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CÉSAR AMBROGI FERREIRA DO LAGO

**IMPACTOS DAS MUDANÇAS CLIMÁTICAS SOBRE A DRENAGEM
URBANA SUBTROPICAL COM TÉCNICAS COMPENSATORIAS**

VERSÃO CORRIGIDA

SÃO CARLOS

2018

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URBANA SUBTROPICAL COM TÉCNICAS COMPENSATORIAS**

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Engenharia de São Carlos, da
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Hidráulica e Saneamento*

*Orientador: Prof. Dr. Eduardo Mario
Mendonça*

VERSÃO CORRIGIDA

SÃO CARLOS

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“I hereby declare this written research is original, with no conflict of interest, and complies with Codes of Ethics of the main research funding agencies and higher education boards, either Brazilian or International ones”.

Resumo

DO LAGO, C. A. F. (2018) **Impactos das mudanças climáticas sobre a drenagem urbana subtropical com técnicas compensatórias**. Dissertação, Escola de Engenharia de São Carlos, Universidade de São Paulo.

Técnicas compensatórias de drenagem (TC) vêm sendo utilizadas para mitigar efeitos da urbanização no ciclo hidrológico. Entretanto faltam estudos sobre a performance destas TCs em clima subtropical e sob potenciais impactos de cenários de mudanças climáticas. Esta dissertação avaliou os impactos de dois cenários de mudanças climáticas (RCP 4.5 e 8.5) sobre o escoamento superficial urbano com poluentes e sua afetação na eficiência da TC localizada em clima subtropical, classificação Cfa segundo Köppen e Geiger. Primeiro se calibrou os parâmetros de quantidade e qualidade do escoamento superficial na entrada da biorretenção. O modelo buildup/washoff foi avaliado, comparando-se calibração da carga e concentração de poluentes: demanda química de oxigênio (DQO), carbono orgânico total (TOC), fosfato (PO₄), nitrato (NO₃), nitrito (NO₂) amônia (NH₃), ferro (Fe), cádmio (Cd) e zinco (Zn). Então se estudou a lavagem de poluentes na área de contribuição da biorretenção com histórico de precipitação entre 2013 e 2017 e analisando a influência dos parâmetros buildup/washoff de cada poluente na entrada de massa. Em seguida, cenários de mudanças climáticas Eta-5x5km (INPE) foram desagregados em intervalos de 5 minutos, pelo método de Bartlett-Lewis modificado. A série desagregada foi utilizada para se estimar os impactos das mudanças climáticas na drenagem urbana, a incidir na biorretenção. Então um modelo simples desenvolvido especificamente para a biorretenção em estudo foi usado para se estimar as eficiências quali-quantitativas de cada período dos cenários de mudanças climáticas. Os dados adquiridos do Inpe mostram que as mudanças climáticas resultarão em uma queda no volume de chuvas em São Carlos, resultando em menores volumes de escoamento superficial. Os impactos na lavagem de poluentes, entretanto, variam de acordo com os parâmetros buildup/washoff, explicados por uma análise de sensibilidade. As mudanças climáticas pouco afetam a eficiência quantitativa da biorretenção, 81.7% no período 1980-1999 para 81.4% e 81.3% no período 2080-2099 para cenários RCP 4.5 e 8.5. Já as eficiências de remoção de poluentes, assim como a lavagem destes, dependem das características buildup/washoff de lavagem. Uma das principais consequências observadas das mudanças climáticas é uma queda na qualidade do escoamento. Porém, mesmo com eficiência quantitativa sendo mantida, a biorretenção é capaz de amenizar essa o aumento na concentração de poluentes na drenagem urbana. Assim, a técnica ajudará a preservar a qualidade dos rios à jusante, que já terão seus volumes diminuídos pela queda no volume de chuva.

Palavras chave: Mudanças climáticas, drenagem urbana subtropical, técnicas compensatórias.

Abstract

DO LAGO, C. A. F. (2018) **Climate Changes Impacts on Subtropical Urban Drainage with Low Impact Developments**. Dissertation, São Carlos School of Engineering, University of São Paulo.

