correspond bottles 1 to 7, and event 2 correspond bottles 8 to 19.

Bottles	Hour	Date	Turb	pH	DO	Temp	Cond	Alka	COD	DOC	NO2-	NH3	TN	TP	TS	FTS	VTS	SS	FSS	VSS
1	02h20	13/03/2015	66,7	7,99	7,38	23,9	275	164.64	40.82	2.95	4.61	23.68	0.51	0.09	304	170	134	151	99	52
2	03h00	13/03/2015	91,0	8,11	7,42	23,7	270	162.40	32.82	1.90	4.35	33.49	0.58	0.06	308	174	134	175	132	43
3	03h20	13/03/2015	114	8,13	7,36	23,5	271	166.88	29.62	1.90	3.49	26.68	0.64	0.05	342	188	154	211	131	80
4	04h10	13/03/2015	113	8,10	7,37	23,5	266	169.12	32.61	4.22	2.71	12.28	0.53	0.07	262	114	148	209	155	54
5	13h10	13/03/2015	212	7,98	7,17	23,4	247	152.32	28.12	9.65	18.17	21.56	0.58	0.46	350	228	122	169	110	59
6	16h00	13/03/2015	146	8,00	7,22	23,5	242	147.84	28.90	10.21	16.88	632.33	0.54	0.19	318	180	138	235	156	79
7	19h30	13/03/2015	110	8,05	7,23	23,3	242	145.60	28.29	9.37	13.43	577.99	0.47	0.04	268	96	172	187	81	105
8	23h40	15/03/2015	44,1	7,98	7,35	23,3	264	161.28	27.27	2.62	8.19	15.18	0.43	0.09	236	124	112	122	65	57
9	23h50	15/03/2015	109	7,77	6,29	23,3	215,1	129.92	43.53	3.01	13.27	131.22	0.51	0.63	360	224	136	295	212	83
10	00h00	16/03/2015	176	7,88	6,77	23,3	180,7	108.64	49.88	2.67	10.62	152.29	0.60	0.27	378	222	156	315	229	86
11	00h10	16/03/2015	854	7,88	6,99	23,2	181,7	107.52	54.18	16.77	10.38	419.06	0.52	0.72	1196	1008	188	1000	898	102
12	00h20	16/03/2015	1100	7,95	6,80	23,0	193	124.32	70.43		13.08	62.99	0.61	0.65	1670	1472	198	1511	1340	171
13	00h33	16/03/2015	1470	8,10	6,44	23,0	187,7	123.20	85.69	4.60	21.08	155.18	0.43	1.41	1738	1418	320	1852	1540	312
14	00h50	16/03/2015	1970	8,18	6,24	23,0	175,5	140.00	85.24	3.78	22.13	115.54	0.62	1.60	1878	1468	410	1768	1386	381
15	05h20	16/03/2015	362	8,00	7,27	23,1	227	136.64	42.50	4.06	10.06	21.10	0.46	0.69	470	316	154	463	280	182
16	06h10	16/03/2015	355	8,13	7,41	23,2	218,5	141.12	52.68	3.80	10.41	23.95	0.42	0.50	420	290	130	335	248	87
17	07h00	16/03/2015	282	8,16	7,42	23,2	213,9	133.28	53.62	7.45	9.60	30.00	0.51	0.26	374	260	114	190	105	85
18	08h00	16/03/2015	230	8,10	7,49	23,2	218,2	135.52	56.65	7.51	9.34	25.46	0.52	0.01	396	164	232	310	158	152
19	10h00	16/03/2015	195	7,99	7,49	23,5	223	136.64	52.94	4.32	9.34	33.06	0.46	0.00	312	178	134	153	103	50

Alkalinity (mg $CaCO_3$/L)

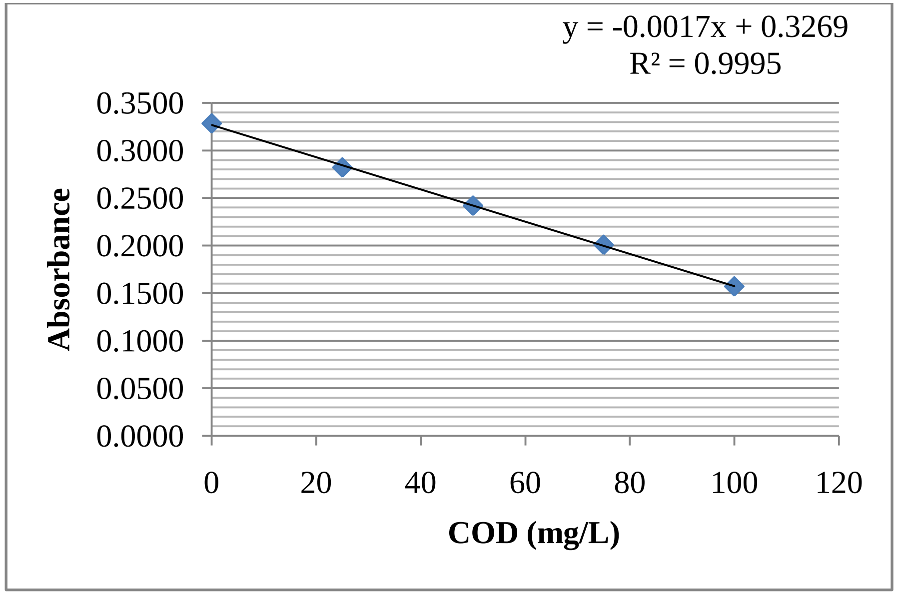
Bottles	Volume consumed (mL)	Alkalinity
1	14.7	164.64
2	14.5	162.40
3	14.9	166.88
4	15.1	169.12
5	13.6	152.32
6	13.2	147.84
7	13	145.60
8	14.4	161.28
9	11.6	129.92
10	9.7	108.64
11	9.6	107.52
12	11.1	124.32
13	11	123.20
14	12.5	140.00
15	12.2	136.64
16	12.6	141.12
17	11.9	133.28
18	12.1	135.52
19	12.2	136.64
Correction Fator = 11,2/10 = 1,12		

DOC (mg/L)

Bottles	TC	IC	DOC
1	3.40	0.45	2.95
2	3.40	1.49	1.90
3	3.71	1.80	1.90
4	4.47	0.25	4.22
5	9.87	0.22	9.65
6	10.42	0.21	10.21
7	9.59	0.22	9.37
8	3.41	0.79	2.62
9	3.20	0.18	3.01
10	2.87	0.21	2.67
11	16.94	0.17	16.77
12	Analytical Error		
13	4.76	0.16	4.60
14	4.14	0.36	3.78
15	4.22	0.16	4.06
16	4.80	1.00	3.80
17	7.62	0.17	7.45
18	7.65	0.14	7.51
19	4.46	0.14	4.32

COD – mg/L

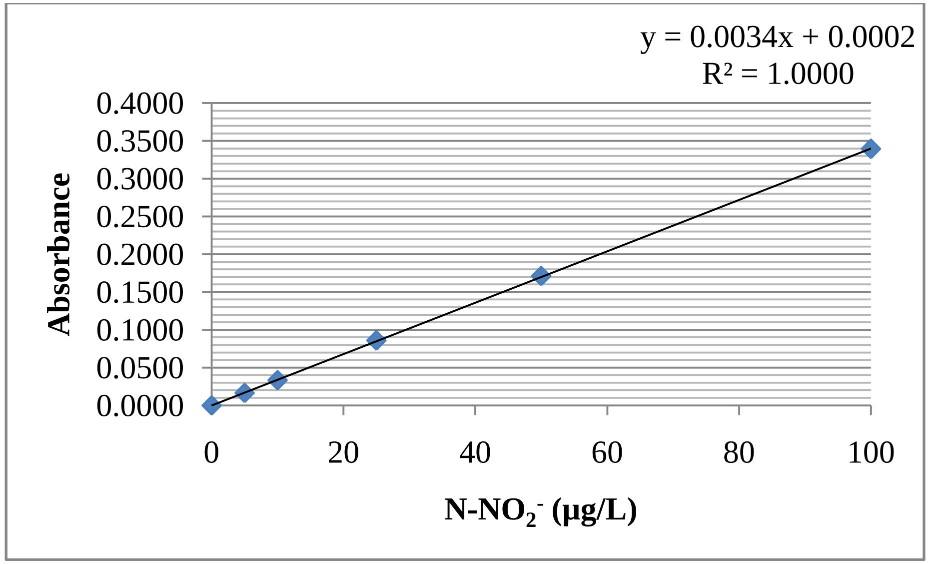
Calibration Curve			
COD (mg/L)	A	B	Aver
0	0.3246	0.3322	0.3284
25	0.2848	0.2795	0.2822
50	0.2430	0.2410	0.2420
75	0.1985	0.2034	0.2010
100	0.1563	0.1582	0.1573



Samples					
Bottles	A	B	C	Aver	Conc (mg/L)
1	0.2743	0.2594	0.2556	0.2575	40.82
2	0.2668	0.2754	0.3340	0.2711	32.82
3	0.2551	0.2755	0.2776	0.2766	29.62
4	0.2767	0.2693	0.2684	0.2715	32.61
5	0.2590	0.2804	0.2778	0.2791	28.12
6	0.2688	0.2776	0.2869	0.2778	28.90
7	0.3728	0.2804	0.2772	0.2788	28.29
8	0.2806	0.2776	0.2834	0.2805	27.27
9	0.2335	0.2542	0.2516	0.2529	43.53
10	0.2432	0.2410	0.2507	0.2421	49.88
11	0.3499	0.2263	0.2433	0.2348	54.18
12	0.2019	0.2062	0.2134	0.2072	70.43
13	0.1749	0.1826	0.1862	0.1812	85.69
14	0.1884	0.1764	0.1812	0.1820	85.24
15	0.2410	0.2538	0.2555	0.2547	42.50
16	0.5090	0.2444	0.2303	0.2374	52.68
17	0.2113	0.2322	0.2393	0.2358	53.62
18	0.2295	0.2317	0.2273	0.2306	56.65
19	0.2368	0.2346	0.2393	0.2369	52.94

Nitrite - µg/L

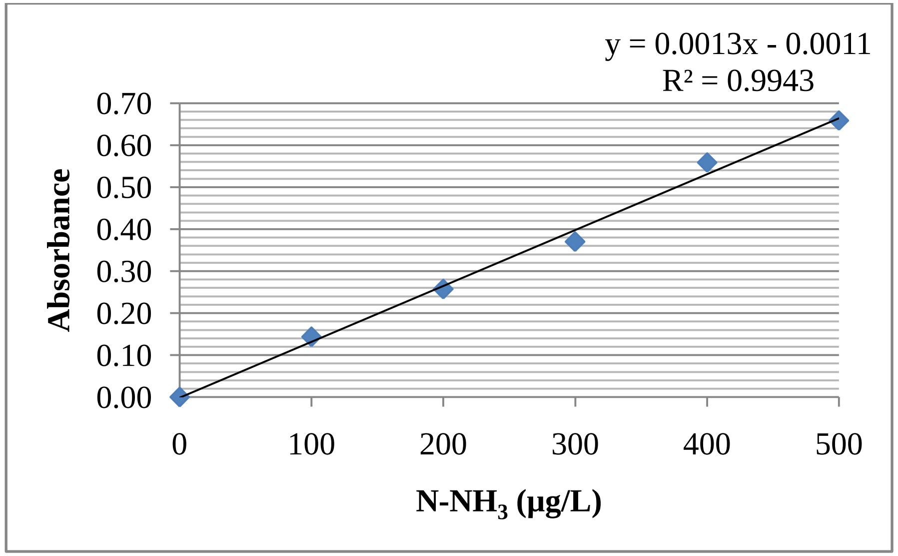
Calibration Curve					
$N\text{-}NO_2^-$ (µg/L)	A	B	C	Aver	Aver-Blank
0	0.0026	0.0026	0.0023	0.0025	0.0000
5	0.0190	0.0194	0.0190	0.0191	0.0166
10	0.0356	0.0366	0.0433	0.0361	0.0336
25	0.0891	0.0891	0.0868	0.0883	0.0858
50	0.1738	0.1719	0.1757	0.1738	0.1713
100	0.3417	0.3436	0.3402	0.3418	0.3393



Sample						
Bottles	A	B	C	Aver	Aver-Blank	Conc (µg/L)
1	0.0190	0.0183	0.0178	0.0184	0.0159	4.61
2	0.0179	0.0171	0.0175	0.0175	0.0150	4.35
3	0.0143	0.0154	0.0140	0.0146	0.0121	3.49
4	0.0120	0.0117	0.0120	0.0119	0.0094	2.71
5	0.0634	0.0638	0.0662	0.0645	0.0620	18.17
6	0.0602	0.0599	0.0602	0.0601	0.0576	16.88
7	0.0490	0.0481	0.0480	0.0484	0.0459	13.43
8	0.0261	0.0306	0.0305	0.0306	0.0281	8.19
9	0.0481	0.0480	0.0474	0.0478	0.0453	13.27
10	0.0405	0.0396	0.0363	0.0388	0.0363	10.62
11	0.0380	0.0377	0.0383	0.0380	0.0355	10.38
12	0.0479	0.0466	0.0470	0.0472	0.0447	13.08
13	0.0754	0.0721	0.0756	0.0744	0.0719	21.08
14	0.0778	0.0778	0.0782	0.0779	0.0754	22.13
15	0.0376	0.0370	0.0361	0.0369	0.0344	10.06
16	0.0380	0.0380	0.0383	0.0381	0.0356	10.41
17	0.0266	0.0359	0.0348	0.0354	0.0329	9.60
18	0.0342	0.0342	0.0350	0.0345	0.0320	9.34
19	0.0343	0.0343	0.0348	0.0345	0.0320	9.34

Amonniacal Nitrogen - µg/L

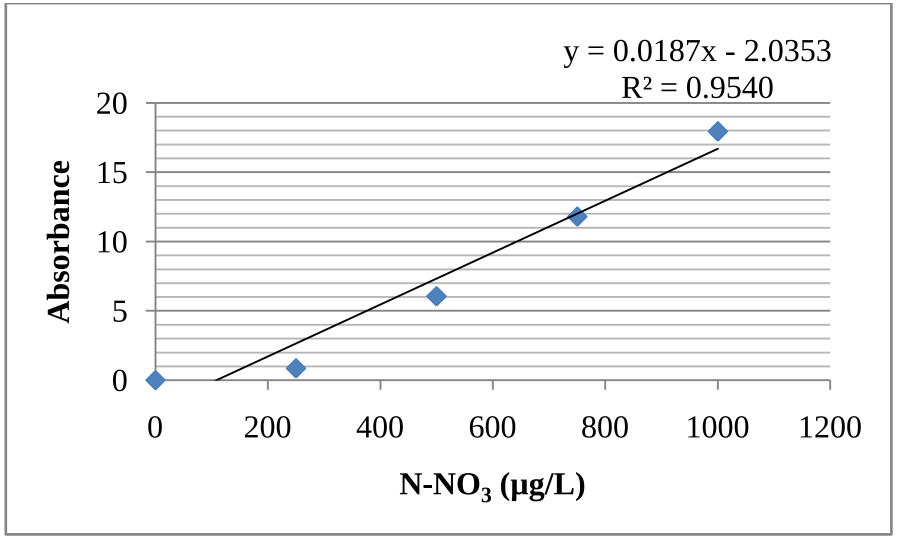
Calibration Curve					
N-NH_3 (µg/L)	A	B	C	Aver	Aver-Blank
0	0.0370	0.0334	0.0363	0.0356	0.0000
100	0.1790	0.3086	0.2789	0.1790	0.1434
200	0.3157	0.2952	0.2902	0.2927	0.2571
300	0.4241	0.3873	0.4784	0.4057	0.3701
400	0.6067	0.5823	0.4528	0.5945	0.5589
500	0.6479	0.7415	0.5527	0.6947	0.6591



Samples						
Bottles	A	B	C	Aver	Aver-Blank	Conc (µg/L)
1	0.0729	0.0667	0.0638	0.0653	0.0297	23.68
2	0.0654	0.0795	0.0765	0.0780	0.0424	33.49
3	0.0651	0.0732	0.1277	0.0692	0.0336	26.68
4	0.0472	0.0494	0.0547	0.0504	0.0149	12.28
5	0.0625	0.0603	0.0647	0.0625	0.0269	21.56
6	0.7631	0.8608	0.8522	0.8565	0.8209	632.33
7	0.7769	0.7948	0.7365	0.7859	0.7503	577.99
8	0.0513	0.0571	0.0410	0.0542	0.0186	15.18
9	0.0841	0.2036	0.2065	0.2051	0.1695	131.22
10	0.2382	0.2267	0.1879	0.2325	0.1969	152.29
11	0.6821	0.6025	0.5560	0.5793	0.5437	419.06
12	0.1156	0.1171	0.1365	0.1164	0.0808	62.99
13	0.2357	0.2335	0.2394	0.2362	0.2006	155.18
14	0.1852	0.1803	0.1885	0.1847	0.1491	115.54
15	0.0612	0.0609	0.0636	0.0619	0.0263	21.10
16	0.0637	0.0675	0.0717	0.0656	0.0300	23.95
17	0.0743	0.0732	0.0729	0.0735	0.0379	30.00
18	0.0659	0.0671	0.0697	0.0676	0.0320	25.46
19	0.0781	0.0768	0.0825	0.0775	0.0419	33.06

Total Nitrogen – mg/L

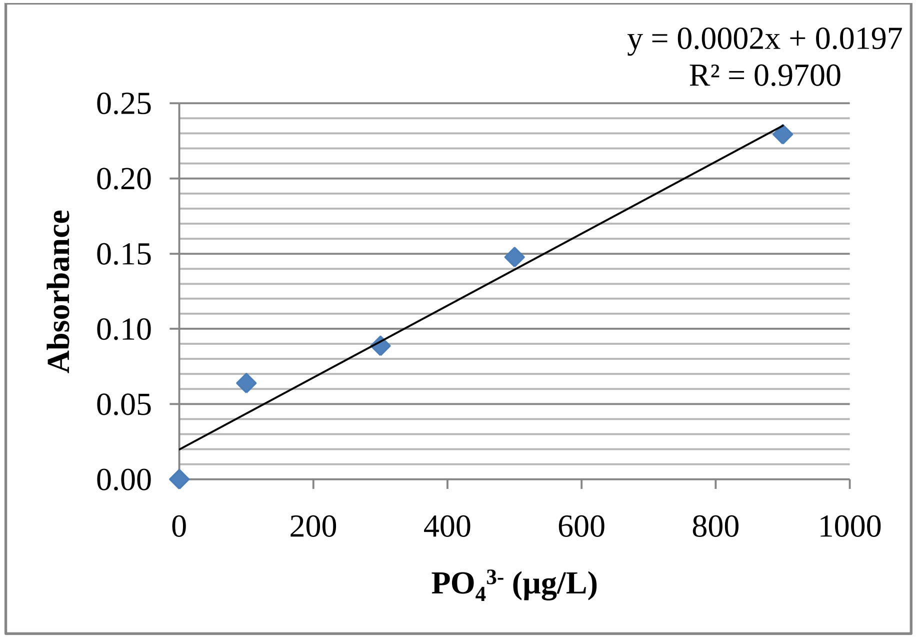
Curva de Calibração						
N-NO$_3$ (µg/L)	A	B	C	Aver	Aver-Blank	x10
0	0.0020	0.0013	0.0009	0.0011	0.0000	0
100	0.0013	0.0013	0.0012	0.0013	0.0002	-
250	0.0828	0.0875	0.0883	0.0862	0.0851	0.851
500	0.5778	0.6040	0.6097	0.6069	0.6058	6.0575
750	1.1742	1.1909	1.0995	1.1826	1.1815	11.8145
1000	1.7931	1.7963	1.8303	1.7947	1.7936	17.936



Amostras								
Bottles	A	B	C	Aver	Aver-Blank	x10	Conc (µg/L)	Conc (mg/L)
1	0.7404	0.7513	0.7683	0.7533	0.7522	7.5223	511.09	0.51
2	0.8450	0.9041	0.8739	0.8890	0.8879	8.8790	583.64	0.58
3	0.9924	0.9841	0.9841	0.9869	0.9858	9.8577	635.97	0.64
4	0.7859	0.7810	0.7645	0.7835	0.7824	7.8235	527.19	0.53
5	0.5831	0.8772	0.8811	0.8792	0.8781	8.7805	578.37	0.58
6	0.7651	0.7961	0.8093	0.8027	0.8016	8.0160	537.49	0.54
7	0.6823	0.6831	0.7039	0.6827	0.6816	6.8160	473.32	0.47
8	0.5972	0.6108	0.6332	0.6040	0.6029	6.0290	431.23	0.43
9	0.7429	0.7435	0.7314	0.7432	0.7421	7.4210	505.67	0.51
10	0.8888	0.9246	0.9211	0.9229	0.9218	9.2175	601.74	0.60
11	0.7559	0.7815	0.7766	0.7791	0.7780	7.7795	524.84	0.52
12	0.9075	0.9336	0.9587	0.9462	0.9451	9.4505	614.20	0.61
13	0.5880	0.6163	0.6714	0.6022	0.6011	6.0105	430.24	0.43
14	0.9579	0.9464	0.9530	0.9524	0.9513	9.5133	617.56	0.62
15	0.6777	0.6633	0.6500	0.6637	0.6626	6.6257	463.14	0.46
16	0.5778	0.5907	0.5903	0.5905	0.5894	5.8940	424.01	0.42
17	0.7214	0.7542	0.7412	0.7477	0.7466	7.4660	508.07	0.51
18	0.7281	0.7671	0.7711	0.7691	0.7680	7.6800	519.52	0.52
19	0.6313	0.6643	0.6930	0.6629	0.6618	6.6177	462.71	0.46

Total Phosphorus (mg/L)

Calibration Curve					
$PO^{4}{}_{3}^{-}$ (μg/L)	A	B	C	Aver	Aver-Blank
0	0.1191	0.2141	0.0616	0.0616	0.0000
100	0.1255	0.0634	-	0.1255	0.0639
300	0.1650	0.1503	0.1356	0.1503	0.0887
500	0.1870	0.2019	0.2167	0.2093	0.1477
900	0.3416	0.2854	0.2965	0.2910	0.2294



Samples							
Bottles	A	B	C	Aver	Aver-Blank	Conc (μg/L)	Conc (mg/L)
1	0.1273	0.0907	0.1066	0.0987	0.0371	86.75	0.09
2	0.0696	0.0972	0.0895	0.0934	0.0318	60.25	0.06
3	0.0616	0.0858	0.0969	0.0914	0.0298	50.25	0.05
4	0.0671	0.0994	0.0914	0.0954	0.0338	70.50	0.07
5	0.0907	0.1676	0.1774	0.1725	0.1109	456.00	0.46
6	0.0717	0.1146	0.1244	0.1195	0.0579	191.00	0.19
7	0.0623	0.0984	0.0815	0.0900	0.0284	43.25	0.04
8	0.2288	0.0934	0.1035	0.0985	0.0369	85.75	0.086
9	0.1047	0.2069	0.2073	0.2071	0.1455	629.00	0.629
10	0.3317	0.1316	0.1375	0.1346	0.0730	266.25	0.266
11	0.1631	0.2338	0.2166	0.2252	0.1636	719.50	0.720
12	0.2981	0.2178	0.2057	0.2118	0.1502	652.25	0.652
13	0.2561	0.3597	0.3652	0.3625	0.3009	1405.75	1.406
14	0.4978	0.3855	0.4188	0.4022	0.3406	1604.25	1.604
15	0.1674	0.2251	0.2141	0.2196	0.1580	691.50	0.692
16	0.1309	0.1931	0.1682	0.1807	0.1191	496.75	0.497
17	0.2173	0.1476	0.1185	0.1331	0.0715	258.75	0.259
18	0.0948	0.0845	0.0835	0.0840	0.0224	13.50	0.014
19	0.2112	0.0775	0.0862	0.0819	0.0203	2.75	0.003

Total Solids							
Bottle	Sample (mL)	P0 (g)	P1 (g)	TS	P2 (g)	FTS	VTS
1	50	46.7531	46.7683	304	46.7616	170	134
2	50	44.2363	44.2517	308	44.2450	174	134
3	50	47.0269	47.0440	342	47.0363	188	154
4	50	48.7350	48.7481	262	48.7407	114	148
5	50	41.3555	41.3730	350	41.3669	228	122
6	50	44.1622	44.1781	318	44.1712	180	138
7	50	50.2192	50.2326	268	50.2240	96	172
8	50	48.3780	48.3898	236	48.3842	124	112
9	50	50.2230	50.2410	360	50.2342	224	136
10	50	51.2816	51.3005	378	51.2927	222	156
11	50	51.1198	51.1796	1196	51.1702	1008	188
12	50	37.6058	37.6893	1670	37.6794	1472	198
13	50	47.4568	47.5437	1738	47.5277	1418	320
14	50	53.8844	53.9783	1878	53.9578	1468	410
15	50	47.4963	47.5198	470	47.5121	316	154
16	50	41.3612	41.3822	420	41.3757	290	130
17	50	49.7042	49.7229	374	49.7172	260	114
18	50	50.0520	50.0718	396	50.0602	164	232
19	50	52.4912	52.5068	312	52.5001	178	134

Suspended Solids							
Bottle	Sample (mL)	P0 (g)	P1 (g)	SS	P2 (g)	FSS	VSS
1	100	27.8790	27.8941	151	27.8889	99	52
2	100	31.1745	31.1920	175	31.1877	132	43
3	100	32.6160	32.6371	211	32.6291	131	80
4	100	34.3962	34.4171	209	34.4117	155	54
5	100	28.4254	28.4423	169	28.4364	110	59
6	68	29.7385	29.7545	235	29.7491	156	79
7	75	31.3795	31.3935	187	31.3856	81	105
8	100	32.1266	32.1388	122	32.1331	65	57
9	100	27.8242	27.8537	295	27.8454	212	83
10	100	30.2777	30.3092	315	30.3006	229	86
11	82	33.4212	33.5032	1000	33.4948	898	102
12	35	26.4814	26.5343	1511	26.5283	1340	171
13	50	27.1190	27.2116	1852	27.196	1540	312
14	37	27.5284	27.5938	1768	27.5797	1386	381
15	56	28.1780	28.2039	463	28.1937	280	182
16	63	26.9592	26.9803	335	26.9748	248	87
17	100	26.9525	26.9715	190	26.963	105	85
18	50	29.6818	29.6973	310	29.6897	158	152
19	70	31.2561	31.2668	153	31.2633	103	50

Campaign SBN 4: This campaign was composed by 11 bottles, where two special events was identified (event 5 and 6). Event 5 correspond bottles 2 to 5, and event 6 correspond bottles 6 to 11. The first bottle below to event 4, diffuse pollution one, not discussed in this thesis.

Bottle	Hour	Date	Turb	pH	DO	Temp	Cond	Alka	NH3	TN	TP	COD	DOC	ST	STF	STV	SS	SSF	SSV
1	11h20	24/03/2015	67.7	8.15	8.74	16.4	252	162.50	14.23	0.42	0.06	8.22	4.36	204	168	36	26	19	8
2	11h10	27/03/2015	59.4	8.11	8.65	15.4	259	168.71	32.91	0.47	0.10	12.42	2.69	250	204	46	241	206	35
3	16h30	27/03/2015	71.6	8.12	8.65	15.5	263	168.71	23.95	0.44	0.08	8.62	-0.83	240	214	26	64	52	13
4	16h40	27/03/2015	83.6	8.21	8.69	15.9	263	173.88	13.55	0.47	0.08	9.52	2.20	308	244	64	77	60	17
5	19h20	27/03/2015	42.8	8.18	8.68	15.9	260	168.71	97.77	0.48	0.02	9.84	-1.44	224	180	44	34	24	9
6	18h10	29/03/2015	80.3	8.00	8.28	15.1	233	150.08	109.53	0.48	0.10	19.55	2.90	248	218	30	79	62	17
7	09h20	30/03/2015	71.0	8.15	8.83	15.4	239	158.36	51.89	0.48	0.07	13.87	1.55	220	172	48	59	41	18
8	09h30	30/03/2015	59.8	8.10	8.73	15.5	236	155.25	66.41	0.47	0.08	14.41	3.50	190	180	10	48	38	10
9	11h50	30/03/2015	56.3	8.04	8.7	14.6	242	162.50	97.89	0.48	0.06	10.25	0.87	204	178	26	61	47	13
10	14h40	30/03/2015	79.2	7.77	7.67	14.8	225	156.29	368.50	0.55	0.23	19.27	1.97	218	210	8	100	75	25
11	11h00	31/03/2015	35.1	8.05	8.68	15.9	251	162.50	48.45	0.47	0.11	9.82	-	198	156	42	30	22	8

Alkalinity – mg $CaCO_3$/L

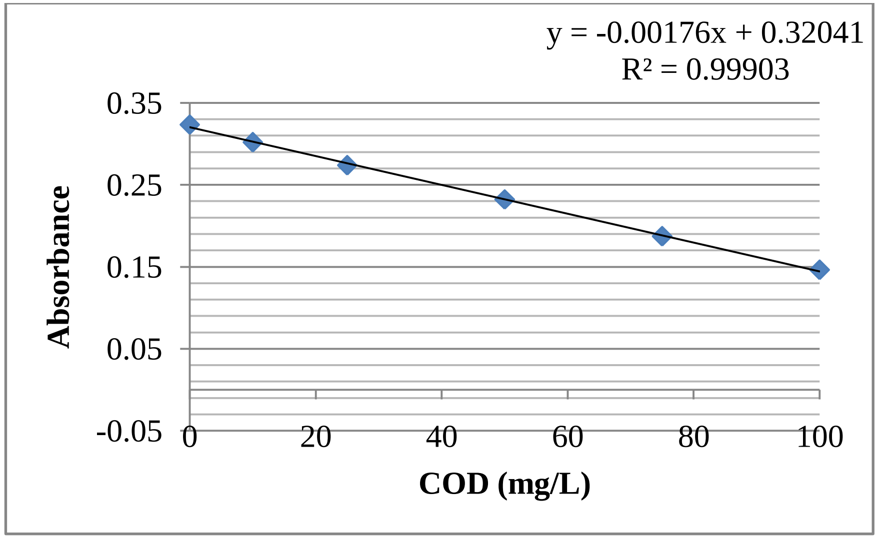
Bottles	Volume Consumed (mL)	Alkalinity
1	15.7	162.50
2	16.3	168.71
3	16.3	168.71
4	16.8	173.88
5	16.3	168.71
6	14.5	150.08
7	15.3	158.36
8	15.0	155.25
9	15.7	162.50
10	15.1	156.29
11	15.7	162.50
Correction Factor = 10.35/10 = 1.035		

DOC – mg/L

Bottle	TC	IC	DOC
1	19.37	15.01	4.36
2	8.746	6.052	2.694
3	33.36	34.19	-0.83
3 rep	19.69	19.88	-0.19
4	12.69	10.49	2.20
5	29.97	31.41	-1.44
5rep	26.67	28.52	-1.85
6	9.746	6.847	2.90
7	18.44	16.89	1.55
8	23.95	20.45	3.50
9	19.63	18.76	0.87
10	19.81	17.84	1.97
11	-	-	-

COD – mg/L

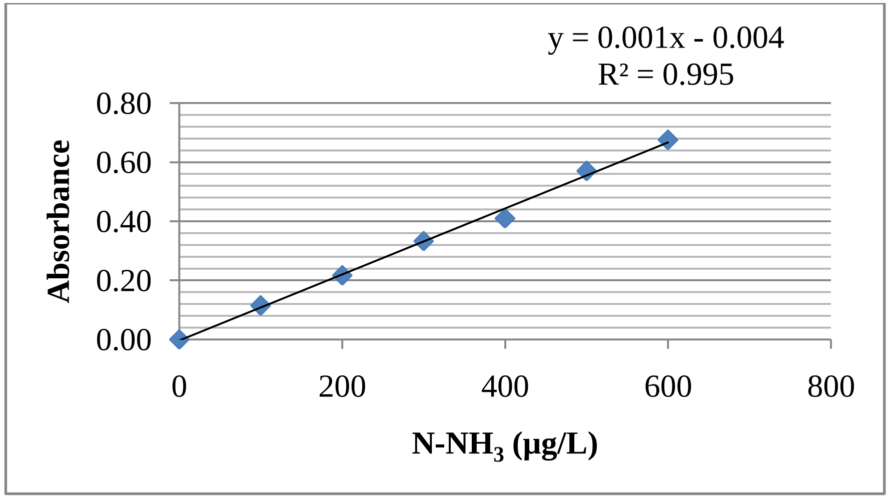
Calibration Curve				
COD	A	B	C	Aver
0	0.3231	0.3232	0.3245	0.3236
10	0.2976	0.3062	0.3114	0.3019
25	0.2662	0.2814	0.3044	0.2738
50	0.2324	0.2321	0.2285	0.2323
75	0.1879	0.1864	0.2048	0.1872
100	0.1411	0.1483	0.1493	0.1462



Samples					
Bottle	A	B	C	Aver	Conc (mg/L)
1	0.3062	0.3057	0.3271	0.3060	8.22
2	0.2997	0.2974	0.3114	0.2986	12.42
3	0.3134	0.2987	0.3036	0.3052	8.62
4	0.3029	0.3044	0.2904	0.3037	9.52
5	0.3035	0.3027	0.6782	0.3031	9.84
6	0.2877	0.2843	0.2925	0.2860	19.55
7	0.2970	0.2925	0.2985	0.2960	13.87
8	0.2947	0.2954	0.3026	0.2951	14.41
9	0.3030	0.2999	0.3042	0.3024	10.25
10	0.3030	0.2850	0.2880	0.2865	19.27
11	0.3114	0.2971	0.3009	0.3031	9.82

Ammoniacal Nitrogen– µg/L

Calibration Curve					
N-NH_3 (µg/L)	A	B	C	Aver	Aver-Blank
0	0.0458	0.0405	0.0564	0.0432	0.0000
100	0.1572	0.1573	0.1630	0.1573	0.1141
200	0.2720	0.2465	0.3278	0.2593	0.2161
300	0.3809	0.3711	0.4526	0.3760	0.3329
400	0.4365	0.4694	0.5115	0.4530	0.4098
500	0.6116	0.6139	0.7488	0.6128	0.5696
600	0.7142	0.7224	0.6742	0.7183	0.6752

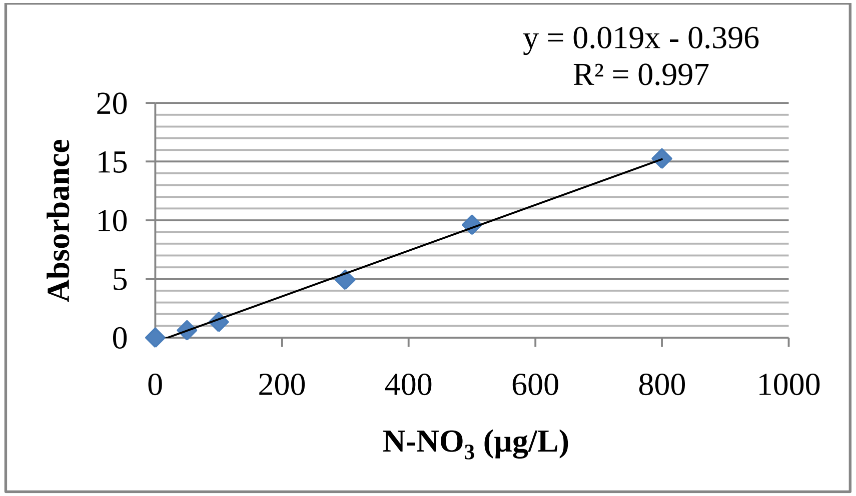


Samples						
Bottle	A	B	C	Aver	Aver-Blank	Conc (µg/L)
1	0.0564	0.0531	0.0540	0.0545	0.0114	14.23
2	0.0769	0.0732	0.0684	0.0751	0.0319	32.91
3	0.0651	0.0653	0.0782	0.0652	0.0221	23.95
4	0.0509	0.0566	0.0667	0.0538	0.0106	13.55
5	0.1528	0.1400	0.1165	0.1464	0.1033	97.77
6	0.1548	0.1635	0.1597	0.1593	0.1162	109.53
7	0.0992	0.0952	0.0934	0.0959	0.0528	51.89
8	0.1202	0.1028	0.1127	0.1119	0.0688	66.41
9	0.1586	0.1371	0.1439	0.1465	0.1034	97.89
10	0.4315	0.4569	0.3970	0.4442	0.4011	368.50
11	0.0924	0.0919	0.0834	0.0922	0.0490	48.45

Total Nitrogen – mg/L

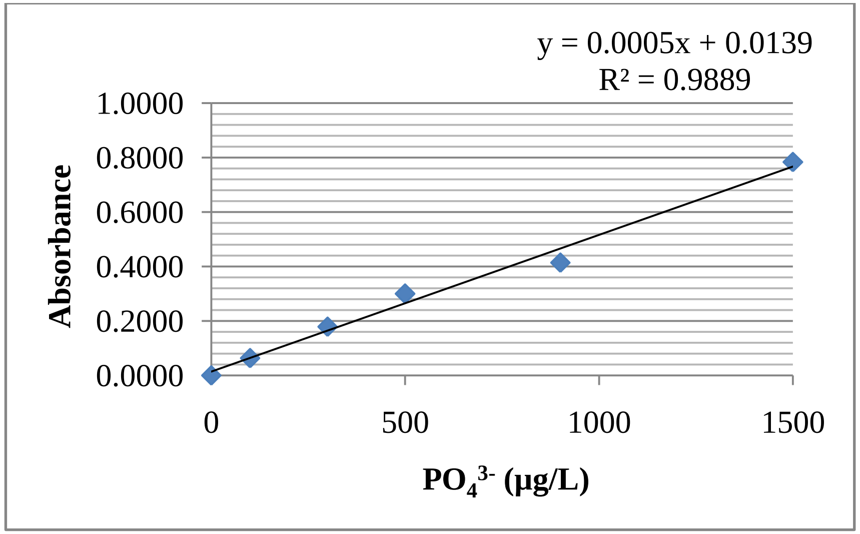
Calibration Curve			
N-NO_3 (µg/L)	Aver	Aver-Blank	x10
0	0.0160	0.0000	0
50	0.0770	0.0610	0.61
100	0.1484	0.1324	1.324
300	0.5089	0.4929	4.929
500	0.9770	0.9610	9.61
800	1.5408	1.5248	15.248

Samples								
Bottles	A	B	C	Aver	Aver-Blank	x10	Conc (µg/L)	Conc (mg/L)
1	0.7753	0.7988	0.8021	0.8005	0.7845	7.8445	422.59	0.42
2	0.8846	0.8860	-	0.8853	0.8693	8.6930	466.11	0.47
3	0.8363	0.8329	0.8173	0.8346	0.8186	8.1860	440.11	0.44
4	0.8956	0.8948	0.8916	0.8940	0.8780	8.7800	470.57	0.47
5	0.9065	0.9117	0.8969	0.9050	0.8890	8.8903	476.23	0.48
6	0.9250	0.9169	0.9130	0.9150	0.8990	8.9895	481.31	0.48
7	0.9894	0.9142	0.9159	0.9151	0.8991	8.9905	481.36	0.48
8	0.8724	0.8943	0.8916	0.8930	0.8770	8.7695	470.03	0.47
9	0.9142	0.9087	0.9041	0.9064	0.8904	8.9040	476.93	0.48
10	1.0585	1.0490	1.0366	1.0480	1.0320	10.3203	549.56	0.55
11	0.9065	0.8818	0.8846	0.8832	0.8672	8.6720	465.03	0.47



Total Phosphorus – mg/L

Curva de Calibração					
$PO^{4}_{3}{}^{-}$ (µg/L)	A	B	C	Aver	Aver-Blank
0	0.0134	0.0117	0.0099	0.0126	0.0000
100	0.0759	0.0773	0.0763	0.0765	0.0640
300	0.1906	0.1913	0.1920	0.1913	0.1788
500	0.3114	0.3131	0.3121	0.3122	0.2997
900	0.4272	0.4254	0.4280	0.4269	0.4143
1500	0.7992	0.7925	0.7964	0.7960	0.7835



Samples							
Bottles	A	B	C	Aver	Aver-Blank	Conc (µg/L)	Conc (mg/L)
1	0.0549	0.0549	0.0537	0.0545	0.0420	56.10	0.06
2	0.0782	0.0784	0.0740	0.0769	0.0643	100.83	0.10
3	0.0625	0.0669	0.0588	0.0647	0.0522	76.50	0.08
4	0.0682	0.0695	0.7360	0.0689	0.0563	84.80	0.08
5	0.0377	0.0386	0.0394	0.0386	0.0260	24.23	0.02
6	0.0763	0.0763	0.0812	0.0763	0.0638	99.70	0.10
7	0.0597	0.0592	0.0592	0.0594	0.0468	65.83	0.07
8	0.0680	0.0619	0.0651	0.0650	0.0525	77.10	0.08
9	0.0597	0.0569	0.0571	0.0579	0.0454	62.90	0.06
10	0.1401	0.1449	0.1465	0.1438	0.1313	234.77	0.23
11	0.0813	0.0839	0.0791	0.0826	0.0701	112.30	0.11

Solids – mg/L

Total Solids							
Bottle	Sample (mL)	P0 (g)	P1 (g)	TS	P2 (g)	FTS	VTS
1	50	52.4888	52.4990	204	52.4972	168	36
2	50	47.4945	47.5070	250	47.5047	204	46
3	50	42.9969	43.0089	240	43.0076	214	26
4	50	51.1188	51.1342	308	51.1310	244	64
5	50	44.3851	44.3963	224	44.3941	180	44
6	50	47.0256	47.0380	248	47.0365	218	30
7	50	39.0283	39.0393	220	39.0369	172	48
8	50	47.4545	47.4640	190	47.4635	180	10
9	50	44.1591	44.1693	204	44.1680	178	26
10	50	44.2343	44.2452	218	44.2448	210	8
11	50	48.3765	48.3864	198	48.3843	156	42

Suspended Solids							
Bottle	Sample (mL)	P0 (g)	P1 (g)	SS	P2 (g)	FSS	VSS
1	200	31.1773	31.1825	26	31.181	19	8
2	200	29.7432	29.7914	241	29.7844	206	35
3	200	33.4205	33.4333	64	33.4308	52	13
4	182	26.8046	26.8186	77	26.8155	60	17
5	200	27.1169	27.1237	34	27.1218	24	9
6	200	30.6673	30.6832	79	30.6797	62	17
7	200	32.5366	32.5485	59	32.5448	41	18
8	200	26.4835	26.4931	48	26.4911	38	10
9	200	28.1800	28.1921	61	28.1895	47	13
10	200	32.6183	32.6384	100	32.6333	75	25
11	200	31.8144	31.8204	30	31.8188	22	8

Campaign SBN 5: This campaign was composed by 6 bottles, where a special events was identified (event 7). Bottles 1 to 4 correspond to discharge conditions and bottles 5 and 6 are sink water.

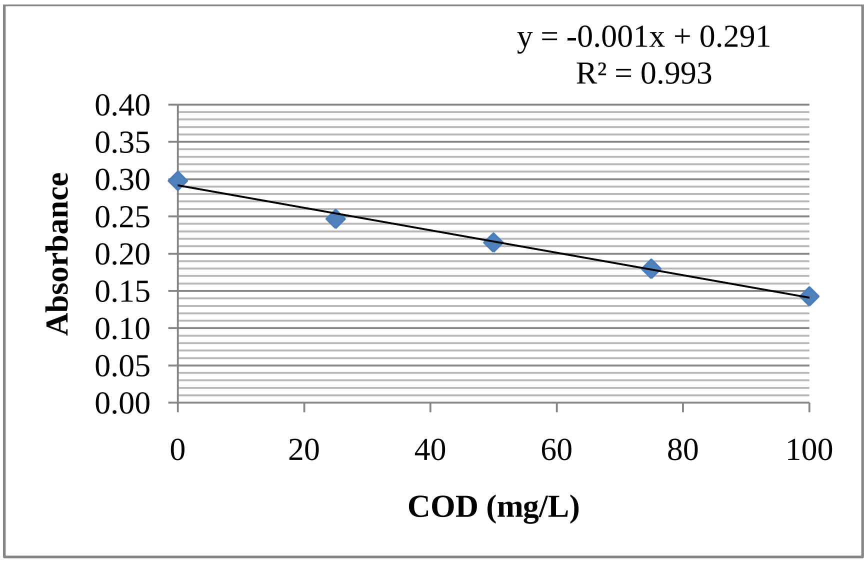
Bottles	Hour	Date	NO2	NO3	NH3	TN	TP	COD	DOC	ST	STF	STV	SS	SSF	SSV
1	02/04/2015	18h10	1.52	6.47	48.79	0.40	0.06	-15.30	-1.02	284	214	70	114	89	25
2	02/04/2015	18h20	0.86	7.40	39.94	0.39	0.09	-8.10	-0.14	292	220	72	126	99	26
3	02/04/2015	19h40	10.82	-3.26	26.25	0.39	0.04	-19.71	3.29	206	152	54	32	22	10
4	02/04/2015	20h00	5.25	2.43	47.04	0.39	0.08	-20.87	3.18	216	150	66	38	28	10
5	07/04/2015	08h30	2.94	3.87	33.50	0.39	0.08	-18.73	1.39	228	162	66	49	32	17
6	07/04/2015	12h10	13.73	-6.61	77.21	0.40	0.06	-44.27	0.92	214	166	48	37	23	14

DOC – mg/L

Bottle	TC	IC	DOC
1	21.27	22.29	-1.02
1rep	11.2	9.853	1.347
2	17.23	17.37	-0.14
2rep	9.516	8.17	1.35
3	5.763	2.471	3.29
4	10.36	7.182	3.18
5	16.31	14.92	1.39
6	16.73	15.81	0.92

COD – mg/L

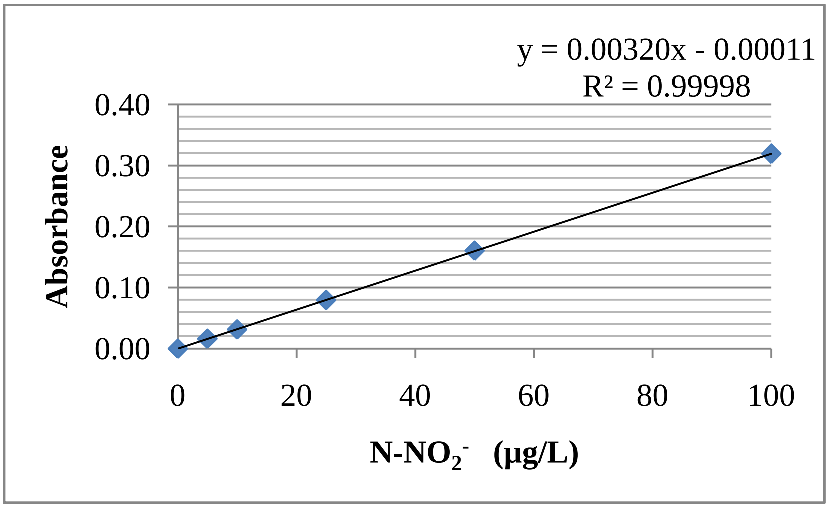
Calibration Curve				
COD	A	B	C	Aver
0	0.3073	0.2886	-	0.2980
25	0.2601	0.2465	0.2469	0.2467
50	0.2048	0.2229	0.2173	0.2150
75	0.1709	0.1881	0.1536	0.1795
100	0.1442	0.1414	0.1573	0.1428



Sample					
Bottle	A	B	C	Aver	Conc (mg/L)
1	0.3188	0.3109	0.3070	0.3149	-15.30
2	0.3066	0.3015	0.3101	0.3041	-8.10
3	0.3207	0.3217	0.3220	0.3215	-19.71
4	0.3168	0.3296	0.3669	0.3232	-20.87
5	0.3220	0.3180	0.3563	0.3200	-18.73
6	0.3588	0.3578	0.3833	0.3583	-44.27