Low impact developments (LID) have been used to mitigate the effects of urbanization on the hydrological cycle. However, there is a lack of studies on LID performance in subtropical climates and under potential impacts of climate change scenarios. This dissertation evaluated the impacts of two climate change scenarios (RCP 4.5 and 8.5) on urban drainage with pollutants and their effect on LID practice efficiency located in a subtropical climate, with Cfa classification according to Köppen and Geiger. First, the inlet quantity and quality parameters were calibrated. The buildup/washoff model was evaluated, comparing load calibration and concentration of pollutants: chemical oxygen demand (COD), total organic carbon (TOC), phosphate (PO₄) (NH₃), iron (Fe), cadmium (Cd) and zinc (Zn). Pollutant washing was studied in the area of the bioretention catchment using historical rainfall data between 2013 and 2017, analyzing the influence of the buildup/washoff parameters of each pollutant in the input mass. Afterwards, Eta-5x5km (INPE) climate change scenarios were disaggregated to 5-minute intervals by the modified Bartlett-Lewis method. The disaggregated series was used to estimate the impacts of climate change on urban drainage into the bioretention. Therefore, a simple model, developed specifically for the study bioretention cell, was used to estimate the qualitative-quantitative efficiencies of each period of the climate change scenarios. According to the data acquired from INPE, climate change will result in a fall in the volume of rainfall in São Carlos, resulting in lower volumes of surface runoff. The impacts on pollutant washing, however, vary according to the buildup/washoff parameters, explained by a sensitivity analysis. Climate change does not affect the bioretention quantitative efficiency very much: 81.7% from 1980 to 1999 to 81.4% and 81.3% from 2080 to 2099 for CPR scenarios 4.5 and 8.5. The pollutant removal efficiencies, as well as the washing, depend on buildup/washoff characteristics. One of the main consequences of climate change is a drop in the runoff quality. However, even with quantitative efficiency being maintained, bioretention is capable of mitigating this increase in the concentration of pollutants in urban drainage. Thus, the LID will help preserve the quality of downstream rivers, whose volumes will already have diminished by the decrease in rainfall volume.

Key words: Climate changes, subtropical urban drainage, low impact developments.

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1. INTRODUCTION

Most of the world population is currently living in urban areas. In Brazil, approximately 185 million people live in cities. This way of life alters the natural environment and one of the impacts is on the hydrologic cycle. Urbanization results in higher imperviousness, increasing runoff volume and its peak flows (Guan, Sillanpää, & Koivusalo, 2015), resulting in more frequent floods (Sun, Tong & Yang 2016, Sun et al. 2017) with a higher amount of pollutants washed-off (Fletcher, Andrieu & Hamel, 2013), degrading the quality of water bodies. Low Impact Developments (LID) practices have been used to prevent and mitigate such impacts, by treating the quantity and the quality of the stormwater.

However, LID in subtropical climates need to be better studied to verify their singularities and what their impacts are on the performance of LID (Macedo et al., 2017) as different rainfall regimes change the runoff generation and pollutant washoff processes. In the tropics, for example, higher intensity rainfall generates runoff more quickly (Le et al., 2007), resulting in major impacts on its quality (Piro & Carbone, 2014) and possibly on pollutants removal efficiency in LID practices. Therefore, the quantity and quality of runoff in tropical regions also needs to be better evaluated to carry out LID studies in these areas.

Rainfall regimes differ not only spatially, but also temporally as climate change models suggest. These changes tend to decrease the rainfall volume and increase its intensity, worsening water insecurity in the country due to more frequent occurrences of floods and droughts (Chou et al., 2014-a; Chou et al., 2014-b; Lyra et al., 2017; Marengo & Ambrizzi, 2014). LID practices are an alternative to mitigate these climate change impacts, which will possibly also alter LID practice performances.

This research studied the quality of stormwater in a subtropical catchment in São Carlos, relating the pollutant washoff process to some rainfall event characteristics such as intensity and previous dry days. Then, climate changes scenarios were evaluated and their impacts on bioretention cell quality and quantity efficiencies were analyzed and discussed.

1.1. Research hypothesis

The effects of a progressive augmentation of rainfall extremes, caused by climate changes, influences the rainfall-runoff process in subtropical urban areas, decreasing stormwater retention and pollutant removal performance of LID practices.

1.2. Purposes

1.3.1. General purpose

To elucidate how runoff generation and pollutant wash-off processes respond to upstream factors of an experimental LID technique and evaluate how this practice would perform as a local adaptation strategy considering rainfall-runoff scenarios under climate change.

3.1.2. Specific purposes

1. Characterize the urban runoff in a subtropical catchment, in terms of volume, flow and water quality, elucidating the runoff generation and pollutant wash-off processing, using a stepwise flowchart including calibration, validation and sensitivity analysis.
2. Analyze the impacts of climate changes on subtropical urban drainage.

1.3. Text organization

Chapter 2 describes the general methodology. It briefly explains how chapters are connected and how they contribute to the general and specific purposes.

In **Chapter 3**, the runoff generation and pollutant washoff processes in a subtropical climate drained to the bioretention are discussed. This was important for better precision in the quality predictions as two calibration methods were compared in this chapter (concentration and load-based calibration).

Chapter 4 analyzes the bioretention performance and verifies the climate changes in São Carlos for the RCP 4.5 and 8.5 scenarios. Future periods (2020-2039, 2040-2059, 2060-2079, and 2080-2099) were compared to the present date (1980-1999), and therefore the changes occurring in one century could be estimated.

Finally, **Chapter 5** includes the general conclusions and recommendations for future research to better understand this dissertation.

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2.GENERAL METHODOLOGY

The study area has 2.3ha, which presents 22% of impervious area. There is a 60m² bioretention downstream, where several events were monitored and used to calibrate and validate the inlet and outlet quantity and quality of the stormwater. Figure 2.1 illustrates the catchment and bioretention location.

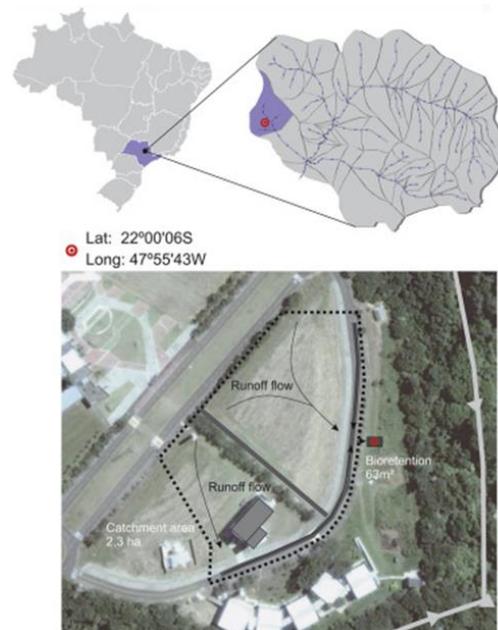


Figure 2.1: The bioretention location and its catchment.
Source: Adapted from Macedo (2017).

In Chapter 3, a sensitivity analysis of the buildup/washoff parameters of the pollutants was performed to understand their influence on the concentrations of the simulated runoff pollutants and better understand this process in the subtropical catchment and minimum warm-up period for reliable quality predictions. Two quality calibration methods were also compared in this chapter, a load-based and a concentration-based calibration to verify which correspond better to the purpose of this study. The quality simulations were done with observed discharge and were optimized using the GRG nonlinear solver tool, and was therefore performed on a spreadsheet.

Chapter 4 aims to evaluate the impacts of climate change on the rainfall regime, runoff and on the bioretention performance. The RCP scenarios 4.5 and 8.5 were used with downscaling based on the Eta Regional Climate Model forced by the global HadGEM2-ES model (Chou et al., 2014-a; Chou et al, 2014-b; Lyra et al, 2017). The data were acquired with a spatial scale of 5km and a 3-hour time scale, which was later reduced to 5min through a modified Bartlett-Lewis rectangular pulse model to simulate the runoff and pollutants into the bioretention. Regarding its outflow, a specific model was used for a greater accuracy of the ponding depth in the surface of the bioretention, which has a triangular weir for the outflow.

Figure 2.2. shows the general methodology flowchart, how chapter 3 and 4 are related and how they contribute to the general and specific purposes.