Nitrite – µg/L

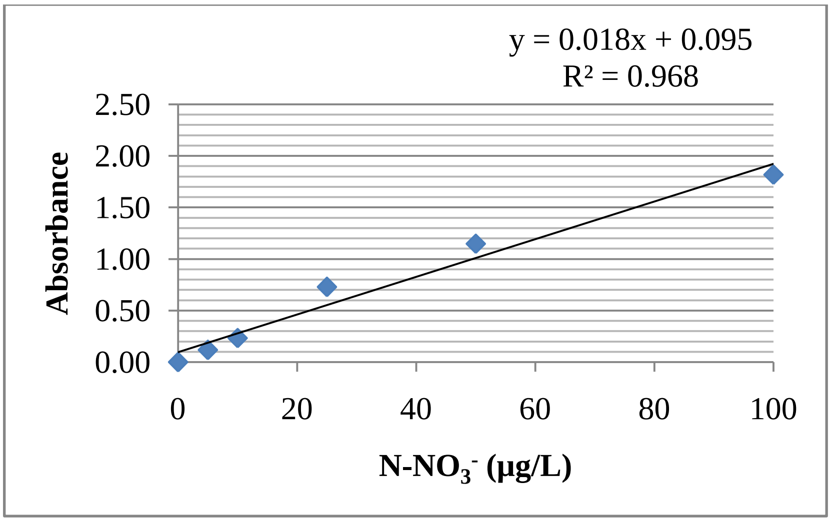
Calibration Curve					
$N\text{-}NO_2^-$ (µg/L)	A	B	C	Aver	Aver-Blank
0	0.0021	0.0020	0.0013	0.0021	0.0000
5	0.0175	0.0183	0.0182	0.0183	0.0162
10	0.0333	0.0334	0.0344	0.0334	0.0313
25	0.0815	0.0811	0.0815	0.0814	0.0793
50	0.1625	0.1625	0.1625	0.1625	0.1605
100	0.3208	0.3215	0.3213	0.3212	0.3192



Samples						
Bottle	A	B	C	Aver	Aver-Blank	Conc (µg/L)
1	0.0068	0.0068	0.0073	0.0068	0.0048	1.52
2	0.0046	0.0048	0.0054	0.0047	0.0027	0.86
3	0.0366	0.0365	0.0386	0.0366	0.0345	10.82
4	0.0192	0.0183	0.0204	0.0188	0.0167	5.25
5	0.0115	0.0112	0.0121	0.0114	0.0093	2.94
6	0.0460	0.0458	0.0458	0.0459	0.0438	13.73

Nitrate – μg/L

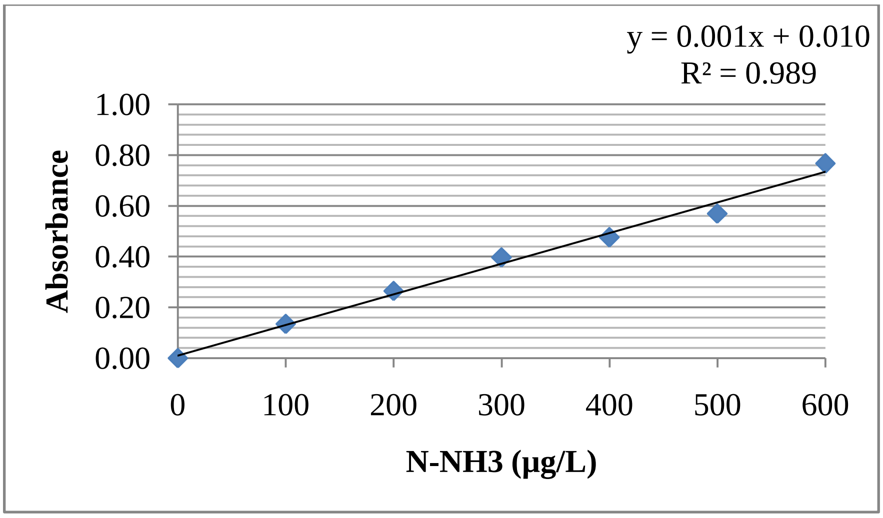
Calibration Curve						
N-NO$_3^-$ (μg/L)	A	B	C	Aver	Aver-Blank	x10
0	0.0270	0.0276	0.0294	0.0273	0.0000	0.000
5	0.1427	0.1467	0.1510	0.1447	0.1174	1.174
10	0.2609	0.2601	0.2574	0.2605	0.2332	2.332
25	0.7548	0.7639	0.7479	0.7555	0.7282	7.282
50	1.1735	1.1798	1.1626	1.1767	1.1494	11.494
100	1.8450	1.8450	1.8130	1.8450	1.8177	18.177



Samples									
Bottle	A	B	C	Aver	Aver-Blank	x10	Conc (μg/L)	Conc NO$_2^-$	Con NO$_3^-$
1	0.2673	0.2700	0.2693	0.2689	0.2416	2.4157	7.99	1.52	6.47
2	0.2748	0.2710	0.2761	0.2740	0.2467	2.4667	8.27	0.86	7.40
3	0.2588	0.2627	0.2612	0.2609	0.2336	2.3360	7.55	10.82	-3.26
4	0.2623	0.2632	0.2646	0.2634	0.2361	2.3607	7.69	5.25	2.43
5	0.2472	0.2482	0.2467	0.2474	0.2201	2.2007	6.81	2.94	3.87
6	0.2537	0.2510	0.2542	0.2530	0.2257	2.2567	7.12	13.73	-6.61

Ammoniacal Nitrogen – µg/L

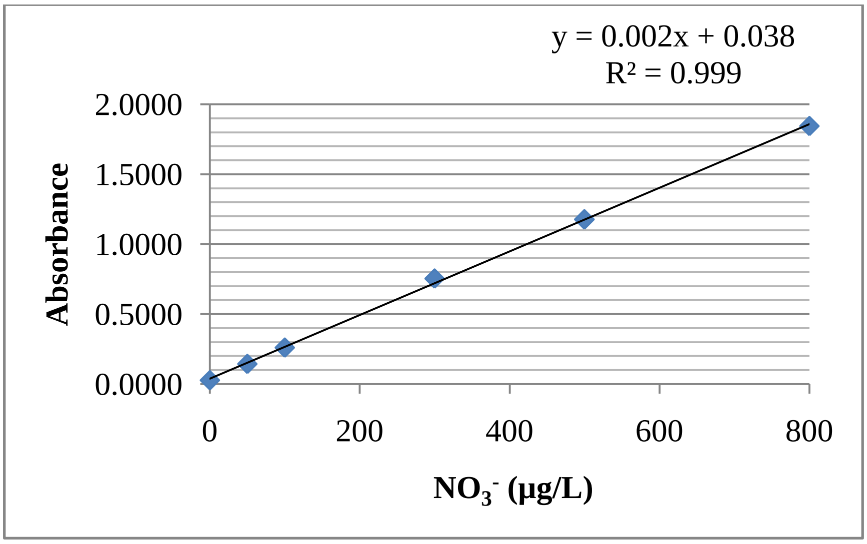
Calibration Curve					
N-NH_3 (µg/L)	A	B	C	Aver	Aver-Blank
0	0.0544	0.0394	0.0403	0.0399	0.0000
100	0.1698	0.1733	0.1755	0.1744	0.1346
200	0.2898	0.3009	0.3071	0.3040	0.2642
300	0.4475	0.4396	0.4338	0.4367	0.3969
400	0.5537	0.5018	0.5292	0.5155	0.4757
500	0.6951	0.6102	0.6088	0.6095	0.5697
600	0.8066	0.8032	0.8097	0.8065	0.7666



Samples						
Bottles	A	B	C	Aver	Aver-Blank	Conc (µg/L)
1	0.0695	0.068	0.1146	0.0688	0.0289	48.79
2	0.0714	0.0437	0.0593	0.0581	0.0183	39.94
3	0.0403	0.0433	0.0415	0.0417	0.0019	26.25
4	0.0815	0.0682	0.0651	0.0667	0.0268	47.04
5	0.052	0.0509	0.0499	0.0504	0.0106	33.50
6	0.0967	0.1028	0.1029	0.1029	0.0630	77.21

Total Nitrogen – mg/L

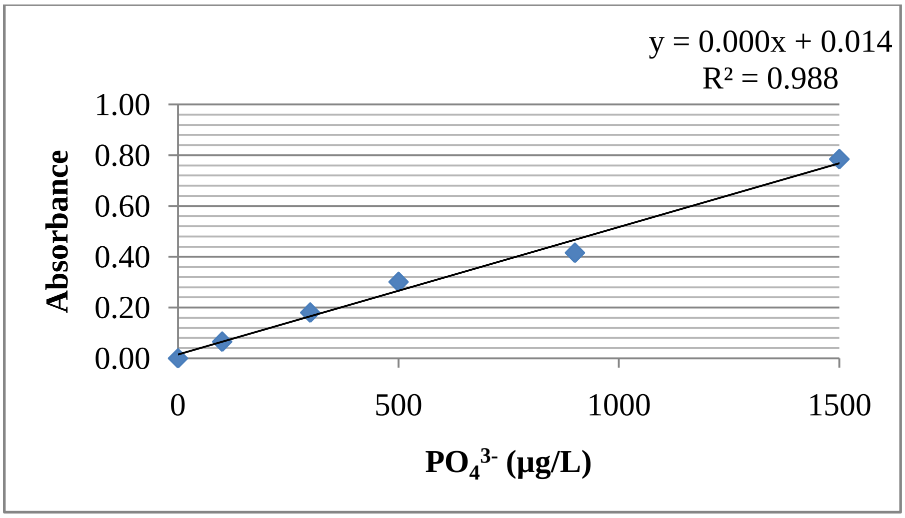
Curva de Calibração					
NO_3 (µg/L)	A	B	C	Aver	Aver-Blank
0	0.0270	0.0276	0.0294	0.0280	0.0000
50	0.1510	0.1427	0.1467	0.1447	0.1167
100	0.2609	0.2601	0.2574	0.2605	0.2325
300	0.7548	0.7639	0.7479	0.7555	0.7275
500	1.1735	1.1798	1.1626	1.1767	1.1487
800	1.8130	1.8450	1.8450	1.8450	1.8170



Samples							
Bottles	A	B	C	Aver	Aver-Blank	Conc (µg/L)	Conc (mg/L)
1	0.9550	0.9872	0.9872	0.9872	0.9592	400.30	0.40
2	0.9675	0.9740	0.9730	0.9735	0.9455	394.35	0.39
3	0.9655	0.9598	0.9595	0.9597	0.9317	388.33	0.39
4	0.9573	0.9724	0.9705	0.9715	0.9435	393.46	0.39
5	0.9559	0.9617	0.9651	0.9634	0.9354	389.96	0.39
6	0.9821	0.9734	0.9795	0.9765	0.9485	395.63	0.40

Total Phosphorus – mg/L

Curva de Calibração				
$PO^{4}_{3}{}^{-}$ (µg/L)	A	B	C	Aver
0	0.0134	0.0099	0.0117	0.0117
100	0.0759	0.0773	0.0763	0.0765
300	0.1906	0.1913	0.1920	0.1913
500	0.3114	0.3131	0.3121	0.3122
900	0.4272	0.4254	0.4280	0.4269
1500	0.7992	0.7925	0.7964	0.7960



Samples						
Bottles	A	B	C	Aver	Conc (µg/L)	Conc (mg/L)
1	0.0466	0.0463	0.0460	0.0463	63.80	0.06
2	0.0594	0.0588	0.0575	0.0586	88.33	0.09
3	0.0328	0.0331	0.0314	0.0324	36.07	0.04
4	0.0568	0.0552	0.0518	0.0546	80.40	0.08
5	0.0569	0.0540	0.0547	0.0552	81.60	0.08
6	0.0537	0.0450	0.0438	0.0444	60.00	0.06

Solids – mg/L

Total Solids							
Bottles	Samples (mL)	P0 (g)	P1 (g)	TS	P2 (g)	FTS	VTS
1	50	48.5537	48.5679	284	48.5644	214	70
2	50	41.2010	41.2156	292	41.2120	220	72
3	50	47.6083	47.6186	206	47.6159	152	54
4	50	47.6987	47.7095	216	47.7062	150	66
5	50	37.0775	37.0889	228	37.0856	162	66
6	50	41.3549	41.3656	214	41.3632	166	48

Suspended Solid							
Bottle	Sample (mL)	P0 (g)	P1 (g)	SS	P2 (g)	FSS	VSS
1	200	30.2807	30.3035	114	30.2984	89	25
2	200	34.4008	34.4259	126	34.4207	99	26
3	200	28.1806	28.1869	32	28.1849	22	10
4	200	26.4838	26.4913	38	26.4893	28	10
5	200	23.6017	23.6116	49	23.6082	32	17
6	200	33.4211	33.4285	37	33.4256	23	14

Campaign SBN 6: This campaign was composed by 21 bottles, where special and diffuse pollution events were identified (event 8 and 9). Event 8 is a special event of water discharge represented by bottles 1 to 12. Event 9 is diffuse pollution event represented by bottles 13 to 21.

Bottle	Hour	Date	Turb	pH	DO	Temp	Cond	Alka	NO2	NO3	NH3	TN	TP	COD	DOC	TS	FTS	VTS	SS	FSS	VSS
1	17h50	17/04/2015	46.0	8.20	7.78	21.7	312	180.79	1.32	8.53	7.95	0.41	0.24	5.97	4.86	272	198	74	115	93	22
2	18h00	17/04/2015	91.4	8.28	8.07	20.6	311	181.83	1.33	8.38	-1.00	0.43	0.32	18.78	6.17	332	248	84	199	164	35
3	18h10	17/04/2015	101.0	8.28	8	20.5	312	173.47	1.39	8.79	-1.73	0.42	0.33	5.85	2.23	332	242	90	207	170	38
4	19h40	17/04/2015	34.3	8.25	8.08	20.4	305	169.29	4.55	4.07	6.14	0.40	0.12	7.75	1.29	226	162	64	46	36	10
5	20h10	17/04/2015	22.6	8.27	8.13	20.2	305	173.47	6.21	2.80	6.36	0.40	0.12	-1.00	2.02	204	136	68	41	30	11
6	12h00	18/04/2015	16.6	8.26	8.1	20.1	311	177.65	4.66	4.27	10.55	0.40	0.13	3.91	1.74	206	128	78	46	32	14
7	08h10	20/04/2015	42.1	8.15	7.87	20	317	180.79	1.33	7.78	33.59	0.41	0.25	8.81	1.47	272	186	86	141	111	30
8	08h20	20/04/2015	70.5	8.24	8.07	20.2	312	183.92	1.01	8.27	-1.65	0.41	0.26	7.69	3.19	360	208	152	176	140	36
9	08h30	20/04/2015	60.1	8.27	8.06	20	308	175.56	1.07	8.11	-1.92	0.41	0.22	0.56	1.65	302	228	74	173	144	29
10	09h40	20/04/2015	21.5	8.21	8.13	20.2	312	179.74	3.08	5.88	6.91	0.40	0.10	11.34	1.84	228	166	62	49	34	15
11	10h00	20/04/2015	17.7	8.21	8.1	20.4	313	177.65	7.45	1.11	23.23	0.40	0.10	-5.67	1.83	232	154	78	37	25	11
12	17h20	20/04/2015	20.2	8.20	8.06	20.1	310	179.74	4.87	3.29	22.41	0.41	0.09	2.19	1.77	360	216	144	35	22	13
13	23h50	20/04/2015	47.8	7.71	4.95	20.2	299	169.29	9.38	-7.18	229.64	0.45	0.63	2.16	2.33	288	182	106	0	0	0
14	00h40	22/04/2015	64.8	7.98	7.54	20.2	263	147.35	7.68	-0.85	83.82	0.42	0.25	12.09	4.39	262	166	96	99	77	21
15	03h10	22/04/2015	135.0	8.09	7.61	20.3	238	125.40	9.88	-3.55	125.17	0.44	0.42	16.91	2.69	288	216	72	144	114	30
16	03h30	22/04/2015	180.0	7.97	7.55	20.2	237	128.54	10.32	-3.90	105.50	0.44	0.49	12.33	2.53	952	382	570	233	199	34
17	08h50	22/04/2015	129.0	8.05	7.83	20.1	256	145.26	4.97	1.36	33.86	0.42	0.30	14.22	2.53	290	146	144	178	157	22
18	17h00	22/04/2015	81.2	7.810	8	20.1	273	150.48	7.14	-0.04	44.45	0.42	0.23	10.88	3.50	236	126	110	109	94	15
19	20h20	22/04/2015	72.9	8.16	8.05	20.2	268	151.53	6.17	0.77	60.59	0.42	0.16	7.41	3.44	254	124	130	67	51	16
20	01h10	23/04/2015	50.5	8.11	8.13	20.3	271	152.57	7.04	0.10	40.17	0.39	0.13	5.16	2.28	224	90	134	0	0	0
21	08h40	23/04/2015	34.9	8.13	8.19	20.4	273	153.615	5.16	1.67	21.82	0.41	0.10	13.44	2.93	204	96	108	32	21	11

Alkalinity – mg $CaCO_3$/L

Bottles	Volume Consumed (mL)	Alkalinity
1	17.3	180.79
2	17.4	181.83
3	16.6	173.47
4	16.2	169.29
5	16.6	173.47
6	17	177.65
7	17.3	180.79
8	17.6	183.92
9	16.8	175.56
10	17.2	179.74
11	17	177.65
12	17.2	179.74
13	16.2	169.29
14	14.1	147.35
15	12	125.40
16	12.3	128.54
17	13.9	145.26
18	14.4	150.48
19	14.5	151.53
20	14.6	152.57
21	14.7	153.62

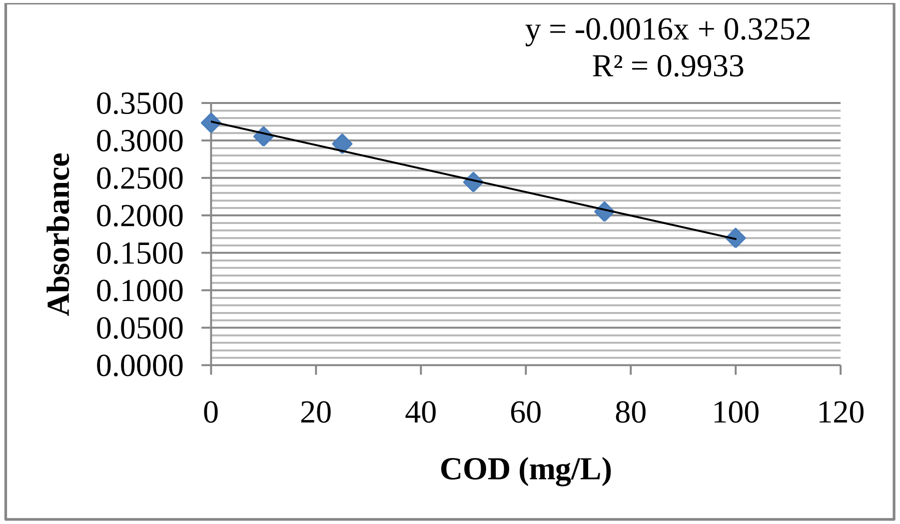
Correction Factor = 10.45/10 = 1.045

DOC – mg/L

Bottles	TC	IC	DOC
1	0.49	0.00	4.86
2	41.32	35.15	6.17
3	2.35	0.12	2.23
4	8.65	7.36	1.29
5	2.15	0.13	2.02
6	1.82	0.09	1.74
7	1.62	0.15	1.47
8	27.13	23.94	3.19
9	2.03	0.38	1.65
10	1.94	0.10	1.84
11	1.91	0.08	1.83
12	1.98	0.21	1.77
13	4.32	2.00	2.33
14	4.52	0.13	4.39
15	2.80	0.12	2.69
16	2.78	0.25	2.53
17	4.65	2.12	2.53
18	3.62	0.12	3.50
19	3.50	0.06	3.44
20	5.75	3.47	2.28
21	10.40	7.47	2.93

COD – mg/L

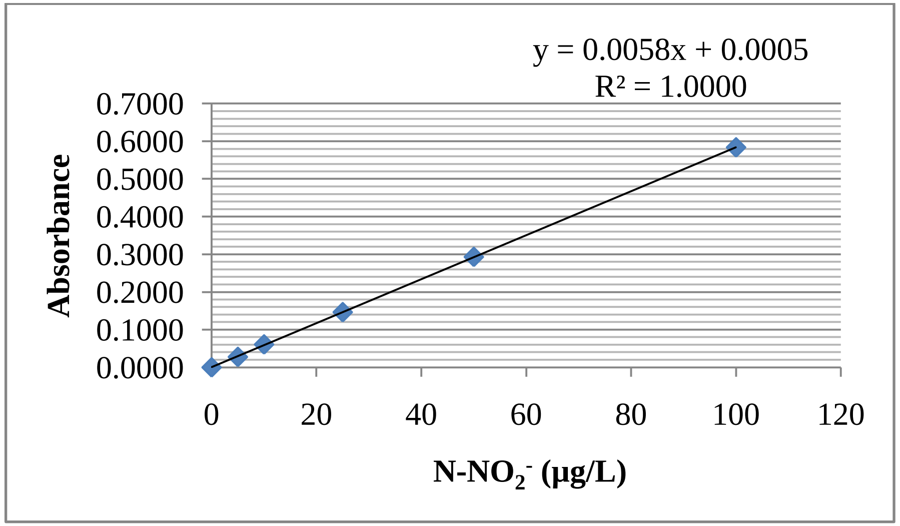
Calibration Curve				
COD (mg/L)	A	B	C	Aver
0	0.3240	0.3228	0.3239	0.3236
10	0.2971	0.3030	0.3079	0.3055
25	0.3036	0.2892	0.2941	0.2956
50	0.2435	0.2460	0.2438	0.2444
75	0.2041	0.2059	0.2275	0.2050
100	0.1698	0.2135	-	0.1698



Samples					
Bottles	A	B	C	Aver	Conc (mg/L)
1	0.3081	0.3232	0.3530	0.3157	5.97
2	0.2994	0.2909	0.3116	0.2952	18.78
3	0.3179	0.3086	0.3210	0.3158	5.85
4	0.3089	0.3167	-	0.3128	7.75
5	0.3268	0.3411	0.3748	0.3268	-1.00
6	0.3206	0.3173	0.4021	0.3190	3.91
7	0.3098	0.3124	0.3353	0.3111	8.81
8	0.3448	0.3619	0.3129	0.3129	7.69
9	0.3458	0.3489	0.3243	0.3243	0.56
10	0.3165	0.2976	0.4191	0.3071	11.34
11	0.3589	0.3088	0.3351	0.3343	-5.67
12	0.4280	0.3979	0.3217	0.3217	2.19
13	0.3220	0.3215	0.3063	0.3218	2.16
14	0.3021	0.3096	0.3232	0.3059	12.09
15	0.2961	0.3002	0.3201	0.2982	16.91
16	0.3081	0.3019	0.3064	0.3055	12.33
17	0.3020	0.3029	0.3221	0.3025	14.22
18	0.3035	0.3121	0.3643	0.3078	10.88
19	0.3124	0.3143	0.3000	0.3134	7.41
20	0.3081	0.3258	0.3655	0.3170	5.16
21	0.3052	0.3022	0.3199	0.3037	13.44

Nitrite – µg/L

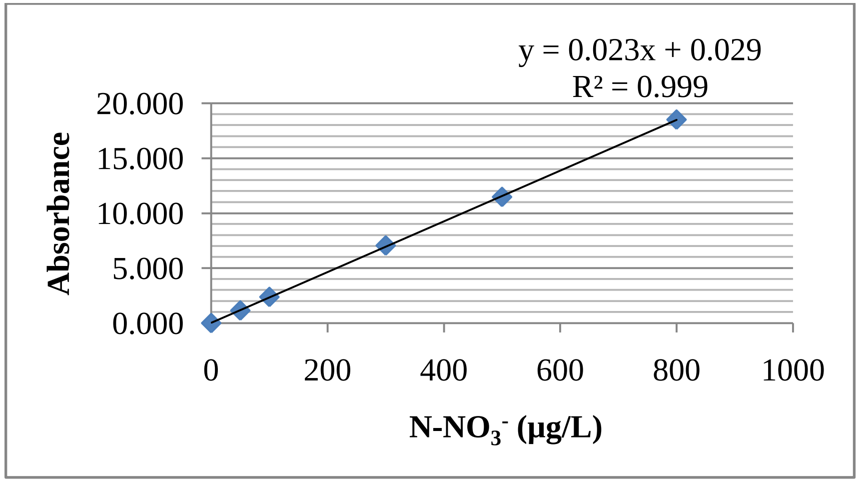
Calibration Curve					
N-NO$_2^-$ (µg/L)	A	B	C	Aver	Aver-Blank
0	0.0010	0.0020	0.0005	0.0015	0.0000
5	0.0287	0.0293	0.0297	0.0292	0.0277
10	0.0602	0.0645	0.0623	0.0623	0.0608
25	0.1476	0.1479	0.1482	0.1479	0.1464
50	0.2920	0.2974	0.2941	0.2945	0.2930
100	0.5865	0.5834	0.5850	0.5850	0.5835