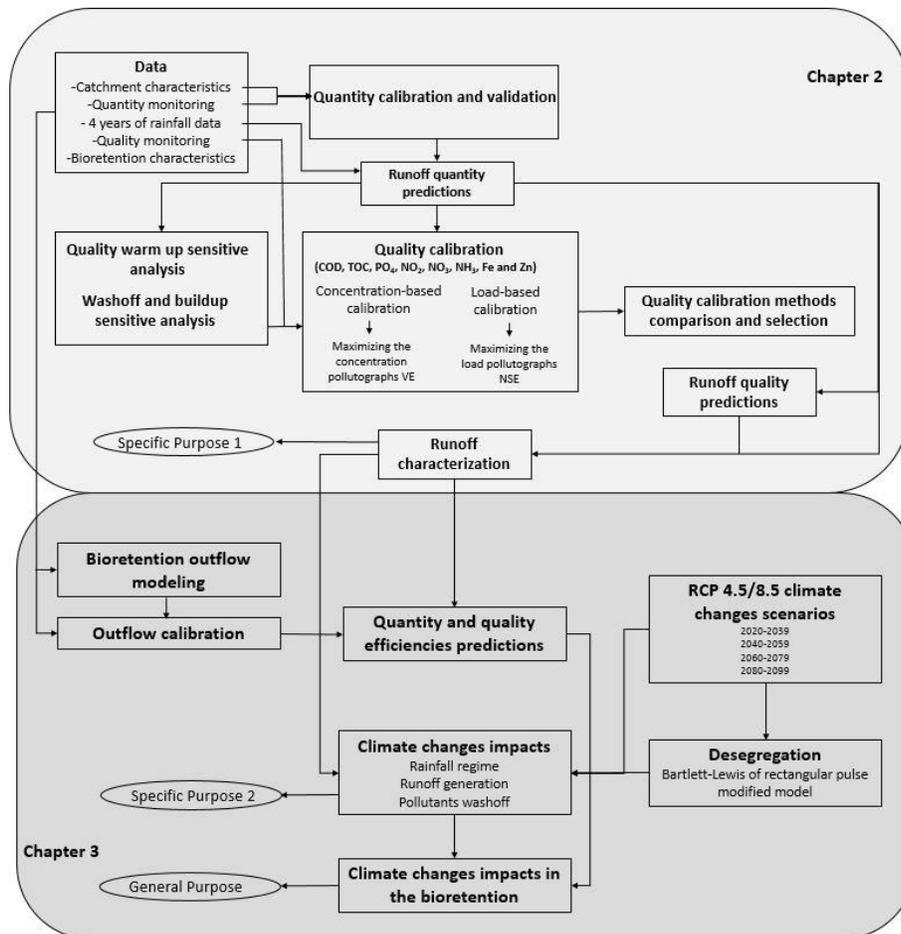


Figure 2.2. General methodology flowchart.

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3.RUNOFF QUALITY AND QUANTITY PREDICTIONS IN A SUBTROPICAL CATCHMENT USING A BUILDUP/WASHOFF MODEL

A modified version of this chapter will be submitted as: César Ambrogi Ferreira do LAGO et al., Runoff quality and quantity predictions in a subtropical catchment using a buildup/washoff model.

Abstract

Hydrological modeling is an important tool for assessing catchment management plans. However, runoff quality modeling in urban catchments requires a better understanding, especially in tropical regions where high intensity rainfalls result in faster hydrological response. The aim of this paper is to qualitatively and quantitatively characterize the urban runoff in a subtropical catchment using a stepwise flowchart including calibration, validation, sensitivity analysis, as well as historical records. The calibration and validation of the runoff quantity were first performed considering six monitored events. Afterwards, different warm up periods of the quality model were analyzed concerning their influence on the initial buildup. In addition, a sensitivity analysis of the buildup and washoff parameters was carried out for a tropical rainfall regime. Then, two types of quality calibrations were evaluated: (1) the maximization of the Volumetric Efficiency (VE) of concentration; and (2) the maximization of the Nash-Sutcliffe Efficiency (NSE) of the pollutant load. Both methods were carried out using observed discharge to avoid propagation of quantitative simulation errors. After validating the quality model, four years of rainfall data were used to simulate and characterize the runoff. Our findings showed that warming up the quality model played an important role in the initial buildup, which could be under-estimated in 93% in one of the events if only considering the previous dry days. Calibrating the concentrations, as expected, generates smaller differences in the predicted and observed mean concentrations. However, by maximizing the NSE of the load pollutograph, the total pollutant mass (and consequently the Event Mean Concentration (EMC)) were more compatible, and were

therefore used for the simulations. Over 4 years, it is estimated that approximately 1223 mm (or 29,000m³) of runoff washed approximately 9659g/ha, 3818.2g/ha, 93.8g/ha, 306.9g/ha, 29731g/ha, 475.5g/ha of Fe, NO₃, NO₂, PO₄, TOC and Zn, respectively. Most of the pollutant mass was generated in the summer (rainy season), while the highest EMCs were found during the winter (dry season). A nonlinear relationship was also observed between the total runoff volume and pollutant mass for higher values of washoff coefficient (w_1).

Key-words: Subtropical quality modeling, buildup/washoff, sensitivity analysis

3.1. Introduction

Urbanization accelerates hydrologic responses increasing runoff volume and peak flows (Guan, Sillanpää, & Koivusalo, 2015), leading to more flood risks (Sun, Tong & Yang 2016, Sun et al. 2017) and the amount of transported pollutants (Fletcher, Andrieu & Hamel, 2013). Monitoring urban catchments requires time, funding and depends on random variables, such as rainfall intensity, making it difficult to understand the system more comprehensively.

Using watershed models to predict runoff discharges can be used as a tool to better evaluate BMPs and watershed management plans (Borah, 2011). Predicting water quality can also be used to support decision makers. Rode et al. (2005) stated that runoff quality models are essential for watershed management plans. However, quality modeling as a management tool is still incipient in Brazilian catchments. For instance, there are considerable uncertainties in studies addressing pollutant load generation under land-use change (Zaffani et al, 2015), qualitative field experiments (Taffarello et al, 2016) and modeling scenarios of nested catchments (Taffarello, 2017).

The phenomenon involved in stormwater quality needs to be better understood for more reliable quality simulations (Obropta & Kardos , 2007; Bonhomme & Petrucci, 2017), especially in the tropics where high intensity rainfall generates faster runoff responses (Le et al., 2007). In wet climates, the interaction between the catchment hydrology and the accumulation and transportation of pollutants has a major impact on the quality of the runoff (Piro & Carbone, 2014).

Liu et al. (2014) and Rosa (2016) analyzed hydrologic models with qualitative aspects, possibly using BMP. In this paper, eight models were analyzed, including the Storm Water Management Model (SWMM), the Hydrologic Modeling System (HEC-HMS), DRAINMOD

and RECARGA in the public domain. They also show that only the SWMM and the RECARGA incorporate qualitative modeling, and the SWMM is most used worldwide.

SWMM uses the buildup/washoff model. It consists of the runoff washing the pollutants, which were deposited during the dry period. The model needs calibration and even doing so, the uncertainties remain (Bertrand-Krajewski, 2007).

This study analyzed the quality of stormwater in a subtropical catchment, classified as Cfa as Köppen e Geiger,. A sensitivity analysis of the buildup/washoff parameters was performed to understand their influence on the concentrations of the simulated runoff pollutants. Two quality calibration methods were also analyzed: a load-based and a concentration-based calibration. The article includes a comprehensive flowchart of the methodology (Section 2), with calibration and validation steps (Sections 2.3 and 2.4), a sensitivity analysis related to the model warm-up (Section 2.5) and results and discussions using a subtropical rainfall regime (Section 3).

3.2. Methodology

The methodology that characterizes the runoff is summarized in a flowchart in Figure 3.1. See further details in the text.