Samples						
Bottles	A	B	C	Aver	Aver-Blank	Conc (µg/L)
1	0.0076	0.0081	0.0082	0.0082	0.0067	1.32
2	0.0077	0.0081	0.0083	0.0082	0.0067	1.33
3	0.0084	0.0068	0.0104	0.0085	0.0070	1.39
4	0.0269	0.0266	0.0271	0.0269	0.0254	4.55
5	0.0344	0.0376	0.0376	0.0365	0.0350	6.21
6	0.0217	0.0273	0.0277	0.0275	0.0260	4.66
7	0.0082	0.0081	0.0084	0.0082	0.0067	1.33
8	0.0065	0.0065	0.0061	0.0064	0.0049	1.01
9	0.0670	0.0071	0.0063	0.0067	0.0052	1.07
10	0.0221	0.0189	0.0178	0.0184	0.0169	3.08
11	0.0355	0.0431	0.0443	0.0437	0.0422	7.45
12	0.0348	0.0286	0.0289	0.0288	0.0273	4.87
13	0.0532	0.0579	0.0536	0.0549	0.0534	9.38
14	0.0546	0.0449	0.0452	0.0451	0.0436	7.68
15	0.0569	0.0579	0.0586	0.0578	0.0563	9.88
16	0.0599	0.0602	0.0609	0.0603	0.0588	10.32
17	0.0315	0.0294	0.0292	0.0293	0.0278	4.97
18	0.0408	0.0413	0.0437	0.0419	0.0404	7.14
19	0.0402	0.0377	0.0349	0.0363	0.0348	6.17
20	0.0413	0.0414	0.0413	0.0413	0.0398	7.04
21	0.0294	0.0304	0.0304	0.0304	0.0289	5.16

Nitrate – μg/L

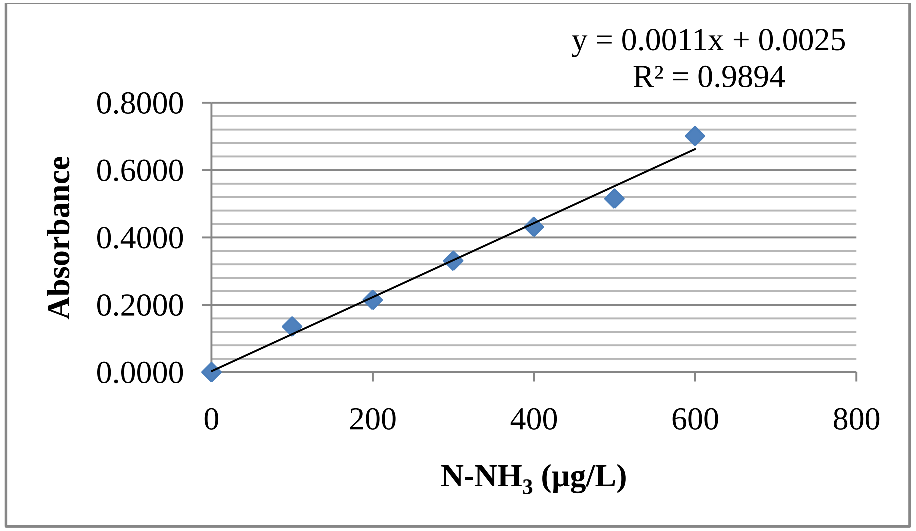
Calibration Curve						
N-NO$_3^-$ (μg/L)	A	B	C	Aver	Aver-Blank	x10
0	0.0277	0.0299	0.0336	0.0288	0.0000	0.000
50	0.1438	0.1425	0.1378	0.1432	0.1144	1.144
100	0.2683	0.2681	0.2633	0.2666	0.2378	2.378
300	0.7368	0.7308	0.7358	0.7345	0.7057	7.057
500	1.1813	1.1711	1.8290	1.1762	1.1474	11.474
800	1.8796	1.8796	1.8599	1.8796	1.8508	18.508



Samples									
Bottles	A	B	C	Aver	Aver-Blank	x10	Conc	Conc NO2	CONC NO3
1	0.2877	0.2864	0.2820	0.2854	0.2566	2.5657	9.85	1.32	8.53
2	0.2839	0.2803	0.2782	0.2821	0.2533	2.5330	9.71	1.33	8.38
3	0.2922	0.2958	0.2902	0.2927	0.2639	2.6393	10.17	1.39	8.79
4	0.2582	0.2554	0.2648	0.2568	0.2280	2.2800	8.61	4.55	4.07
5	0.2661	0.2653	0.2668	0.2661	0.2373	2.3727	9.02	6.21	2.80
6	0.2655	0.2614	0.2648	0.2639	0.2351	2.3510	8.92	4.66	4.27
7	0.2671	0.2689	0.2689	0.2683	0.2395	2.3950	9.11	1.33	7.78
8	0.2726	0.2712	0.2731	0.2723	0.2435	2.4350	9.29	1.01	8.27
9	0.2697	0.2698	0.2755	0.2698	0.2410	2.4095	9.18	1.07	8.11
10	0.2670	0.2649	0.2625	0.2648	0.2360	2.3600	8.96	3.08	5.88
11	0.2496	0.2648	0.2524	0.2556	0.2268	2.2680	8.56	7.45	1.11
12	0.2477	0.2474	0.2439	0.2463	0.2175	2.1753	8.16	4.87	3.29
13	0.1085	0.1089	0.1107	0.1087	0.0799	0.7990	2.20	9.38	-7.18
14	0.2128	0.2173	0.2167	0.2156	0.1868	1.8680	6.83	7.68	-0.85
15	0.2026	0.2054	0.1982	0.2040	0.1752	1.7520	6.33	9.88	-3.55
16	0.2054	0.2065	0.2157	0.2060	0.1772	1.7715	6.41	10.32	-3.90
17	0.2076	0.2032	0.2008	0.2039	0.1751	1.7507	6.32	4.97	1.36
18	0.2202	0.2238	0.2186	0.2220	0.1932	1.9320	7.11	7.14	-0.04
19	0.2181	0.2181	0.2223	0.2181	0.1893	1.8930	6.94	6.17	0.77
20	0.2230	0.2234	0.2217	0.2227	0.1939	1.9390	7.14	7.04	0.10
21	0.2157	0.2151	0.2158	0.2155	0.1867	1.8673	6.83	5.16	1.67

Ammoniacal Nitrogen – μg/L

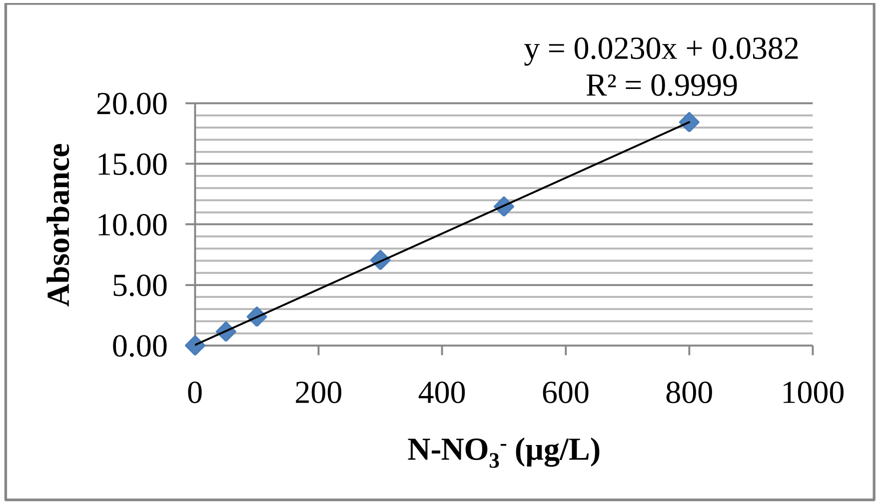
Calibration Curve					
N-NH_3 (μg/L)	A	B	C	Aver	Aver-Blank
0	0.0464	0.0457	0.0507	0.0461	0.0000
100	0.1835	0.1794	0.2010	0.1815	0.1354
200	0.2545	0.2661	0.2954	0.2603	0.2143
300	0.3691	0.3843	0.4250	0.3767	0.3307
400	0.4756	0.4794	0.4326	0.4775	0.4315
500	0.5630	0.5593	0.6606	0.5612	0.5151
600	0.7563	0.7383	0.6454	0.7473	0.7013



Samples						
Bottles	A	B	C	Aver	Aver-Blank	Conc (μg/L)
1	0.0592	0.0537	0.0590	0.0573	0.0113	7.95
2	0.0502	0.0455	0.0494	0.0475	0.0014	-1.00
3	0.0514	0.0475	0.0458	0.0467	0.0006	-1.73
4	0.0459	0.0599	0.0507	0.0553	0.0093	6.14
5	0.0499	0.0540	0.0571	0.0556	0.0095	6.36
6	0.0529	0.0593	0.0610	0.0602	0.0141	10.55
7	0.0612	0.0819	0.0891	0.0855	0.0395	33.59
8	0.0494	0.0459	0.0449	0.0467	0.0007	-1.65
9	0.0486	0.0443	0.0464	0.0464	0.0004	-1.92
10	0.0612	0.0577	0.0546	0.0562	0.0101	6.91
11	0.0631	0.0758	0.0724	0.0741	0.0281	23.23
12	0.0756	0.0717	0.0723	0.0732	0.0272	22.41
13	0.2750	0.2971	0.3052	0.3012	0.2551	229.64
14	0.1157	0.1344	0.1471	0.1408	0.0947	83.82
15	0.1754	0.1980	0.1853	0.1862	0.1402	125.17
16	0.1768	0.1639	0.1653	0.1646	0.1186	105.50
17	0.0909	0.0835	0.0881	0.0858	0.0398	33.86
18	0.1101	0.0963	0.0986	0.0975	0.0514	44.45
19	0.1069	0.1125	0.1179	0.1152	0.0692	60.59
20	0.0906	0.0820	0.1056	0.0927	0.0467	40.17
21	0.1013	0.0726	0.0725	0.0726	0.0265	21.82

Total Nitrogen – mg/L

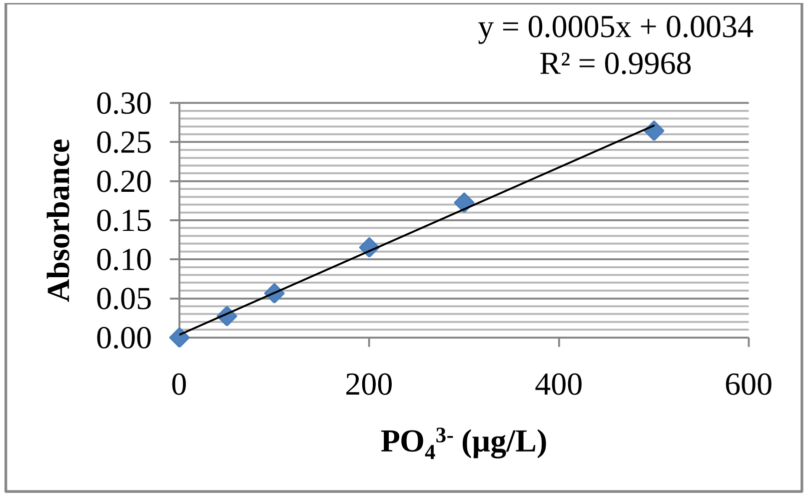
Calibration Curve						
$N-NO_3^-$ (μg/L)	A	B	C	Aver	Aver-Blank	x10
0	0.0336	0.0277	0.0299	0.0288	0.0000	0.0000
50	0.1378	0.1425	0.1438	0.1432	0.1144	1.1435
100	0.2683	0.2681	0.2633	0.2666	0.2378	2.3777
300	0.7368	0.7308	0.7358	0.7345	0.7057	7.0567
500	1.8290	1.1813	1.1711	1.1762	1.1474	11.4740
800	1.8796	1.8796	1.8599	1.8730	1.8442	18.4423



Samples								
Bottles	A	B	C	Aver	Aver-Blank	x10	Conc (μg/L)	Conc (mg/L)
1	0.9904	0.9507	0.9740	0.9717	0.9429	9.4290	408.30	0.41
2	1.0106	1.0216	1.0308	1.0210	0.9922	9.9220	429.73	0.43
3	0.9795	1.0068	0.9944	1.0006	0.9718	9.7180	420.86	0.42
4	0.9559	0.9454	0.9408	0.9431	0.9143	9.1430	395.86	0.40
5	0.9331	0.9446	0.9446	0.9446	0.9158	9.1580	396.51	0.40
6	0.9617	0.9579	0.9540	0.9560	0.9272	9.2715	401.45	0.40
7	0.9716	0.9655	0.9695	0.9675	0.9387	9.3870	406.47	0.41
8	0.9769	0.9835	0.9825	0.9830	0.9542	9.5420	413.21	0.41
9	0.9655	0.9867	0.9852	0.9860	0.9572	9.5715	414.49	0.41
10	0.9482	0.9446	0.9497	0.9475	0.9187	9.1870	397.77	0.40
11	0.9418	0.9583	0.9564	0.9574	0.9286	9.2855	402.06	0.40
12	0.9734	0.9695	0.9686	0.9691	0.9403	9.4025	407.14	0.41
13	1.0916	1.0779	1.0697	1.0738	1.0450	10.4500	452.69	0.45
14	0.9872	0.9913	0.9961	0.9937	0.9649	9.6490	417.86	0.42
15	1.0443	1.0560	1.0647	1.0550	1.0262	10.2620	444.51	0.44
16	1.0472	1.0580	1.0343	1.0465	1.0177	10.1770	440.82	0.44
17	0.9883	1.0013	0.9983	0.9998	0.9710	9.7100	420.51	0.42
18	1.0084	0.9950	1.0020	1.0018	0.9730	9.7300	421.38	0.42
19	0.9977	0.9956	0.9956	0.9963	0.9675	9.6750	418.99	0.42
20	0.9186	0.9264	0.9259	0.9262	0.8974	8.9735	388.49	0.39
21	0.9583	0.9701	0.9755	0.9728	0.9440	9.4400	408.77	0.41

Total Phosphorus – mg/L

Calibration Curve					
$PO^{4}_{3}{}^{-}$ (µg/L)	A	B	C	Aver	Aver-Blank
0	0.0076	0.0095	0.0100	0.0098	0.0000
50	0.0341	0.0376	0.0366	0.0371	0.0274
100	0.0662	0.0667	0.0660	0.0663	0.0566
200	0.1256	0.1251	0.1244	0.1250	0.1153
300	0.1836	0.1820	0.1813	0.1823	0.1726
500	0.2755	0.2756	0.2719	0.2743	0.2646



Samples							
Bottles	A	B	C	Aver	Aver-Blank	Conc (µg/L)	Conc (mg/L)
1	0.1262	0.1273	0.1229	0.1255	0.1157	244.13	0.24
2	0.1631	0.1624	0.1616	0.1624	0.1526	317.93	0.32
3	0.1609	0.1687	0.1682	0.1659	0.1562	325.07	0.33
4	0.0626	0.0619	0.0643	0.0629	0.0532	119.07	0.12
5	0.0631	0.0618	0.0626	0.0625	0.0528	118.20	0.12
6	0.0582	0.0696	0.0624	0.0660	0.0563	125.20	0.13
7	0.1249	0.1278	0.1281	0.1269	0.1172	247.07	0.25
8	0.1346	0.1322	0.1357	0.1342	0.1244	261.53	0.26
9	0.0906	0.1328	0.1194	0.1143	0.1045	221.73	0.22
10	0.0525	0.0550	0.0514	0.0530	0.0432	99.13	0.10
11	0.0505	0.0537	0.0553	0.0532	0.0434	99.53	0.10
12	0.0500	0.0497	0.0485	0.0494	0.0397	92.00	0.09
13	0.3196	0.3102	0.3242	0.3180	0.3083	629.20	0.63
14	0.1293	0.1292	0.1301	0.1295	0.1198	252.27	0.25
15	0.2134	0.2062	0.2141	0.2112	0.2015	415.67	0.42
16	0.2402	0.2520	0.2487	0.2470	0.2372	487.13	0.49
17	0.4930	0.1489	0.1548	0.1519	0.1421	296.90	0.30
18	0.1252	0.1119	0.1241	0.1204	0.1107	234.00	0.23
19	0.0725	0.0812	0.0968	0.0835	0.0738	160.20	0.16
20	0.0745	0.0618	0.0621	0.0661	0.0564	125.47	0.13
21	0.0546	0.0542	0.0558	0.0549	0.0451	102.93	0.10

Solids – mg/L

Total Solids							
Bottles	Samples (mL)	P0 (g)	P1 (g)	TS	P2 (g)	FTS	VTS
1	50	50.2179	50.2315	272	50.2278	198	74
2	50	51.2824	51.2990	332	51.2948	248	84
3	50	47.5849	47.6015	332	47.5970	242	90
4	50	49.7045	49.7158	226	49.7126	162	64
5	50	48.7315	48.7417	204	48.7383	136	68
6	50	50.8056	50.8159	206	50.8120	128	78
7	50	48.4225	48.4361	272	48.4318	186	86
8	50	44.3134	44.3314	360	44.3238	208	152
9	50	49.7484	49.7635	302	49.7598	228	74
10	50	48.0239	48.0353	228	48.0322	166	62
11	50	51.5975	51.6091	232	51.6052	154	78
12	50	51.3401	51.3581	360	51.3509	216	144
13	50	50.2175	50.2319	288	50.2266	182	106
14	50	49.7183	49.7314	262	49.7266	166	96
15	50	56.4570	56.4714	288	56.4678	216	72
16	50	50.0493	50.0969	952	50.0684	382	570
17	50	42.0124	42.0269	290	42.0197	146	144
18	50	35.8071	35.8189	236	35.8134	126	110
19	50	50.6416	50.6543	254	50.6478	124	130
20	50	38.8680	38.8792	224	38.8725	90	134
21	50	42.9085	42.9187	204	42.9133	96	108

Suspended Solids							
Bottles	Sample (mL)	P0 (g)	P1 (g)	SS	P2 (g)	FSS	VSS
1	200	26.8060	26.8291	115	26.8247	93	22
2	200	31.2823	31.3221	199	31.315	164	35
3	200	31.3817	31.4231	207	31.4156	170	38
4	200	29.7429	29.7522	46	29.7501	36	10
5	200	32.6185	32.6267	41	32.6245	30	11
6	200	27.1172	27.1264	46	27.1236	32	14
7	200	33.5060	33.5341	141	33.5282	111	30
8	200	27.8840	27.9193	176	27.9121	140	36
9	200	31.1767	31.2112	173	31.2055	144	29
10	200	30.6686	30.6784	49	30.6754	34	15
11	200	32.5359	32.5432	37	32.5409	25	11
12	200	27.8290	27.8360	35	27.8334	22	13
13	200	-	-	0	-	0	0
14	200	28.4254	28.4451	99	28.4409	77	21
15	171	31.8149	31.8395	144	31.8344	114	30
16	200	26.9635	27.0101	233	27.0034	199	34
17	200	25.0671	25.1028	178	25.0984	157	22
18	200	32.1277	32.1494	109	32.1464	94	15
19	200	27.5318	27.5452	67	27.542	51	16
20	200	-	-	0	-	0	0
21	200	32.9609	32.9673	32	32.965	21	11

Campaign SBN 7: This campaign was composed by 21 bottles, where two diffuse pollution events was identified (event 10 and 11). Event 10 correspond bottles 1 to 12, and event 6 correspond bottles 13 to 21.

Bottle	Hour	Date	Turb	pH	DO	Temp	Cond	Alka	NO2	NO3	NH3	TN	TP	COD	DOC	ST	STF	STV	SS	SSF	SSV
1	00h20	04/05/2015	96.0	7.940	8.23	17.1	254	156.75	41.27	86.78	27.70	0.16	0.17	27.17	0.99	384	260	124	198	169	29
2	00h30	04/05/2015	246	7.589	6.80	16.8	197.9	129.58	54.78	-26.78	169.47	0.20	0.26	112.25	2.33	654	492	162	225	187	38
3	01h00	04/05/2015	920	7.828	6.96	16.6	198.8	147.35	88.52	-24.28	110.07	0.18	0.47	65.15	1.75	1100	902	198	448	395	53
4	01h40	04/05/2015	110	7.951	6.88	13.9	194.7	180.79	134.20	-19.68	235.43	0.26	0.49	58.60	2.52	1306	1034	272	1073	924	149
5	01h50	04/05/2015	950	7.912	7.02	13.5	191.4	190.19	89.49	26.71	102.67	0.22	0.49	38.95	2.50	1098	860	238	900	803	97
6	03h30	04/05/2015	666	7.957	8.80	13.0	193	137.94	29.71	76.33	29.00	0.18	0.29	23.40	9.44	722	548	174	513	451	62
7	05h40	04/05/2015	186	8.059	8.43	15.1	243	155.71	17.29	86.48	26.50	0.19	0.61	23.70	1.68	420	284	136	159	132	27
8	08h40	04/05/2015	234.0	8.026	8.68	13.3	215	138.99	8.78	102.43	23.47	0.16	0.17	19.30	1.82	466	326	140	245	206	39
9	11h40	04/05/2015	256	7.914	8.70	12.8	190.9	123.31	15.93	95.82	23.83	0.14	0.16	11.45	6.66	424	296	128	168	143	25
10	15h20	04/05/2015	79	8.171	9.01	12.7	239	159.89	15.07	105.72	32.73	0.12	0.09	-0.30	1.75	304	186	118	83	67	16
11	18h20	04/05/2015	82	8.130	8.98	13.1	236	156.75	24.39	85.43	24.53	0.11	0.10	4.80	2.79	290	170	120	91	75	16
12	23h00	04/05/2015	47	8.085	9.02	12.8	232	153.62	28.31	79.70	24.03	0.10	0.06	-	11.34	248	142	106	38	30	8
13	07h50	10/05/2015	60	7.792	7.79	13.0	250	167.20	14.46	86.68	99.80	0.14	0.15	4.65	6.93	312	196	116	100	80	20
14	08h30	10/05/2015	68	7.899	8.00	14.2	212	142.12	14.03	78.33	42.97	0.10	0.09	20.93	2.58	268	180	88	76	60	16
15	09h00	10/05/2015	163	7.912	8.25	13.8	210	138.99	16.90	79.01	137.67	0.14	0.15	19.30	2.43	370	250	120	84	69	16
16	12h50	10/05/2015	140	7.958	8.43	13.7	223	150.48	14.86	85.08	85.50	0.13	0.11	20.30	2.71	310	190	120	103	85	17
17	15h10	10/05/2015	157	8.076	8.67	13.5	220	146.30	11.32	81.33	46.27	0.11	0.12	18.80	5.31	336	222	114	119	96	23
18	23h10	10/05/2015	98	7.978	8.70	13.5	219	147.35	15.32	79.86	60.50	0.11	0.08	17.35	11.87	278	166	112	62	48	14
19	02h30	11/05/2015	74	7.997	8.73	13.6	226	151.53	14.82	84.09	52.13	0.11	0.06	-0.35	3.33	240	134	106	35	27	8
20	07h10	11/05/2015	41.5	7.980	8.79	14.0	234	155.705	12.62	85.98	53.20	0.10	0.10	22.70	3.64	260	152	108	42.5	34.5	8
21	14h10	11/05/2015	31.3	7.860	8.72	15.6	238	150.48	12.67	82.89	75.42	0.09	0.04	11.10	3.11	242	126	116	12.5	8	4.5

Alkalinity – mg $CaCO_3$/L

Bottles	Volume Consumed (mL)	Alkalinity
1	15.0	156.75
2	12.4	129.58
3	14.1	147.35
4	17.3	180.79
5	18.2	190.19
6	13.2	137.94
7	14.9	155.71
8	13.3	138.99
9	11.8	123.31
10	15.3	159.89
11	15.0	156.75
12	14.7	153.62
13	16.0	167.20
14	13.6	142.12
15	13.3	138.99
16	14.4	150.48
17	14.0	146.30
18	14.1	147.35
19	14.5	151.53
20	14.9	155.71
21	14.4	150.48

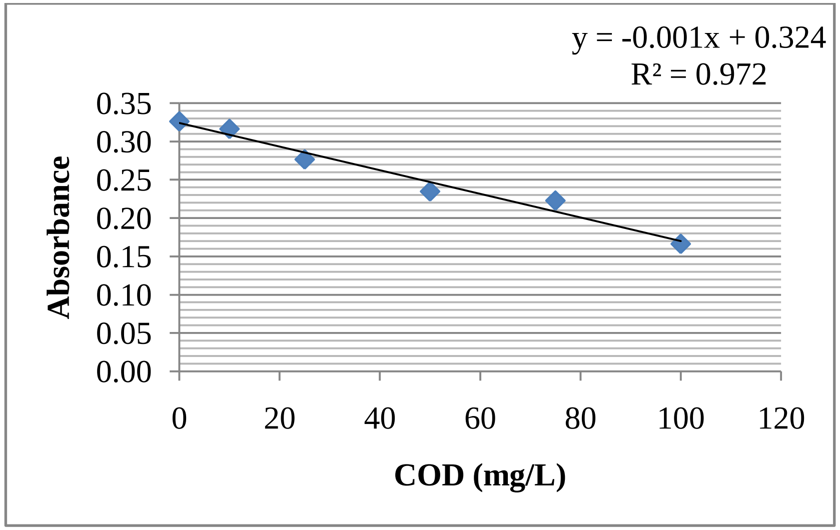
Correction Factor = 10.45/10 = 1.045

DOC – mg/L

Bottle	TC	IC	DOC
1	0.99	0.00	0.99
2	2.35	0.02	2.33
3	1.87	0.12	1.75
4	3.07	0.55	2.52
5	2.50	0.00	2.50
6	12.95	3.51	9.44
7	1.70	0.02	1.68
8	1.82	0.00	1.82
9	8.21	1.55	6.66
10	1.83	0.08	1.75
11	2.91	0.12	2.79
12	15.32	3.98	11.34
13	15.52	8.59	6.93
14	2.73	0.15	2.58
15	6.04	3.61	2.43
16	2.79	0.09	2.71
17	25.19	19.88	5.31
18	22.80	10.93	11.87
19	3.51	0.18	3.33
20	3.66	0.01	3.64
21	3.17	0.06	3.11

COD – mg/L

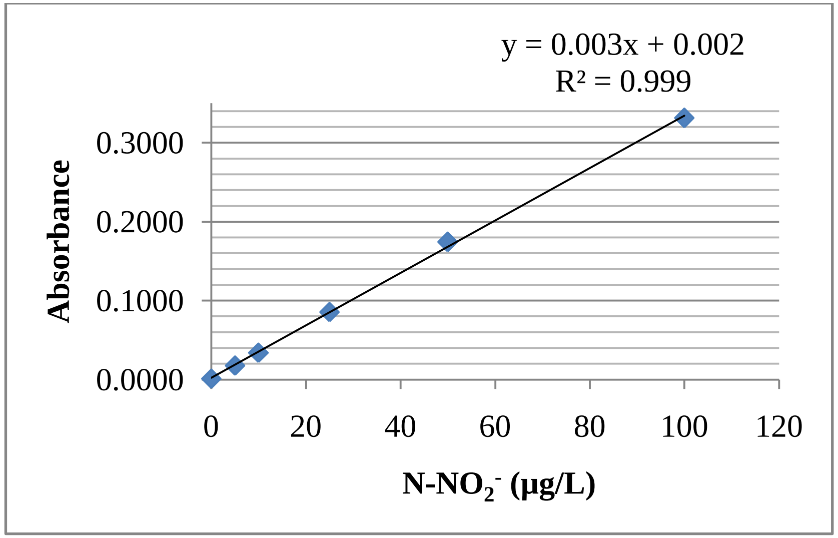
Curva de Calibração				
COD (mg/L)	A	B	C	Aver
0	0.3058	0.3242	0.3285	0.3264
10	0.3273	0.3160	0.3170	0.3165
25	0.2800	0.2765	0.2769	0.2767
50	0.2306	0.2329	0.2412	0.2349
75	0.2216	0.2242	0.2087	0.2229
100	0.1635	0.1692	0.1710	0.1664



Samples					
Bottles	A	B	C	Aver	Conc (mg/L)
1	0.2997	0.2971	0.2937	0.2968	27.17
2	0.2465	0.2126	0.2109	0.2118	112.25
3	0.2922	0.2661	0.2516	0.2589	65.15
4	0.2771	0.2675	0.2633	0.2654	58.60
5	0.2957	0.2810	0.2891	0.2851	38.95
6	0.3232	0.3051	0.2961	0.3006	23.40
7	0.3387	0.3007	0.2999	0.3003	23.70
8	0.2850	0.3059	0.3035	0.3047	19.30
9	0.3416	0.3009	0.3242	0.3126	11.45
10	0.3433	0.3280	0.3206	0.3243	-0.30
11	0.3456	0.3425	0.3192	0.3192	4.80
12	0.3670	0.3362	0.3523	*	*
13	0.3157	0.3230	0.4757	0.3194	4.65
14	0.3076	0.3007	0.3009	0.3031	20.93
15	0.3057	0.3157	0.2927	0.3047	19.30
16	0.3037	-	-	0.3037	20.30
17	0.3038	0.3066	0.3246	0.3052	18.80
18	0.3074	0.3059	0.3799	0.3067	17.35
19	0.3308	0.3179	0.4218	0.3244	-0.35
20	0.3120	0.2906	0.3523	0.3013	22.70
21	0.3113	0.3145	0.3070	0.3129	11.10

Nitrite – µg/L

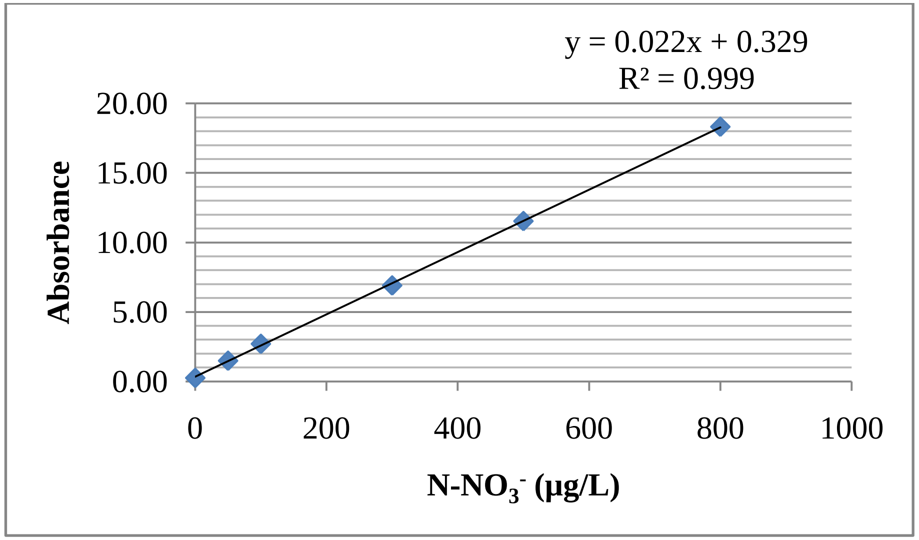
Calibration Curve				
N-NO_2^- (µg/L)	A	B	C	Aver
0	0.0011	0.0010		0.0011
5	0.0177	0.0170	0.0184	0.0177
10	0.0330	0.0345	0.0341	0.0339
25	0.0839	0.0863	0.0859	0.0854
50	0.1763	0.1742	0.1719	0.1741
100	0.3308	0.3308	0.3322	0.3313



Samples					
Bottle	A	B	C	Aver	Conc (µg/L)
1	0.1257	0.1260	0.1257	0.1258	41.27
2	0.1655	0.1653	0.1682	0.1663	54.78
3	0.2683	0.2671	0.2673	0.2676	88.52
4	0.4049	0.4037	0.4052	0.4046	134.20
5	0.2810	0.2830	0.2474	0.2705	89.49
6	0.0912	0.0913	0.0909	0.0911	29.71
7	0.0137	0.0139	0.1340	0.0539	17.29
8	0.0281	0.0283	0.0286	0.0283	8.78
9	0.0500	0.0500	0.0494	0.0498	15.93
10	0.0470	0.0474	0.0472	0.0472	15.07
11	0.0763	0.0768	0.0724	0.0752	24.39
12	0.0869	0.0870	0.0869	0.0869	28.31
13	0.0453	0.0453	0.0455	0.0454	14.46
14	0.0441	0.0441	0.0441	0.0441	14.03
15	0.0530	0.0531	0.0520	0.0527	16.90
16	0.0466	0.0465	0.0466	0.0466	14.86
17	0.0355	0.0363	0.0361	0.0360	11.32
18	0.0488	0.0477	0.0474	0.0480	15.32
19	0.0464	0.0465	0.0465	0.0465	14.82
20	0.0392	0.0402	0.0402	0.0399	12.62
21	0.0402	0.0396	0.0402	0.0400	12.67

Nitrate – µg/L

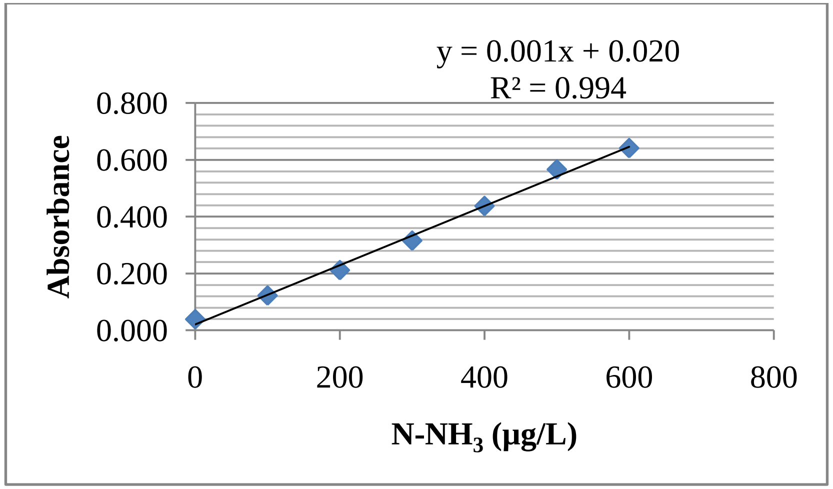
Calibration Curve					
N-NO$_3^-$ (µg/L)	A	B	C	Aver	x10
0	0.0264	0.0264	0.0262	0.0263	0.2633
50	0.1500	0.1494	0.1497	0.1497	1.4970
100	0.2686	0.2733	0.2716	0.2712	2.7117
300	0.6866	0.6969	0.6890	0.6908	6.9083
500	1.1595	1.1603	1.1409	1.1536	11.5357
800	1.8303	1.8165	1.8486	1.8318	18.3180



Samples								
Bottles	A	B	C	Aver	x10	Conc (µg/L)	NO2 (µg/L)	NO3- (µg/L)
1	0.3246	0.3094	0.3098	0.3146	3.1460	128.05	41.3	86.78
2	0.0975	0.0933	0.0927	0.0945	0.9450	28.00	54.8	-26.78
3	0.1742	0.1725	0.1760	0.1742	1.7423	64.24	88.5	-24.28
4	0.2820	0.2869	0.2856	0.2848	2.8483	114.52	134.2	-19.68
5	0.2876	0.2886	0.2894	0.2885	2.8853	116.20	89.5	26.71
6	0.2645	0.2682	0.2659	0.2662	2.6620	106.05	29.7	76.33
7	0.2625	0.2581	0.2630	0.2612	2.6120	103.77	17.3	86.48
8	0.2782	0.2740	0.2805	0.2776	2.7757	111.21	8.8	102.43
9	0.2755	0.2798	0.2810	0.2788	2.7877	111.76	15.9	95.82
10	0.2964	0.2993	0.3002	0.2986	2.9863	120.79	15.1	105.72
11	0.2758	0.2738	0.2739	0.2745	2.7450	109.82	24.4	85.43
12	0.2693	0.2704	0.2719	0.2705	2.7053	108.02	28.3	79.70
13	0.2552	0.2542	0.2568	0.2554	2.5540	101.14	14.5	86.68
14	0.2352	0.2373	0.2358	0.2361	2.3610	92.36	14.0	78.33
15	0.2474	0.2417	0.2426	0.2439	2.4390	95.91	16.9	79.01
16	0.2534	0.2529	0.2520	0.2528	2.5277	99.94	14.9	85.08
17	0.2346	0.2360	0.2396	0.2367	2.3673	92.65	11.3	81.33
18	0.2410	0.2435	0.2424	0.2423	2.4230	95.18	15.3	79.86
19	0.2511	0.2493	0.2511	0.2505	2.5050	98.91	14.8	84.09
20	0.2509	0.2502	0.2484	0.2498	2.4983	98.61	12.6	85.98
21	0.2418	0.2448	0.2428	0.2431	2.4313	95.56	12.7	82.89

Ammoniacal Nitrogen

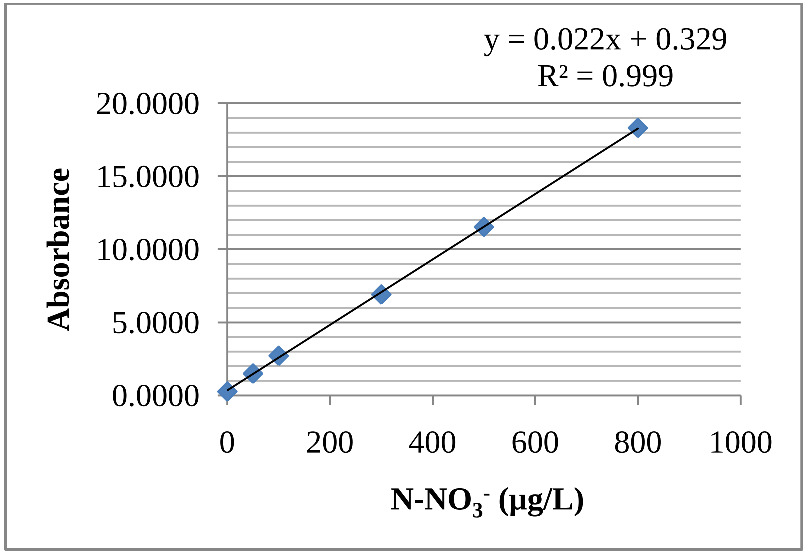
Calibration Curve				
N-NH_3 (µg/L)	A	B	C	Aver
0	0.0341	0.0387	0.0430	0.0386
100	0.1364	0.1086	0.1216	0.1222
200	0.2050	0.2137	0.2159	0.2115
300	0.3179	0.3218	0.3066	0.3154
400	0.4489	0.4254	0.4380	0.4374
500	0.5615	0.5753	0.5616	0.5661
600	0.6595	0.6183	0.6458	0.6412



Samples						
Bottles	A	B	C	Aver	Conc (µg/L)	Conc (mg/L)
1	0.0481	0.0443	0.0507	0.0477	27.70	0.0277
2	0.1929	0.1836	0.1919	0.1895	169.47	0.1695
3	0.1271	0.1298	0.1333	0.1301	110.07	0.1101
4	0.2803	0.2135	0.2725	0.2554	235.43	0.2354
5	0.1249	0.1302	0.1129	0.1227	102.67	0.1027
6	0.0529	0.0470	0.0471	0.0490	29.00	0.0290
7	0.0463	0.0474	0.0458	0.0465	26.50	0.0265
8	0.0417	0.0435	0.0452	0.0435	23.47	0.0235
9	0.0444	0.0430	0.0441	0.0438	23.83	0.0238
10	0.0594	0.0551	0.0437	0.0527	32.73	0.0327
11	0.0405	0.0468	0.0463	0.0445	24.53	0.0245
12	0.0433	0.0458	0.0430	0.0440	24.03	0.0240
13	0.1180	0.1206	0.1208	0.1198	99.80	0.0998
14	0.0625	0.0621	0.0643	0.0630	42.97	0.0430
15	0.1648	0.1567	0.1515	0.1577	137.67	0.1377
16	0.1111	0.1085	0.0969	0.1055	85.50	0.0855
17	0.0669	0.0703	0.0616	0.0663	46.27	0.0463
18	0.0818	0.0808	0.0789	0.0805	60.50	0.0605
19	0.0752	0.0732	0.0680	0.0721	52.13	0.0521
20	0.0725	0.0756	0.0715	0.0732	53.20	0.0532
21	0.0136	0.1345	0.1382	0.0954	75.42	0.0754

Total Nitrogen – mg/L

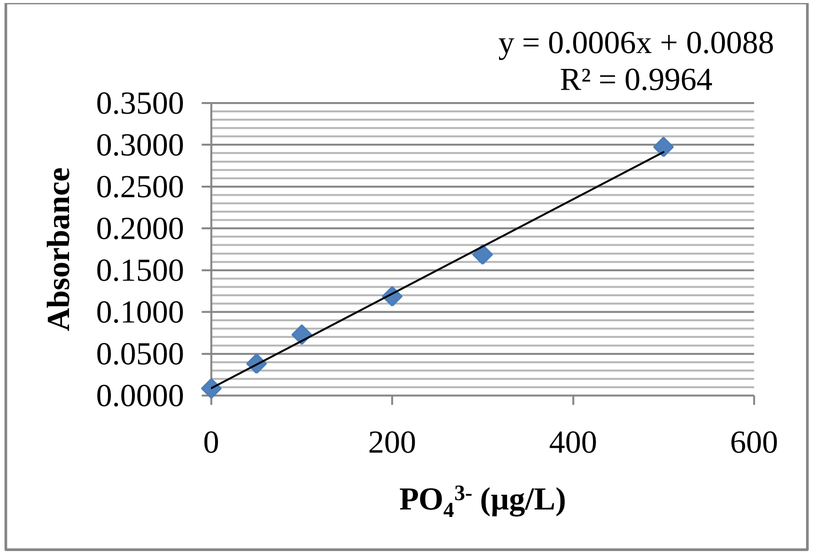
Calibration Curve					
N-NO_3^- (µg/L)	A	B	C	Aver	x10
0	0.0264	0.0264	0.0262	0.0263	0.2633
50	0.1500	0.1494	0.1497	0.1497	1.4970
100	0.2686	0.2733	0.2716	0.2712	2.7117
300	0.6866	0.6969	0.6890	0.6908	6.9083
500	1.1595	1.1603	1.1409	1.1536	11.5357
800	1.8303	1.8165	1.8486	1.8318	18.3180



Samples								
Bottles	A	B	C	Aver	Aver-Blank	x10	Conc (µg/L)	Conc (mg/L)
B	0.6857	0.6932	0.6853	0.6881	0.0000	0.0000		
1	1.0677	1.0741	1.0691	1.0703	0.3822	3.8223	158.79	0.16
2	1.1542	1.1453	1.1566	1.1520	0.4640	4.6397	195.94	0.20
3	1.1173	1.1124	1.1329	1.1209	0.4328	4.3280	181.77	0.18
4	1.2776	1.2877	1.2981	1.2878	0.5997	5.9973	257.65	0.26
5	1.2102	1.2059	1.2283	1.2148	0.5267	5.2673	224.47	0.22
6	1.1194	1.1272	1.1315	1.1260	0.4380	4.3797	184.12	0.18
7	1.0172	1.0354	1.3960	1.1495	0.4615	4.6147	194.80	0.19
8	1.0603	1.0591	1.0779	1.0658	0.3777	3.7770	156.73	0.16
9	1.0354	1.0320	1.0389	1.0354	0.3474	3.4737	142.94	0.14
10	0.9944	0.9919	0.9967	0.9943	0.3063	3.0627	124.26	0.12
11	0.9745	0.9716	0.9636	0.9699	0.2818	2.8183	113.15	0.11
12	0.9318	0.9353	0.9468	0.9380	0.2499	2.4990	98.64	0.10
13	1.0343	1.0325	1.0483	1.0384	0.3503	3.5030	144.27	0.14
14	0.9515	0.9202	0.9535	0.9417	0.2537	2.5367	100.35	0.10
15	1.0262	1.0273	1.0245	1.0260	0.3379	3.3793	138.65	0.14
16	0.9999	1.0051	0.9983	1.0011	0.3130	3.1303	127.33	0.13
17	0.9583	0.9755	0.9690	0.9676	0.2795	2.7953	112.11	0.11
18	0.9587	0.9573	0.9740	0.9633	0.2753	2.7527	110.17	0.11
19	0.9636	0.9545	0.9540	0.9574	0.2693	2.6930	107.45	0.11
20	0.9353	0.9408	0.9309	0.9357	0.2476	2.4760	97.59	0.10
21	0.9291	0.9291	0.9237	0.9273	0.2392	2.3923	93.79	0.09

Total Phosphorus – mg/L

Calibration Curve				
$PO^{4}{}_{3}^{-}$ (µg/L)	A	B	C	Aver
0	0.0084	0.0082	0.0137	0.0083
50	0.0371	0.0392	0.0376	0.0380
100	0.0729	0.0714	0.0736	0.0726
200	0.1187	0.1191	0.1176	0.1185
300	0.1692	0.1674	0.1691	0.1686
500	0.2999	0.2959	0.2961	0.2973



Samples						
Bottles	A	B	C	Aver	Conc (µg/L)	Conc (mg/L)
1	0.1074	0.1089	0.1215	0.1126	173.00	0.17
2	0.1610	0.1724	0.1683	0.1672	264.06	0.26
3	0.2864	0.2893	0.2885	0.2881	465.44	0.47
4	0.3035	0.3037	0.3022	0.3031	490.56	0.49
5	0.2981	0.2985	0.3105	0.3024	489.28	0.49
6	0.1859	0.1703	0.1919	0.1827	289.83	0.29
7	0.0842	0.0854	0.9480	0.3725	606.22	0.61
8	0.1089	0.1101	0.1082	0.1091	167.11	0.17
9	0.1061	0.1071	0.1082	0.1071	163.89	0.16
10	0.0695	0.0657	0.0619	0.0657	94.83	0.09
11	0.0688	0.0681	0.0673	0.0681	98.78	0.10
12	0.0463	0.0460	0.0458	0.0460	62.06	0.06
13	0.0974	0.0961	0.0992	0.0976	147.94	0.15
14	0.0658	0.0638	0.0632	0.0643	92.44	0.09
15	0.0992	0.0976	0.0962	0.0977	148.11	0.15
16	0.0769	0.0753	0.0746	0.0756	111.33	0.11
17	0.0818	0.0775	0.0795	0.0796	118.00	0.12
18	0.0513	0.0507	0.0599	0.0540	75.28	0.08
19	0.0446	0.0446	0.0479	0.0457	61.50	0.06
20	0.0638	0.0791	0.0669	0.0699	101.89	0.10
21	0.0366	0.0297	0.0314	0.0326	39.61	0.04

Solids – mg/L

Total Solids							
Bottle	Sample (mL)	P0 (g)	P1 (g)	TS	P2 (g)	FTS	VTS
1	50	44.3852	44.4044	384	44.3982	260	124
2	50	44.2346	44.2673	654	44.2592	492	162
3	50	42.9935	43.0485	1100	43.0386	902	198
4	50	48.3757	48.4410	1306	48.4274	1034	272
5	50	52.4897	52.5446	1098	52.5327	860	238
6	50	38.0308	38.0669	722	38.0582	548	174
7	50	37.0760	37.0970	420	37.0902	284	136
8	50	47.0286	47.0519	466	47.0449	326	140
9	50	44.7893	44.8105	424	44.8041	296	128
10	50	49.1112	49.1264	304	49.1205	186	118
11	50	47.6978	47.7123	290	47.7063	170	120
12	50	37.3169	37.3293	248	37.3240	142	106
13	50	47.4968	47.5124	312	47.5066	196	116
14	50	41.3544	41.3678	268	41.3634	180	88
15	50	39.0290	39.0475	370	39.0415	250	120
16	50	46.7510	46.7665	310	46.7605	190	120
17	50	44.1590	44.1758	336	44.1701	222	114
18	50	51.1215	51.1354	278	51.1298	166	112
19	50	53.8835	53.8955	240	53.8902	134	106
20	50	41.2001	41.2131	260	41.2077	152	108
21	50	52.0069	52.019	242	52.0132	126	116

Suspended Solids							
Bottles	Sample (mL)	P0 (g)	P1 (g)	SS	P2 (g)	FSS	VSS
1	150	27.8265	27.8562	198	27.8519	169	29
2	200	23.6003	23.6454	225	23.6377	187	38
3	200	27.8815	27.9710	448	27.9604	395	53
4	100	32.6156	32.7229	1073	32.708	924	149
5	100	31.1750	31.265	900	31.2553	803	97
6	100	32.1254	32.1767	513	32.1705	451	62
7	150	33.5030	33.5269	159	33.5228	132	27
8	100	28.4230	28.4475	245	28.4436	206	39
9	200	30.6647	30.6983	168	30.6933	143	25
10	200	26.8041	26.8207	83	26.8175	67	16
11	200	30.2740	30.2923	91	30.289	75	16
12	200	29.6820	29.6896	38	29.688	30	8
13	200	27.5286	27.5486	100	27.5446	80	20
14	200	26.9614	26.9766	76	26.9734	60	16
15	200	28.3633	28.3802	84	28.377	69	16
16	200	25.0653	25.0859	103	25.0824	85	17
17	200	27.1163	27.14	119	27.1354	96	23
18	190	31.3787	31.3904	62	31.3878	48	14
19	200	33.4179	33.425	35	33.4234	27	8
20	200	31.811	31.8195	42.5	31.8179	34.5	8
21	200	31.2537	31.2562	12.5	31.2553	8	4.5

Data of the tests performed to verify automatic sampler limitations

Alkalinity

IG 2A	ALKALINITY					
	Ambience Sample			Refrigerated Sample		
	CF	VC	Conc	CF	VC	Conc
29-Sep	10.50	7.50	78.75	-	-	-
30-Sep	10.50	7.50	78.75	10.50	7.20	75.60
01-Oct	10.10	6.60	66.66	10.10	6.60	66.66
02-Oct	10.55	7.00	73.85	10.55	7.00	73.85
03-Oct	10.20	6.50	66.30	10.20	6.50	66.30
04-Oct	-	-	-	10.25	6.80	69.70

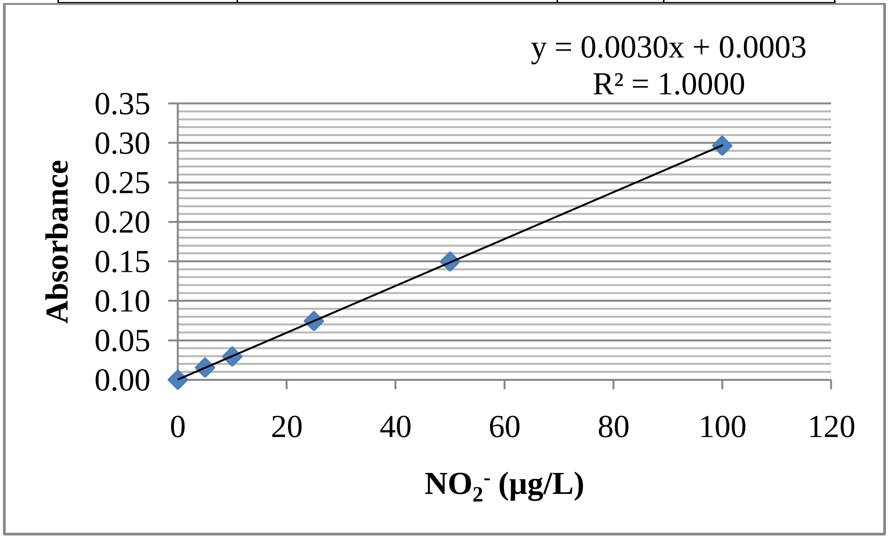
IG 2B	ALKALINITY					
	Ambience Sample			Refrigerated Sample		
	CF	VC	Conc	CF	VC	Conc
29-Sep	10.50	12.10	127.05	-	-	-
30-Sep	10.50	12.20	128.10	10.50	12.60	132.30
01-Oct	10.10	12.30	124.23	10.10	12.00	121.20
02-Oct	10.55	12.40	130.82	10.55	11.80	124.49
03-Oct	10.20	12.30	125.46	10.20	12.50	127.50
04-Oct	-	-	-	10.25	13.00	133.25

Where CF is correction factor and VC is volume consumed of reagents, both used in alkalinity analytical procedure

Nitrite

Calibration Curve					
NO_2^- (µg/L)	A	B	C	Aver	Aver-Blank
0	0,0012	0,0013	0,0012	0,0012	0,0000
5	0,059	0,0172	0,0161	0,0167	0,0154
10	0,0306	0,0304	0,0309	0,0306	0,0294
25	0,0741	0,0762	0,0763	0,0755	0,0743
50	0,1506	0,1504	0,1516	0,1509	0,1496
100	0,2974	0,2993	0,2958	0,2975	0,2963

Standard Proposed	A	B	C	Aver	Values Measured
30	0,0909	0,0918	0,093	0,0919	30,53
80	0,2411	0,2393	0,2396	0,2400	79,90



Ambient Sample		
Tuesday, Sep 29	IG2A	IG2B
	0,4001	0,6614
	0,4036	0,6550
	0,4027	0,6595
	0,4005	0,6633
	0,3999	0,6610
Aver	0,4014	0,6600
Aver-Blank	0,4001	0,6588
Conc	133,28	219,50

	Ambient Sample		Ambient Acidified Samples		Refrigerated Sample		Refrigerated Acidified Samples		Branco	P30	P80
Wednesday, Sep 30	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0005	0,0917	0,2465
	0,4349	1,1512	0,2092	0,2158	0,4152	0,6355	0,2378	0,2227	0,0005	0,0907	0,2439
	0,4381	1,1534	0,2097	0,2186	0,4053	0,6410	0,2373	0,2216	0,0011	0,0928	0,2448
	0,4374	1,1549	0,2109	0,2185	0,4139	0,6414	0,2363	0,2246			
	0,4050	1,1542	0,2131	0,2148	0,4137	0,6387	0,2366	0,2191			
	0,4353	1,1527	0,2107	0,2144	0,4137	0,6362	0,2363	0,2224			
Aver	0,4301	1,1533	0,2107	0,2164	0,4124	0,6386	0,2369	0,2221	0,0007	0,0917	0,2451
Aver-Blank	0,4294	1,1526	0,2100	0,2157	0,4117	0,6379	0,2362	0,2214	0,0000	0,0910	0,2444
Conc	143,05	384,09	69,91	71,81	137,12	212,52	78,62	73,69	0,00	30,24	81,36

	Ambient Sample		Ambient Acidified Samples		Refrigerated Sample		Refrigerated Acidified Samples		Branco	P30	P80
Thrusday, Oct 01	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0013	0,0935	0,2437
	0,5239	1,1886	0,2098	0,2522	0,4066	0,6973	0,2728	0,2400	0,0017	0,0927	0,2460
	0,5284	1,1710	0,2113	0,2509	0,4017	0,6959	0,2670	0,2400	0,0012	0,0922	0,2462
	0,5282	1,1727	0,2097	0,2522	0,4044	0,6903	0,2322	0,2383			
	0,5226	1,1727	0,2104	0,2504	0,4020	0,6963	0,2711	0,2440			
	0,5210	1,1719	0,2098	0,2412	0,4006	0,7045	0,2667	-			
Aver	0,5248	1,1754	0,2102	0,2494	0,4031	0,6969	0,2620	0,2406	0,0014	0,0928	0,2453
Aver-Blank	0,5234	1,1740	0,2088	0,2480	0,4017	0,6955	0,2606	0,2392	0	0,0914	0,2439
Conc	174,37	391,23	69,50	82,56	133,79	231,72	86,75	79,63	0,00	30,37	81,20

	Ambient Sample		Ambient Acidified Samples		Refrigerated Sample		Refrigerated Acidified Samples		Branco	P30	P80
Friday, Oct 02	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0011	0,0930	0,2480
	0,5729	0,9108	0,1915	0,2572	0,4005	0,7473	0,2510	0,2098	0,0010	0,0933	0,2455
	0,6644	0,9078	0,1934	0,2606	0,3975	0,7450	0,2526	0,2085	0,0011	0,0941	0,2421
	0,6655	0,9054	0,1946	0,2618	0,3971	0,7450	0,2523	0,2085			
	0,6641	0,9094	0,1962	0,2582	0,4001	0,7438	0,2538	0,2062			
	0,6606	0,9058	0,1949		0,3962	0,7433	0,2529	0,2079			
Aver	0,6455	0,9078	0,1941	0,2595	0,3983	0,7449	0,2525	0,2082	0,0011	0,0935	0,2452
Aver-Blank	0,6444	0,9068	0,1931	0,2584	0,3972	0,7438	0,2515	0,2071	0,0000	0,0924	0,2441
Conc	214,71	302,16	64,25	86,03	132,30	247,84	83,72	68,94	0,00	30,70	81,28

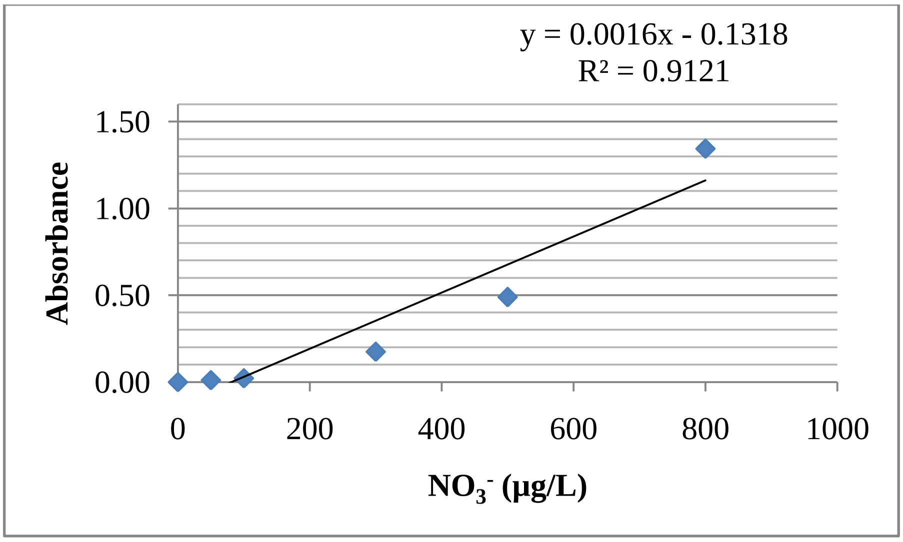
	Ambient Sample		Ambient Acidified Samples		Refrigerated Sample		Refrigerated Acidified Samples		Branco	P30	P80
Saturday, Oct 03	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0045	0,0924	0,2388
	1,0437	0,5905	0,1760	0,1703	0,4036	0,7433	0,2460	0,2162	0,0016	0,0914	0,2378
	1,0454	0,5958	0,1771	0,1724	0,4053	0,7373	0,2465	0,2173	0,0009	0,093	0,2412
	1,0454	0,5952	0,1781	0,1720	0,4053	0,7456	0,2454	0,2166			
	1,0560	0,5903	0,1770	0,1687		0,7371	0,2472	0,2170			
			0,1731	0,1725		0,5957	0,2451				
Aver	1,0476	0,5930	0,1763	0,1712	0,4047	0,7408	0,2460	0,2168	0,0013	0,0923	0,2393
Aver-Blank	1,0464	0,5917	0,1750	0,1699	0,4035	0,7396	0,2448	0,2155	0,0000	0,0910	0,2380
Conc	348,69	197,13	58,24	56,54	134,39	246,43	81,50	71,74	0,00	30,24	79,24

	Ambient Acidified Samples		Refrigerated Sample		Refrigerated Acidified Samples		Branco	P30	P80
Sunday, Oct 04	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0016	0,0912	0,2415
	0,1531	0,2611	0,3975	0,7323	0,2333	0,2649	0,0004	0,0902	0,2444
	0,1544	0,2594	0,3933	0,7391	0,2343	0,2637	0,0004	0,0909	0,2454
	0,1525	0,2579	0,3959	0,7350	0,2343	0,2627			
	0,1516	0,2623	0,3645	0,7383	0,2316	0,2614			
	0,1515	0,2596		0,7404	0,2339	0,2640			
Aver	0,1526	0,2601	0,3878	0,7370	0,2335	0,2633	0,0008	0,0908	0,2438
Aver-Blank	0,1518	0,2593	0,3870	0,7362	0,2327	0,2625	0,0000	0,0900	0,2430
Conc	50,51	86,32	128,90	245,31	77,46	87,41	0,00	29,89	80,89

Nitrate

Calibration Curve					
NO_3^-	A	B	C	Aver	Aver-Blank
0	0,0042	0,0028	0,0032	0,0030	0,0000
50	0,0139	0,0128	0,0115	0,0134	0,0104
100	0,0284	0,0256	0,0222	0,0254	0,0224
300	0,1827	0,1794	0,1704	0,1775	0,1745
500	0,4923	0,4951	0,4891	0,4922	0,4892
800	1,3003	1,3596	1,3822	1,3474	1,3444

Standard Proposed	A	B	C	Aver	Aver-Blank	Values Measured
150	0,0599	0,0552	0,0513	0,0555	0,0525	115,17
650	0,894	0,9436	0,9545	0,9307	0,9277	662,19



	Ambient Sample	
	IG2A	IG2B
Tuesday, Sep 29	0,0676	0,1178
	0,0586	0,1234
	0,0618	0,1193
	0,0931	0,1609
	0,0889	0,1545
	0,0819	0,1444
Aver	0,0753	0,1367
Aver-Blank	0,0723	0,1337
Conc	127,57	165,95

	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P150	P650
Wednesday, Sep 30	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0244	0,3783	1,5222
	0,2667	0,2935	0,2454	0,2363	0,2804	0,2507	0,2264	0,2401	0,0273	0,3949	1,5087
	0,2631	0,2806	0,2433	0,2325	0,2789	0,2555	0,2296	0,2378	0,0265	0,3895	1,5018
	0,2681	0,2775	0,2400	0,2306	0,2791	0,2587	0,2238	0,2339			
Aver	0,2660	0,2839	0,2429	0,2331	0,2795	0,2550	0,2266	0,2373	0,0261	0,3876	1,5109
Aver-Blank	0,2399	0,2578	0,2168	0,2071	0,2534	0,2289	0,2005	0,2112	0,0000	0,3615	1,4848
Conc	232,31	243,50	217,90	211,79	240,75	225,44	207,71	214,38		308,31	1010,40

	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P150	P650
Thursday, Oct 01	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0302	0,3822	1,5348
	0,2764	0,4768	0,2726	0,2271	0,2548	0,0302	0,2299	0,2410	0,032	0,3893	1,5420
	0,2529	0,4734	0,2524	0,2323	0,2576	0,0315	0,2314	0,2322	0,0306	0,395	1,5365
	0,2739	0,4768	0,2385	0,2422	0,2588	0,0302	0,2321	0,2311			
Aver	0,2677	0,4757	0,2545	0,2339	0,2571	0,0306	0,2311	0,2348	0,0309	0,3888	1,5378
Aver-Blank	0,2368	0,4447	0,2236	0,2029	0,2261	-0,0003	0,2002	0,2038	0,0000	0,3579	1,5068
Conc	230,38	360,33	222,10	209,21	223,71	82,19	207,50	209,77		306,06	1024,15

	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P150	P650
Friday, Oct 02	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0292	0,3871	1,5531
	0,2943	0,1175	0,0953	0,2172	0,2549	0,3062	0,1238	0,2380	0,0254	0,3910	1,5686
	0,3002	0,1187	0,0850	0,2235	0,2538	0,3077	0,1228	0,2411	0,0262	0,3899	1,5311
	0,3116	0,1158		0,2227	0,2474	0,3079	0,1093	0,2432			
Aver	0,3020	0,1173	0,0902	0,2211	0,2520	0,3073	0,1186	0,2408	0,0269	0,3893	1,5509
Aver-Blank	0,2751	0,0904	0,0632	0,1942	0,2251	0,2803	0,0917	0,2138	0,0000	0,3624	1,5240
Conc	254,31	138,88	121,89	203,75	223,06	257,58	139,69	216,02		308,9	1034,9

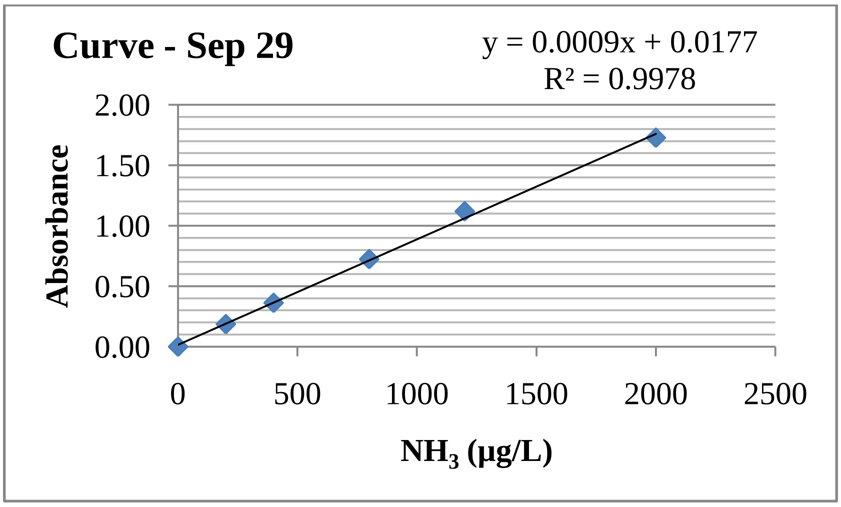
	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P150	P650
Saturday, Oct 03	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0425	0,3757	1,4559
	0,3751	0,0859	0,2036	0,2128	0,2455	0,2847	0,1997	0,2178	0,0442	0,3898	1,476
	0,3591	0,0878	0,2007	0,2087	0,2452	0,2828	0,1992	0,2151	0,043	0,391	1,4808
	0,3484	0,0895	0,2000	0,2092	0,2489	0,2805	0,1962	0,2148			
Aver	0,3609	0,0877	0,2014	0,2102	0,2465	0,2827	0,1984	0,2159	0,0432	0,3855	1,4709
Aver-Blank	0,3176	0,0445	0,1582	0,1670	0,2033	0,2394	0,1551	0,1727	0,0000	0,3423	1,4277
Conc	280,90	110,19	181,25	186,75	209,44	232,02	179,33	190,29		296,29	974,67

	Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco
Sunday, Oct 04	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0270
	0,1816	0,2258	0,2147	0,2426	0,1173	0,1860	0,0262
	0,1769	0,2185	0,2198	0,2493	0,1057	0,1859	0,0248
	0,1639	0,2124	0,2206	0,2515	0,0935	0,1759	
Aver	0,1741	0,2189	0,2184	0,2478	0,1055	0,1826	
Aver-Blank	0,1481	0,1929	0,1924	0,2218	0,0795	0,1566	0,0260
Conc	174,96	202,94	202,60	221,00	132,06	180,25	0,0000

Ammoniacal Nitrogen

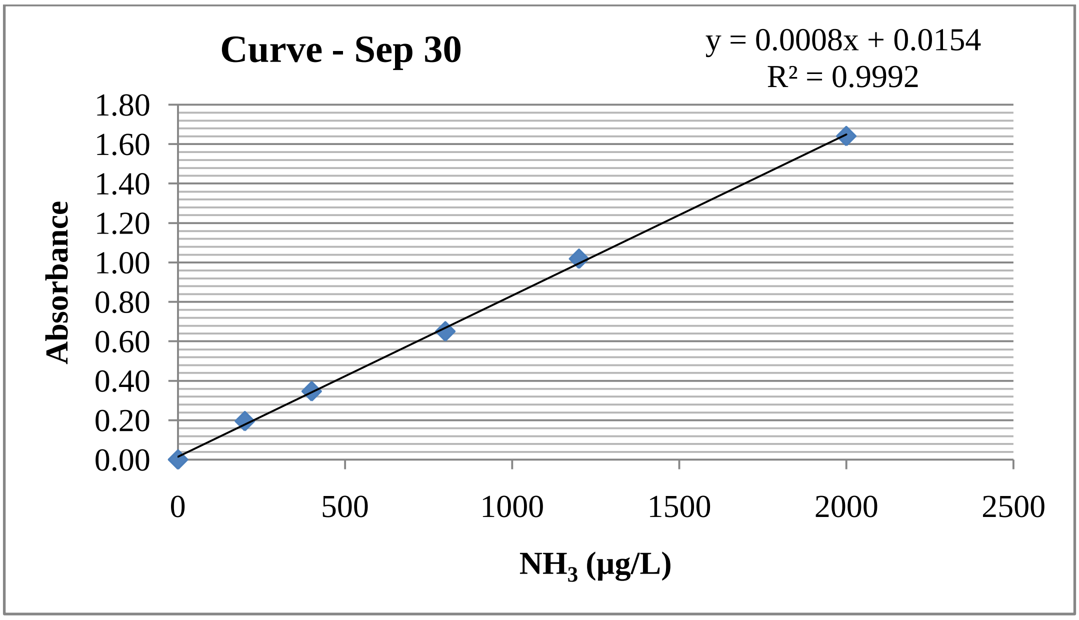
Calibration Curve					
NH_3 (µg/L)	A	B	C	Aver	Aver-Blank
0	0,0112	0,0088	0,0104	0,0101	0,0000
200	0,2115	0,2097	0,1672	0,1961	0,1860
400	0,3602	0,3531	0,4028	0,3720	0,3619
800	0,6887	0,7709	0,7397	0,7331	0,7230
1200	1,1124	1,1742	1,0983	1,1283	1,1182
2000	1,5928	1,7931	1,8234	1,7364	1,7263

Standard Proposed	A	B	C	Aver	Aver-Blank	Values Measured
300	0,3387	0,3373	0,3257	0,3339	0,3238	340,07
1500	1,3335	1,4384	1,1926	1,3215	1,3114	1437,41



	Ambient Sample		
	IG2A	IG2B - diluted 2x	IG2B
Tuesday, Sep 29	1,3966	2,9138	5,8276
	1,6300	2,8721	5,7442
	1,5867	2,7668	5,5336
	1,4823	2,9597	5,9194
	1,3846		
Aver	1,4960		5,7562
Aver-Blank	1,4859		5,7461
Conc	1631,34		6364,85

Calibration Curve					
NH_3 (µg/L)	A	B	C	Aver	Aver-Blank
0	0,0321	0,0286	0,0286	0,0298	0,0000
200	0,2084	0,2572	0,2079	0,2245	0,1947
400	0,3993	0,3712	0,3569	0,3758	0,3460
800	0,6692	0,6472	0,7233	0,6799	0,6501
1200	1,056	1,0812	1,0062	1,0478	1,0180
2000	1,6416	1,6558	1,7125	1,6700	1,6402



	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		P300	P1500
Wednesday, Sep 30	IG2A	IG2B - 5x	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,2699	1,3123
	1,2560	7,8335	1,0078	9,2995	1,3822	8,8850	1,0200	8,9655	0,3583	1,3335
	1,2068	7,2060	0,9390	7,6825	1,5138	8,8230	0,8604	8,9990	0,2842	1,2145
	1,2815	6,8165	0,8871	8,9165	1,2266	8,0280	1,0343	9,1700		
	1,2391	6,6450	0,8724	7,5775	1,2578	8,6180	0,9054	8,2670		
	1,0709	6,9435	0,7676	9,0485	1,0513	7,1340	1,0325	9,7015		
Aver	1,2109	7,0889	0,8948	8,5049	1,2863	8,2976	0,9705	9,0206	0,3041	1,2868
Aver-Blank	1,1811	7,0591	0,8650	8,4751	1,2566	8,2678	0,9408	8,9908	0,2744	1,2570
Conc	1457,12	8804,67	1062,02	10574,67	1551,47	10315,54	1156,69	11219,29	323,71	1552,00

	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P300	P1500
Thursday, Oct 01	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0337	0,2803	1,6534
	1,5293	6,1330	1,0162	6,6390	1,6805	6,8855	0,9440	7,2205	0,0222	0,3444	1,5725
	1,5365	6,3230	0,8623	6,9110	1,5206	6,7090	0,9716	8,2435	0,0206	0,3588	1,6034
	1,3108	7,1770	0,9535	8,2790	1,5070	6,0040	0,9805	6,6225			
	1,6208	5,8950	0,9255	8,2320	1,6534	5,6325	0,9579	6,8415			
	1,5104	5,6435	0,8888	6,3485	1,4681	6,1060	0,9403	8,3250			
Aver	1,5016	6,2343	0,9293	7,2819	1,5659	6,2674	0,9589	7,4506	0,0255	0,3278	1,6098
Aver-Blank	1,4761	6,2088	0,9038	7,2564	1,5404	6,2419	0,9334	7,4251	0,0000	0,3023	1,5843
Conc	1825,83	7741,75	1110,45	9051,25	1906,28	7783,13	1147,45	9262,13	0,00	358,67	1961,08

	Ambient Sample	Ambient Acidified Sample	Refrigerated Sample	Refrigerated Acidified Sample	Blank	P300	P1500
Friday, Oct 02	IG2A	IG2A	IG2A	IG2A	0,0219	0,3539	1,5383
	1,0956	0,9719	1,4470	0,9846	0,0200	0,3656	1,6370
	1,2484	0,9423	1,2744	0,8940	0,0197	0,3679	1,5928
	1,2338	0,8940	1,3132	0,9730			
	1,2474	0,8943	1,3669	1,0046			
	1,1877	1,0112	1,4745	0,9497			
Aver	1,2026	0,9427	1,3752	0,9612	0,0205	0,3625	1,5894
Aver-Blank	1,1820	0,9222	1,3547	0,9406	0,0000	0,3419	1,5688
Conc	1458,31	1133,51	1674,08	1156,56	0,00	408,17	1941,79

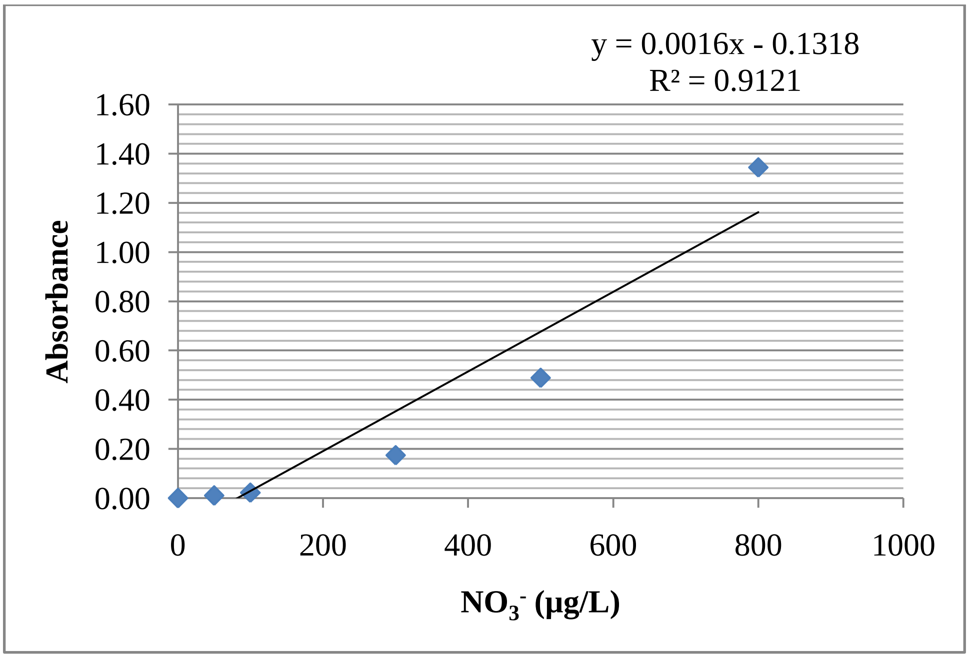
	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P300	P1500
Saturday, Oct 03	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0269	0,3533	1,6056
	1,0767	7,4595	0,9835	7,8230	1,3669	7,7470	0,9207	7,8930	0,0277	0,3535	1,6300
	1,2776	7,6740	1,3335	9,5220	1,3441	6,3485	1,0580	8,9970	0,0306	0,3354	1,6233
	1,3170	6,9765	1,1416	7,9640	1,5970	6,8920	0,9719	9,1875			
	1,3633	7,7190	1,0697	8,9330	1,3145	6,6620	1,0297	7,8625			
	1,2726	7,7850	0,9856	8,0935	1,5420	6,1550	1,1173	9,2995			
Aver	1,2614	7,5228	1,1028	8,4671	1,4329	6,7609	1,0195	8,6479	0,0284	0,3474	1,6196
Aver-Blank	1,2330	7,4944	1,0744	8,4387	1,4045	6,7325	0,9911	8,6195	0,0000	0,3190	1,5912
Conc	1522,05	9348,75	1323,73	10529,13	1736,38	8396,38	1219,65	10755,13		379,50	1969,79

	Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P300	P1500
Sunday, Oct 04	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0186	0,2977	1,8027
	0,7595	5,7265	1,2310	6,4025	0,9215	6,2465	0,0146	0,3323	1,7739
	0,8477	5,8480	1,1649	6,4130	0,8356	6,5880	0,0155	0,3312	1,7407
	0,9418	5,5420	1,1512	6,0805	0,9446	6,1150			
	1,0206	5,4540	1,1483	6,9630	0,8888	6,1110			
	0,9468	6,4330	1,3267	7,3875	0,8132	8,3400			
Aver	0,9033	5,8007	1,2044	6,6493	0,8807	6,6801	0,0162	0,3204	1,7724
Aver-Blank	0,8870	5,7845	1,1882	6,6331	0,8645	6,6639	0,0000	0,3042	1,7562
Conc	1089,56	7211,33	1465,98	8272,08	1061,38	8310,58	0,00	360,96	2176,00

Total Nitrogen

Calibration Curve					
NO_3^- (µg/L)	A	B	C	Aver	Aver-Blank
0	0,0042	0,0028	0,0032	0,0030	0,0000
50	0,0139	0,0128	0,0115	0,0134	0,0104
100	0,0284	0,0256	0,0222	0,0254	0,0224
300	0,1827	0,1794	0,1704	0,1775	0,1745
500	0,4923	0,4951	0,4891	0,4922	0,4892
800	1,3003	1,3596	1,3822	1,3474	1,3444

Standard Proposed	A	B	C	Aver	Aver-Blank	Values Measured
150	0,1136	0,125	0,1113	0,1166	0,1136	235,11
750	0,2858	0,302		0,2939	0,2909	826,00



	Ambient Sample	
Tuesday, Sep 29	IG2A	IG2B
	1,8918	2,6128
	1,8486	2,6351
	1,8450	2,6128
	1,7931	2,6128
	1,7898	2,6128
	1,7994	2,6128
Aver	1,8280	2,6165
Conc	1224,84	1717,70

	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample	
Wednesday, Sep 30	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B
	1,5551	2,4982	0,2163	0,6606	1,6300	2,6351	0,4269	0,5643
	1,5846	2,4982	0,1913	0,5865	1,6393	2,6351	0,4143	0,5398
	1,5258	2,5151	0,1747	0,5231	1,6464	2,5710	0,3927	0,4939
Aver	1,5552	2,5038	0,1941	0,5901	1,6386	2,6137	0,4113	0,5327
Conc	1054,35	1647,27	203,69	451,17	1106,48	1715,96	339,44	415,29

	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample	
Thursday, Oct 01	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B
	1,6781	2,5151	0,1329	0,4296	1,4576	2,6587	0,1223	0,2555
	1,7153	2,5151	0,1090	0,3408	1,4240	2,6587	0,1041	0,2366
	1,7017	2,5331	0,0883	0,2899	1,4115	2,6833	0,0919	0,2059
Aver	1,6984	2,5211	0,1101	0,3534	1,4310	2,6669	0,1061	0,2327
Conc	1143,85	1658,06	151,17	303,27	976,77	1749,19	148,69	227,79

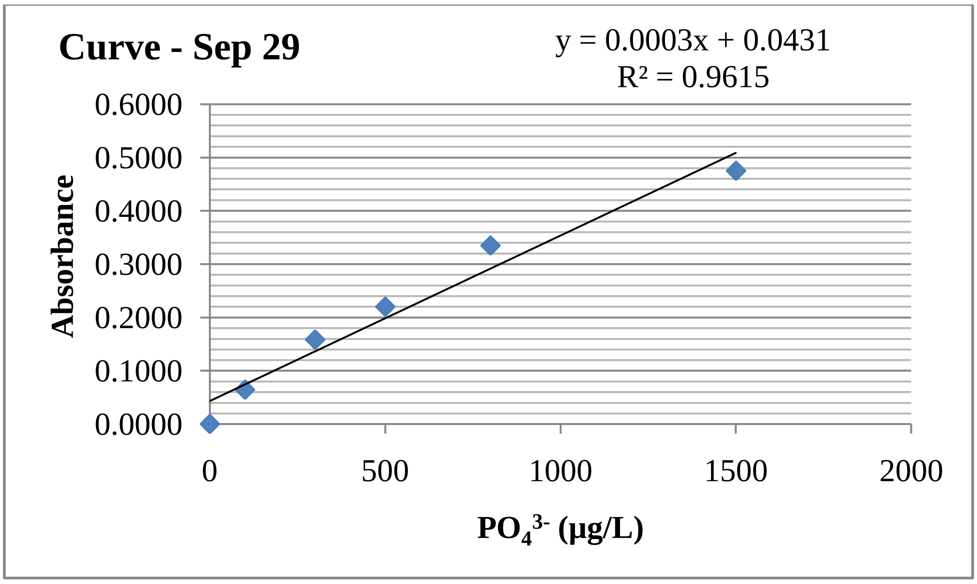
	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample	
Friday, Oct 02	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B
	1,2646	1,7350	0,2041	0,4874	1,4310	1,8961	0,1918	0,3541
	1,2836	1,7646	0,1666	0,4115	1,4226	1,8677	0,1716	0,3287
	1,2887	1,7495	0,1332	0,3528	1,4073	1,9001	0,1504	0,2911
Aver	1,2862	1,7497	0,1680	0,4172	1,4203	1,8880	0,1713	0,3246
Conc	886,22	1175,94	187,35	343,15	970,06	1262,35	189,42	285,27

	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample	
Saturday, Oct 03	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B
	1,6606	1,9044	0,1091	0,7552	1,5494	1,8961	0,1292	0,6940
	1,6255	1,9001	0,0939	0,7368	1,5970	1,9175	0,1039	0,6338
	1,6187	1,8918	0,0806	0,7246	1,6143	1,8677	0,0867	0,5940
Aver	1,6349	1,8988	0,0945	0,7389	1,5869	1,8938	0,1066	0,6406
Conc	1104,21	1269,10	141,46	544,17	1074,19	1265,98	149,00	482,75

Total Phosphorus

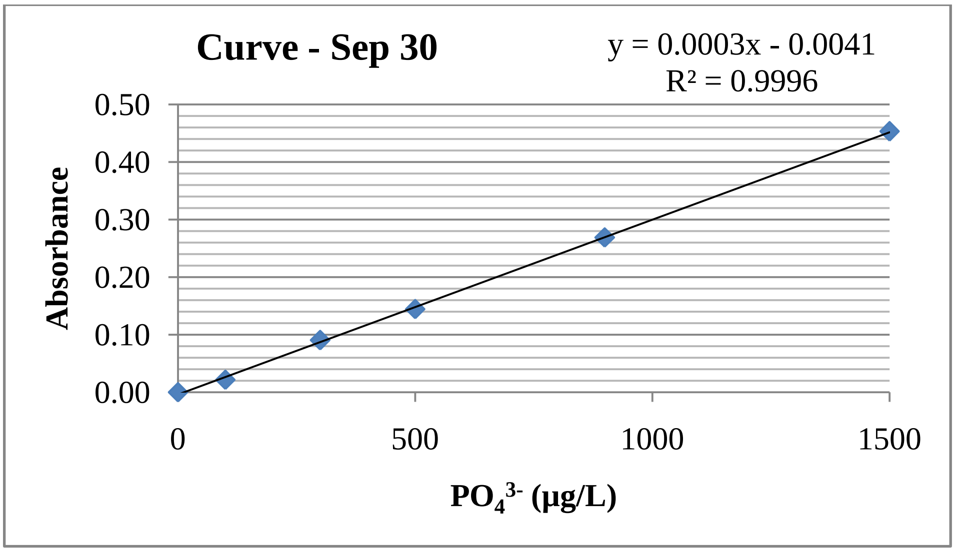
Calibration Curve					
PO_4^{3-} (µg/L)	A	B	C	Aver	Aver-Blank
0	0,0121	0,0172	0,0242	0,0178	0,0000
100	0,0763	0,0880	*	0,0822	0,0643
300	0,1616	0,1805	0,1864	0,1762	0,1583
500	0,2181	0,2836	0,212	0,2379	0,2201
800	0,3285	0,3856	0,344	0,3527	0,3349
1500	0,5146	0,4531	0,5112	0,4930	0,4751

Standard Proposed	A	B	C	Aver	Aver-Blank	Values Measured
150	0,1136	0,125	0,1113	0,1166	0,0988	185,67
750	0,2858	0,302		0,2939	0,2761	776,56



	Ambient Sample	
Tuesday, Sep 29	IG2A	IG2B
	0,1223	0,2402
	0,1221	0,2445
	0,1108	0,2388
	0,1310	0,2313
		0,2284
Aver	0,1216	0,2366
Aver-Blank	0,1037	0,2188
Conc	202,06	585,69

Calibration Curve					
PO_4^{3-} (μg/L)	A	B	C	Aver	Aver-Blank
0	0,0055	0,0054	0,0129	0,0079	0,0000
100	0,0293	0,0302	0,0300	0,0298	0,0219
300	0,1017	0,0940	0,0991	0,0983	0,0903
500	0,1490	0,1559	0,3145	0,1525	0,1445
900	0,2709	0,2795	0,2800	0,2768	0,2689
1500	0,4502	0,4680	0,4651	0,4611	0,4532



	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P150	P750
Wednesday. Sep 30	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0055	0,0437	0,2273
	0,0599	0,1918	0,0787	0,3085	0,0553	0,2777	0,0768	0,2964	0,0054	0,056	0,2354
	0,0703	0,1899	0,0787	0,2992	0,0459	0,2604	0,0845	0,2941	0,0129	0,0564	0,1709
	0,0665	0,1179	0,0630	0,3158	0,0443	0,2610	0,0837	0,2913			
	0,0575	0,2196	0,0804	0,2990	0,0497	0,2527	0,0759	0,2944			
	0,0610	0,1613	0,1381	0,2601	0,0413	0,2182	0,0443	0,2913			
Aver	0,0630	0,1761	0,0752	0,3056	0,0473	0,2540	0,0802	0,2935	0,0079	0,0520	0,2314
Aver-Blank	0,0551	0,1682	0,0673	0,2977	0,0394	0,2461	0,0723	0,2856	0,0000	0,0441	0,2234
Conc	197,36	574,22	237,89	1005,97	144,89	833,89	254,64	965,56		160,67	758,39

	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P150	P750
Thursday, Oct 01	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,005	0,0543	0,2332
	0,0542	0,1859	0,0847	0,2943	0,0509	0,2655	0,0804	0,3065	0,0035	0,0492	0,2411
	0,0441	0,1825	0,0808	0,3009	0,0496	0,2645	0,0790	0,3285	0,0046	0,0475	0,2324
	0,0513	0,1907	0,0870	0,2897	0,0544	0,2640	0,0885	0,2971			
	0,0472	0,1886	0,0862	0,2950	0,0532	0,2537	0,0826	0,2985			
	0,0535	0,1868	0,0719	0,2994	0,0518	0,2587	0,0837	0,2977			
Aver	0,0501	0,1869	0,0821	0,2959	0,0520	0,2613	0,0828	0,3057	0,0044	0,0503	0,2356
Aver-Blank	0,0457	0,1825	0,0778	0,2915	0,0476	0,2569	0,0785	0,3013	0,0000	0,0460	0,2312
Conc	165,98	622,11	272,84	985,31	172,38	870,04	275,24	1017,98		166,89	784,33

	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P150	P750
Friday, Oct 02	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0076	0,0518	0,2280
	0,0479	0,2025	0,0782	0,3008	0,0690	0,2013	0,0585	0,2761	0,0062	0,0522	0,2323
	0,0687	0,1965	0,0862	0,2942	0,0686	0,2107	0,0847	0,2697	0,0056	0,0515	0,2213
	0,0687	0,2173	0,0721	0,2861	0,0630	0,1998	0,0898	0,2775			
	0,0723	0,2019	0,1035	0,2949	0,0826	0,2085	0,0753	0,2625			
	0,0675	0,1926	0,1694	0,2949	0,0868	0,2001	0,0712	0,2793			
Aver	0,0693	0,2022	0,0850	0,2942	0,0740	0,2041	0,0803	0,2730	0,0065	0,0518	0,2272
Aver-Blank	0,0628	0,1957	0,0785	0,2877	0,0675	0,1976	0,0738	0,2666	0,0000	0,0454	0,2207
Conc	223,11	665,98	275,44	972,71	238,78	672,38	259,61	902,18		164,89	749,44

	Ambient Sample		Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P150	P750
Saturday, Oct 03	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,009	0,0564	0,2335
	0,0577	0,1906	0,0695	0,2968	0,0599	0,2072	0,0718	0,2844	0,0205	0,0569	0,2432
	0,0518	0,1876	0,0740	0,2897	0,0668	0,2065	0,0769	0,2792	0,0121	0,0562	0,2332
	0,0510	0,1921	0,0737	0,3042	0,0647	0,2025	0,0767	0,2841			
	0,0515	0,1963	0,0690	0,3066	0,0640	0,1985	0,0765	0,2786			
	0,0540	0,1893	0,0709	0,2939	0,0636	0,1992		0,2820			
Aver	0,0532	0,1912	0,0714	0,2982	0,0638	0,2028	0,0755	0,2817	0,0139	0,0565	0,2366
Aver-Blank	0,0393	0,1773	0,0576	0,2844	0,0499	0,1889	0,0616	0,2678	0,0000	0,0426	0,2228
Conc	144,78	604,71	205,51	961,56	180,11	643,38	219,03	906,31		155,78	756,22

	Ambient Acidified Sample		Refrigerated Sample		Refrigerated Acidified Sample		Branco	P150	P750
Sunday, Oct 04	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,0085	0,0479	0,2251
	0,0797	0,2200	0,0424	0,2380	0,0568	0,2778	0,0125	0,0466	0,2328
	0,0789	0,2294	0,0430	0,2579	0,0608	0,2664			
	0,0818	0,2047	0,0430	0,2251	0,0590	0,2789			
	0,0775	0,2284	0,0452	0,2294	0,0560	0,2717			
	0,0776	0,2122	0,0471	0,2302	0,0558	0,2745			
Aver	0,0791	0,2189	0,0441	0,2361	0,0577	0,2739	0,0105	0,0473	0,2290
Aver-Blank	0,0686	0,2084	0,0336	0,2256	0,0472	0,2634	0,0000	0,0368	0,2185
Conc	242,33	708,47	125,80	765,73	170,93	891,53		136,17	741,83

Dissolved Organic Carbon - DOC

Tuesday, September 29												
	TC		IC		DOC			TC		IC		DOC
IG2A	Area	Conc	Area	Conc	5,51		IG2B	Area	Conc	Area	Conc	4,21
	51,83	16,62	25,2	11,2				64,35	20,6	36,86	16,39	
	51,87	16,63	24,86	11,05				63,33	20,31	35,74	15,89	
	51,37	16,47	24,63	10,95				62,37	20	36,01	16,01	
Average	51,69	16,57	24,90	11,07			Average	63,35	20,30	36,20	16,10	

IG2A	Wednesday, October 30				
Ambient Sample	TC		IC		DOC
	Area	Conc	Area	Conc	5,54
	51,97	18,50	30,71	13,10	
	51,90	18,47	29,92	12,76	
	51,04	18,17	29,70	12,67	
Average	51,64	18,38	30,11	12,84	
Ambient Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	6,78
	26,80	9,54	6,13	2,61	
	26,28	9,35	6,06	2,58	
	25,65	9,13	5,85	2,50	
Average	26,24	9,34	6,01	2,57	
Refrigerated Sample	TC		IC		DOC
	Area	Conc	Area	Conc	9,14
	59,02	21,01	29,69	12,67	
	61,36	21,84	29,62	12,64	
	61,86	22,02	28,46	12,14	
Average	60,75	21,62	29,26	12,48	
Refrigerated Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	11,63
	40,25	14,40	7,48	3,19	
	42,81	15,24	7,32	3,12	
	41,25	14,68	7,31	3,12	
Average	41,44	14,77	7,37	3,14	

IG2B	Wednesday, October 30				
Ambient Sample	TC		IC		DOC
	Area	Conc	Area	Conc	7,77
	57,82	20,58	30,26	12,91	
	60,76	21,63	31,58	13,47	
	58,52	20,83	31,29	13,35	
Average	59,03	21,01	31,04	13,24	
Ambient Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	7,67
	31,32	11,15	8,08	3,45	
	31,83	11,33	8,36	3,57	
	31,29	11,14	8,44	3,60	
Average	31,48	11,21	8,29	3,54	
Refrigerated Sample	TC		IC		DOC
	Area	Conc	Area	Conc	6,68
	73,86	26,29	49,35	21,05	
	74,05	26,36	45,35	19,35	
	73,26	26,08	42,85	18,28	
Average	73,72	26,24	45,85	19,56	
Refrigerated Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	5,72
	31,59	11,24	8,98	3,83	
	31,83	11,33	8,93	8,81	
	31,04	11,05	8,94	3,81	
Average	31,49	11,21	8,95	5,49	

IG2A	Thursday, Oct 01				
Ambient Sample	TC		IC		DOC
	Area	Conc	Area	Conc	3,84
	49,77	15,96	25,59	11,38	
	47,28	15,16	25,41	11,30	
	45,14	14,47	25,59	11,38	
Average	47,40	15,20	25,53	11,35	
Ambient Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	6,49
	40,96	13,13	14,88	6,62	
	40,15	12,87	14,22	6,32	
	39,05	12,52	13,76	6,12	
Average	40,05	12,84	14,29	6,35	
Refrigerated Sample	TC		IC		DOC
	Area	Conc	Area	Conc	18,62
	82,11	29,23	26,13	11,15	
	81,97	29,18	26,42	11,27	
	86,33	30,73	25,47	10,87	
Average	83,47	29,71	26,01	11,10	

IG2B	Thursday, Oct 01				
Ambient Sample	TC		IC		DOC
	Area	Conc	Area	Conc	11,51
	88,18	31,39	48,47	20,68	
	87,15	31,02	45,17	19,27	
	86,27	30,71	43,70	18,64	
Average	87,20	31,04	45,78	19,53	
Ambient Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	12,03
	49,92	17,77	12,99	5,54	
	47,59	16,94	11,72	5,00	
	47,61	16,95	11,76	5,02	
Average	48,37	17,22	12,16	5,19	
Refrigerated Sample	TC		IC		DOC
	Area	Conc	Area	Conc	6,73
	74,89	26,66	48,33	20,62	
	75,10	26,73	45,38	19,36	
	73,70	26,23	45,61	19,46	
Average	74,56	26,54	46,44	19,81	
Refrigerated Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	16,68
	64,04	22,80	14,51	6,19	
	61,21	21,79	14,03	5,99	
	66,31	23,60	14,01	5,98	
Average	63,85	22,73	14,18	6,05	

IG2A	Friday, Oct 02				
Ambient Sample	TC		IC		DOC
	Area	Conc	Area	Conc	5,28
	38,66	13,76	18,56	7,92	
	37,27	13,27	18,90	8,06	
	35,94	12,79	18,72	7,99	
Average	37,29	13,27	18,73	7,99	
Ambient Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	8,44
	34,89	12,42	8,53	3,64	
	32,81	11,68	8,47	3,61	
	37,26	11,84	7,87	3,36	
Average	34,99	11,98	8,29	3,54	
Refrigerated Sample	TC		IC		DOC
	Area	Conc	Area	Conc	5,00
	38,42	13,68	20,79	8,87	
	37,98	13,52	20,70	8,83	
	37,88	13,48	18,70	7,98	
Average	38,09	13,56	20,06	8,56	
Refrigerated Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	7,35
	38,89	12,47	14,28	3,35	
	40,12	12,86	14,01	6,23	
	38,41	12,32	13,58	6,04	
Average	39,14	12,55	13,96	5,20	

IG2B	Friday, Oct 02				
Ambient Sample	TC		IC		DOC
	Area	Conc	Area	Conc	10,80
	95,47	33,98	54,99	23,46	
	94,53	33,65	55,22	23,56	
	97,15	34,58	53,41	22,79	
Average	95,72	34,07	54,54	23,27	
Ambient Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	-0,69
	54,56	17,49	41,56	18,47	
	54,39	17,44	38,47	17,10	
	53,39	17,12	41,76	18,56	
Average	54,11	17,35	40,60	18,04	
Refrigerated Sample	TC		IC		DOC
	Area	Conc	Area	Conc	5,89
	77,98	27,26	50,59	21,58	
	77,45	27,57	50,42	21,51	
	75,77	26,97	49,32	21,04	
Average	77,07	27,27	50,11	21,38	
Refrigerated Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	8,90
	46,65	16,61	19,05	8,13	
	48,12	17,13	18,59	7,93	
	47,63	16,95	18,62	7,94	
Average	47,47	16,90	18,75	8,00	

IG2A	Saturday, Oct 03				
Ambient Sample	TC		IC		DOC
	Area	Conc	Area	Conc	4,14
	72,98	23,40	43,57	19,37	
	70,20	22,51	41,45	18,43	
	69,74	22,36	40,62	18,06	
Average	70,97	22,76	41,88	18,62	
Ambient Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	5,64
	39,93	14,21	19,89	8,49	
	40,25	14,33	19,87	8,48	
	38,99	13,88	20,00	8,53	
Average	39,72	14,14	19,92	8,50	
Refrigerated Sample	TC		IC		DOC
	Area	Conc	Area	Conc	3,94
	61,47	19,71	35,55	15,80	
	59,52	19,09	34,51	15,34	
	59,72	19,15	33,74	15,00	
Average	60,24	19,32	34,60	15,38	
Refrigerated Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	5,58
	42,34	15,07	21,47	9,16	
	41,58	14,80	21,60	9,22	
	41,50	14,77	22,34	9,53	
Average	41,81	14,88	21,80	9,30	

IG2B	Saturday, Oct 03				
Ambient Sample	TC		IC		DOC
	Area	Conc	Area	Conc	4,24
	80,63	28,70	57,20	24,40	
	80,41	28,62	57,14	24,50	
	79,36	28,25	56,15	23,95	
Average	80,13	28,52	56,83	24,28	
Ambient Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	8,14
	54,17	19,28	27,43	11,70	
	55,09	19,61	25,87	11,01	
	53,81	19,15	25,56	10,90	
Average	54,36	19,35	26,29	11,20	
Refrigerated Sample	TC		IC		DOC
	Area	Conc	Area	Conc	6,05
	103,40	33,16	59,80	26,49	
	98,07	31,45	58,44	25,98	
	100,40	32,19	58,90	26,18	
Average	100,62	32,27	59,05	26,22	
Refrigerated Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	8,15
	63,28	20,29	27,14	12,06	
	61,66	19,77	25,47	11,32	
	58,54	18,77	24,75	11,00	
Average	61,16	19,61	25,79	11,46	

IG2A	Sunday, Oct 04				
Ambient Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	7,15
	44,06	15,68	19,93	8,50	
	44,18	15,06	19,60	8,36	
	44,28	15,76	19,19	8,19	
Average	44,17	15,50	19,57	8,35	

Refrigerated Sample	TC		IC		DOC
	Area	Conc	Area	Conc	4,97
	43,38	13,91	19,64	8,73	
	42,10	13,50	19,51	8,67	
	41,11	13,18	18,59	8,26	
Average	42,20	13,53	19,25	8,56	

Refrigerated Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	5,03
	40,87	13,11	18,29	8,13	
	39,76	12,75	17,88	7,95	
	40,78	13,08	17,51	7,78	
Average	40,47	12,98	17,89	7,95	

IG2B	Sunday, Oct 04				
Ambient Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	5,15
	55,89	19,89	30,96	13,21	
	44,35	15,79	29,88	12,75	
	51,14	18,20	29,21	12,46	
Average	50,46	17,96	30,02	12,81	

Refrigerated Sample	TC		IC		DOC
	Area	Conc	Area	Conc	2,84
	85,72	30,51	63,21	26,97	
	83,54	29,74	64,05	27,32	
	83,81	29,83	63,91	27,26	
Average	84,36	30,03	63,72	27,18	

Refrigerated Acidified Sample	TC		IC		DOC
	Area	Conc	Area	Conc	5,85
	54,63	19,45	32,18	13,73	
	55,00	19,58	32,21	13,74	
	54,15	19,27	31,13	13,28	
Average	54,59	19,43	31,84	13,58	

Biochemical Oxygen Demand - BOD

AMBIENT SAMPLE – IG2A

Date	Volume Sample	Tiossulfate Volume (mL)			Pratical Volume	Correction Factor	DO (mg/L)	BOD_5 (mg/L)
29-Set	280	2,9	2,9	2,9	20,2	1,01	5,86	9,14
30-Set	280	3	2,8	2,9	20,5	1,025	5,95	
1-Oct	280	2,8	3	2,9	20,4	1,02	5,92	
2-Oct	280	2,5	2,5	2,5	20,3	1,015	5,08	
3-Oct	280	2,4	2,4	2,4	20,6	1,03	4,94	
30-Set	280	3,6	3,6	3,6	20,5	1,025	7,38	12,61
1-Oct	280	2,7	2,7	2,7	20,4	1,02	5,51	
2-Oct	280	2,3	2,3	2,3	20,3	1,015	4,67	
3-Oct	280	2,9	2,8	2,85	20,6	1,03	5,87	
4-Oct	280	2,9	2,9	2,9	21,1	1,055	6,12	
1-Oct	280	2,7	2,7	2,7	20,4	1,02	5,51	1,275
2-Oct	280	2,7	2,8	2,75	20,3	1,015	5,58	
3-Oct	280	3	3	3	20,6	1,03	6,18	
4-Oct	280	2,3	2,4	2,35	21,1	1,055	4,96	
5-Oct	280	2,5	2,6	2,55	21,1	1,055	5,38	
2-Oct	280	2,6	2,8	2,7	20,3	1,015	5,48	-23,63
3-Oct	280	2,7	2,8	2,75	20,6	1,03	5,67	
4-Oct	280	2,5	2,4	2,45	21,1	1,055	5,17	
5-Oct	280	2,3	2,6	2,45	21,1	1,055	5,17	
6-Oct	280	3,7	3,7	3,7	21,2	1,06	7,84	
3-Oct	280	1,4	1,4	1,4	20,6	1,03	2,88	-9,35
4-Oct	280	2,2	2,3	2,25	21,1	1,055	4,75	
5-Oct	280	2,6	2,6	2,6	21,1	1,055	5,49	
6-Oct	280	2,9	2,9	2,9	21,2	1,06	6,15	
7-Oct	280	1,8	2	1,9	20,1	1,005	3,82	

	Day 1	Day 2	Day 3	Day 4	Day 5	BOD_5
1	5,86	*	*	*	*	9,14
2	7,38	5,95	*	*	*	12,61
3	5,51	5,51	5,92	*	*	1,275
4	5,48	5,58	4,67	5,08	*	-23,63
5	2,88	5,67	6,18	5,87	4,94	-9,35
6	*	4,75	5,17	4,96	6,12	
7	*	*	5,49	5,17	5,38	
8	*	*	*	6,15	7,84	
9	*	*	*	*	3,82	

REFRIGERATED SAMPLE – IG2A

Date	Volume Sample	Tiossulfate Volume (mL)			Pratical Volume	Correction Factor	DO (mg/L)	BOD$_5$ (mg/L)
30-Sep	280	3	3	3	20,5	1,025	6,15	8,75
1-Oct	280	2,8	3,2	3	20,4	1,02	6,12	
2-Oct	280	2,3	2,3	2,3	20,3	1,015	4,67	
3-Oct	280	2,9	2,9	2,9	20,6	1,03	5,97	
4-Oct	280	2,5	2,5	2,5	21,1	1,055	5,28	
1-Oct	280	3,5	3,5	3,5	20,4	1,02	7,14	3,88
2-Oct	280	3	3	3	20,3	1,015	6,09	
3-Oct	280	2,8	2,9	2,85	20,6	1,03	5,87	
4-Oct	280	3,6	3,6	3,6	21,1	1,055	7,60	
5-Oct	280	3,2	3,2	3,2	21,1	1,055	6,75	
2-Oct	280	3	3	3	20,3	1,015	6,09	21,68
3-Oct	280	2,9	3,2	3,05	20,6	1,03	6,28	
4-Oct	280	3	2,7	2,85	21,1	1,055	6,01	
5-Oct	280	2,7	2,9	2,8	21,1	1,055	5,91	
6-Oct	280	1,8	1,9	1,85	21,2	1,06	3,92	
3-Oct	280	2,7	2,7	2,7	20,6	1,03	5,56	21,45
4-Oct	280	2,7	3,2	2,95	21,1	1,055	6,22	
5-Oct	280	3,5	3,5	3,5	21,1	1,055	7,39	
6-Oct	280	3	3	3	21,2	1,06	6,36	
7-Oct	280	1,7	1,7	1,7	20,1	1,005	3,42	
4-Oct	280	3,7	3,6	3,65	21,1	1,055	7,70	53,9
5-Oct	280	3,5	3,5	3,5	21,1	1,055	7,39	
6-Oct	280	1,8	1,9	1,85	21,2	1,06	3,92	
7-Oct	280	3,7	3,7	3,7	20,1	1,005	7,44	
8-Oct	280	1	1,3	1,15	20,1	1,005	2,31	

	Day 1	Day 2	Day 3	Day 4	Day 5	BOD$_5$
1	6,15	*	*	*	*	8,75
2	7,14	6,12	*	*	*	3,88
3	6,09	6,09	4,669	*	*	21,68
4	5,562	6,28	5,871	5,974	*	21,45
5	7,7015	6,2245	6,01	7,596	5,275	53,9
6	*	7,385	7,385	5,91	6,752	
7	*	*	3,922	6,36	3,92	
8	*	*	*	7,437	3,417	
9	*	*	*	*	2,3115	

AMBIENT SAMPLE – IG 2B

Date	Volume Sample	Tiossulfate Volume (mL)			Pratical Volume	Correction Factor	DO (mg/L)	BOD_5 (mg/L)
29-Set	280	1,5	1,7	1,6	20,2	1,01	3,23	7,60
30-Set	280	1,1	1,1	1,1	20,5	1,03	2,26	
1-Oct	208	1,1	1,1	1,1	20,4	1,02	2,24	
2-Oct	280	0,6	0,6	0,6	20,3	1,02	1,22	
3-Oct	280	1,2	1,2	1,2	20,6	1,03	2,47	
30-Set	280	1,6	1,5	1,6	20,5	1,03	3,18	-17,81
1-Oct	280	1,1	1	1,1	20,4	1,02	2,14	
2-Oct	280	1	0,7	0,9	20,3	1,02	1,73	
3-Oct	280	0,9	1	1,0	20,6	1,03	1,96	
4-Oct	280	2,4	2,3	2,4	21,1	1,06	4,96	
1-Oct	280	1,4	1,4	1,4	20,4	1,02	2,86	-14,70
2-Oct	280	1	0,8	0,9	20,3	1,02	1,83	
3-Oct	280	1,2	1,1	1,2	20,6	1,03	2,37	
4-Oct	280	2	1,9	2,0	21,1	1,06	4,11	
5-Oct	280	2	2,1	2,1	21,1	1,06	4,33	
2-Oct	280	1,7	1,6	1,7	20,3	1,02	3,35	13,36
3-Oct	280	2,5	2,7	2,6	20,6	1,03	5,36	
4-Oct	280	2,5	2,5	2,5	21,1	1,06	5,28	
5-Oct	280	1,3	1,4	1,4	21,1	1,06	2,85	
6-Oct	280	0,9	1	1,0	21,2	1,06	2,01	
3-Oct	280	0,6	0,5	0,6	20,6	1,03	1,13	-25,86
4-Oct	280	1,7	1,6	1,7	21,1	1,06	3,48	
5-Oct	280	1,9	2	2,0	21,1	1,06	4,11	
6-Oct	280	1,4	1,3	1,4	21,2	1,06	2,86	
7-Oct	280	1,7	2	1,9	20,1	1,01	3,72	

	Day 1	Day 2	Day 3	Day 4	Day 5	BOD_5
1	3,23					7,6
2	3,18	2,26				-17,8
3	2,86	2,14	2,24			-14,7
4	3,35	1,83	1,73	1,22		13,4
5	1,13	5,36	2,37	1,96	2,47	-25,9
6		3,48	5,28	4,11	4,96	
7			4,11	2,85	4,33	
8				2,86	2,01	
9					3,72	

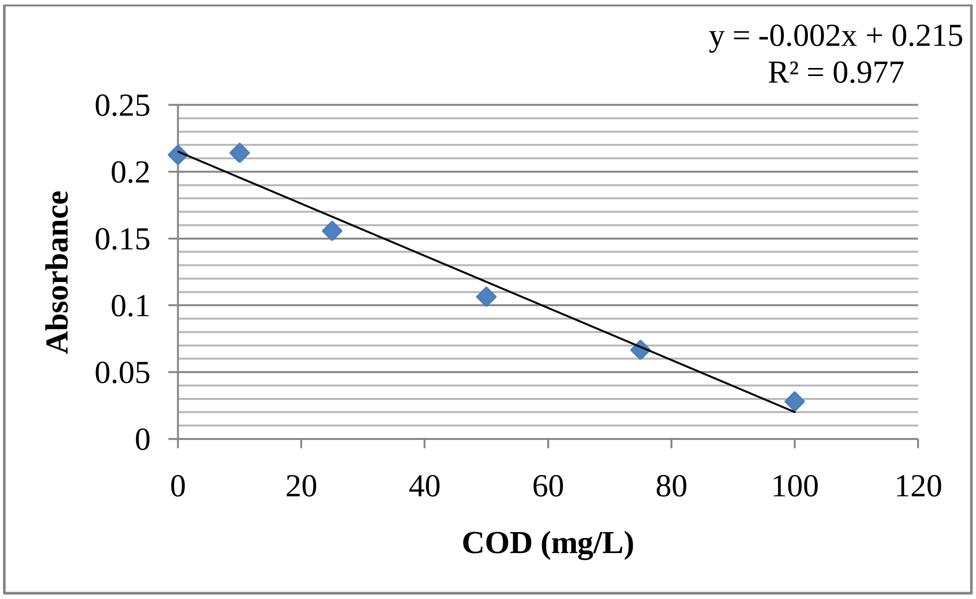
REFRIGERATED SAMPLE - IG 2B								
Date	Volume Sample	Tiossulfate Volume (mL)			Pratical Volume	Correction Factor	DO (mg/L)	BOD_5 (mg/L)
30-Set	280	1,4	1,5	1,5	20,5	1,03	2,97	-4,04
1-Oct	280	1,8	1,9	1,9	20,4	1,02	3,77	
2-Oct	280	0,7	0,6	0,7	20,3	1,02	1,32	
3-Oct	280	1,2	1,1	1,2	20,6	1,03	2,37	
4-Oct	280	1,7	1,5	1,6	21,1	1,06	3,38	
1-Oct	280	1,7	1,5	1,6	20,4	1,02	3,26	-3,23
2-Oct	280	0,6	0,7	0,7	20,3	1,02	1,32	
3-Oct	280	1,6	1,5	1,6	20,6	1,03	3,19	
4-Oct	280	0,7	0,8	0,8	21,1	1,06	1,58	
5-Oct	280	1,7	1,7	1,7	21,1	1,06	3,59	
2-Oct	280	1,6	1,6	1,6	20,3	1,02	3,25	19,76
3-Oct	280	3,1	3,2	3,2	20,6	1,03	6,49	
4-Oct	280	1,4	1,4	1,4	21,1	1,06	2,95	
5-Oct	280	1,7	1,6	1,7	21,1	1,06	3,48	
6-Oct	280	0,6	0,6	0,6	21,2	1,06	1,27	
3-Oct	280	1,3	1,2	1,3	20,6	1,03	2,58	5,65
4-Oct	280	2,3	2,2	2,3	21,1	1,06	4,75	
5-Oct	280	2,8	2,7	2,8	21,1	1,06	5,80	
6-Oct	280	0,6	0,6	0,6	21,2	1,06	1,27	
7-Oct	280	1	1	1,0	20,1	1,01	2,01	
4-Oct	280	2,5	2,5	2,5	21,1	1,06	5,28	-9,56
5-Oct	280	1	1	1,0	21,1	1,06	2,11	
6-Oct	280	1,5	1,4	1,5	21,2	1,06	3,07	
7-Oct	280	0,9	0,9	0,9	20,1	1,01	1,81	
8-Oct	280	3	3,2	3,1	20,1	1,01	6,23	

	Day 1	Day 2	Day 3	Day 4	Day 5	BOD_5
1	2,9725					-4,0
2	3,26	3,774				-3,23
3	3,248	1,32	1,3195			19,76
4	2,575	6,489	3,19	2,369		5,65
5	5,275	4,7475	2,954	1,58	3,376	-9,56
6		2,11	5,8025	3,4815	3,59	
7			3,074	1,272	1,27	
8				1,809	2,01	
9					6,231	

Chemical Oxygen Demand

Calibration Curve				
COD (mg/L)	A	B	C	Aver
0	0,2128	0,1702	0,2122	0,213
10	0,3116	0,2115	0,2164	0,214
25	0,1595	0,1389	0,1517	0,156
50	0,1097	0,1063	0,1029	0,106
75	0,0621	0,0594	0,0782	0,067
100	0,0287	0,0265	0,0289	0,028

Standard Proposed	A	B	C	Aver	Values Measured
30	0,1595	0,1389	0,1517	0,1556	29,70
80	0,0621	0,0594	0,0782	0,0666	74,22



Ambient Sample		
	IG2A	IG2B
Tuesday, Sep 29	0,1537	0,1353
	0,1615	0,1359
	0,1580	0,1312
	0,1558	0,1404
	0,1597	0,1185
Aver	0,1577	0,1323
Conc	28,63	41,37

	Ambient Sample		Ambient Acidified Samples		Refrigerated Sample		Refrigerated Acidified Samples		Branco	P30	P80
Wednesday, Sep 30	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,1840	0,1431	0,2371
	0,1619	0,1345	0,1724	0,1168	0,1814	0,1266	0,1809	0,1285	0,1913	0,1508	0,1298
	0,1654	0,1312	0,3577	0,1202	0,1724	0,1423	0,1619	0,1270	0,2043	0,1559	0,1344
	0,1665	0,1229	0,1720	0,1233	0,1843	0,1317	0,1843	0,1346			
	0,1632	0,1501	0,1907	0,1207	0,1744	0,1237	0,1687	0,1249			
	0,1637	0,1597	0,4694	0,1266	0,1968	0,1456	0,1943	0,1108			
Aver	0,1641	0,1397	0,2724	0,1215	0,1819	0,1340	0,1780	0,1252	0,1932	0,1499	0,1671
Conc	25,43	37,66	-28,72	46,74	16,57	40,51	18,49	44,92		32,53	23,95

	Ambient Sample		Ambient Acidified Samples		Refrigerated Sample		Refrigerated Acidified Samples		Branco	P30	P80
Thrusday, Oct 01	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,1899	0,1460	0,0497
	0,1626	0,0881	0,1569	0,1123	0,1548	0,1144	0,1483	0,1089	0,4922	0,1223	0,0277
	0,1791	0,0356	0,1205	0,0809	0,1298	0,1344	0,1353	0,0992	0,1973	0,1400	0,0430
	0,1500	0,1112	0,1401	0,1097	0,1288	0,1097	0,1396	0,1033			
	0,0620	0,3409	0,1223	0,1163	0,1598	0,1136	0,1544	0,0968			
	0,1588	0,2091	0,1553	0,1135	0,1604	0,1293	0,1108	0,0470			
Aver	0,1425	0,1570	0,1390	0,1065	0,1467	0,1203	0,1377	0,0910		0,1361	0,0401
Conc	36,25	29,01	37,99	54,23	34,14	47,36	38,66	61,98		39,45	87,43

	Ambient Sample		Ambient Acidified Samples		Refrigerated Sample		Refrigerated Acidified Samples		Branco	P30	P80
Friday, Oct 02	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,1836	0,1353	0,1292
	0,1843	0,1458	0,1741	0,2163	0,1550	0,1447	0,1742	0,1179	0,2040	0,1476	0,2402
	0,3114	0,1459	0,1503	0,1000	0,2676	0,1530	0,1770	0,1473	0,2185	0,1816	0,1680
	0,1855	0,1503	0,1595	0,0983	0,1710	0,1559	0,1559	0,1255			
	0,1689	0,1677	0,1563	0,1848	0,1764	0,1493	0,1555	0,1233			
	0,2001	0,1543	0,2817	0,1233	0,1616	0,1472	0,1559	0,1624			
Aver	0,2100	0,1528	0,1844	0,1445	0,1863	0,1500	0,1637	0,1353	0,2020	0,1548	0,1791
Conc	2,48	31,10	15,31	35,23	14,34	32,49	25,65	39,86		30,08	17,93

	Ambient Sample		Ambient Acidified Samples		Refrigerated Sample		Refrigerated Acidified Samples		Branco	P30	P80
Saturday, Oct 03	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,2145	0,138	0,0466
	0,1682	0,1814	0,1746	0,0968	0,1593	0,1547	0,1841	0,1184	0,4435	0,1353	0,0437
	0,1654	0,187	0,1814	0,0994	0,2208	0,1323	0,1718	0,1123	0,2107	0,1295	0,0327
	0,166	0,1754	0,1821	0,0983	0,2595	0,1389	0,1703	0,1047			
	0,1637	0,3265	0,3868	0,0997	0,1849	0,1395	0,1757	0,1074			
	0,163	0,2461	0,1809	0,1104	0,1588	0,1313	0,1814	0,1068			
Aver	0,1653	0,2233	0,2212	0,1009	0,1967	0,1393	0,1767	0,1099	0,2896	0,1343	0,0410
Conc	24,87	-4,14	-3,08	57,04	9,17	37,83	19,17	52,54		40,37	87,00

	Ambient Acidified Samples		Refrigerated Sample		Refrigerated Acidified Samples		Branco	P30	P80
Sunday, Oct 04	IG2A	IG2B	IG2A	IG2B	IG2A	IG2B	0,1954	0,1478	0,0543
	0,1442	0,1307	0,1857	0,1563	0,4073	0,1375	0,2047	0,1471	0,0452
	0,1508	0,1212	0,1755	0,1699	0,1959	0,3035	0,2029	0,1487	
	0,1541	0,1169	0,179	0,352	0,1829	0,174			0,0564
	0,1501	0,0551	0,1782	0,1605	0,1757	0,1166			
	0,1447	0,1317	0,1779	0,1479	0,2943	0,1227			
Aver	0,1488	0,1111	0,1793	0,1973	0,2512	0,1709	0,2010	0,1479	0,0498
Conc	33,11	51,94	17,87	8,84	-18,11	22,07		33,57	82,63