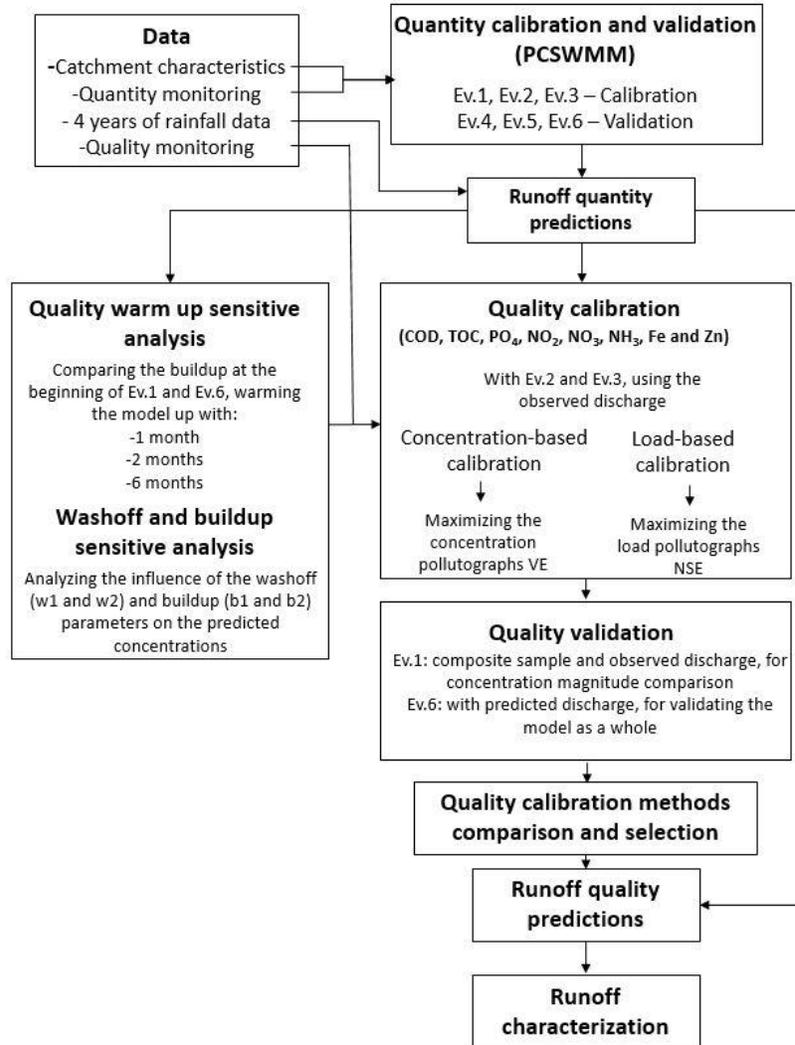


Figure 3.1: Methodology flowchart used in this chapter.

3.2.1. Study Area

The studied catchment is located at Campus 2 at the University of São Paulo (USP), São Carlos, Brazil. The city has a subtropical climate with an average annual rainfall of 1422mm. January (summer) is the month that has a higher precipitation volume with an average of 269mm, while July (winter) has the lowest with an average of 15.5mm (Miranda et al., 2012).

The area has 2.3 hectares, which presents 22% of impervious area related to buildings, roads and footpaths, while the pervious part is mainly covered by short grass. The local soil was analyzed, resulting in 20% clay, 10% silt and 70% sand, and was classified between sandy clay loam and sandy loam soils (*USDA, 2017*). The average slope of the area is 3.5%, which was obtained using the Digital Elevation Model (DEM). Downstream of the area is a 60.6m³ bioretention, where the data were collected (Macedo et al., 2017).

The campus is under an occupation process and the impervious area is expected to reach 50% by 2025 and 80% by 2100 (Rosa, 2016). However, no building was under construction during the data collection, which would have had a strong impact on the generation of pollutants (Sillanpää & Koivusalo, 2015).

3.2.2. Data collection

Data from seven monitored events were used for the quali-quantity calibration and their characteristics are shown in Table 3.1. A rain gauge with a 0.2mm precision was used to obtain the rainfall data, installed at the campus about 400m from the catchment. Quality data in Ev.1 was collected as composite sample and Ev. 6 has no quantity data.

Table 3.1: Monitored events and their characteristics.

| | Day | Prior dry period (days) | Observed runoff duration (min) | Total precipitation (mm) | Average precipitation intensity (mm/hr) | Monitoring Type |
|-------------|------------|-------------------------|--------------------------------|--------------------------|---|-----------------------|
| Ev.1 | 25/08/2015 | 29 | 89 | 3.8 | 3.3 | Quantity and quality* |
| Ev.2 | 27/08/2015 | 0 | 137 | 1.8 | 1.7 | Quantity and quality |
| Ev.3 | 08/09/2015 | 1 | 478 | 37.8 | 5.1 | Quantity and quality |
| Ev.4 | 02/09/2016 | 1 | 118 | 6.4 | 11.6 | Quantity |
| Ev.5 | 06/09/2016 | 3 | 211 | 7.0 | 2.8 | Quantity |
| Ev.6 | 16/05/2016 | 0 | **53 | 5.8 | 20.5 | Quality |
| Ev.7 | 26/04/2017 | 0 | 632 | 18.4 | 2 | Quantity |

Note: *Composite sample ** Predicted runoff duration

The quantity data was obtained by a water level sensor (HOBO Water Level U20I-02) placed in a composed weir, both triangular and rectangular, located at the bioretention entrance.

The water level, which was registered every minute, was then converted to discharge with calibrated weir.

Concerning the quality, Event (Ev)1 presents a composite sample acquired during the first 30 minutes. Samples from Ev.2 and Ev.3 were collected every 4 minutes in the first 24 minutes of the events. In Ev.6, they were collected every 5 minutes during the first 50 minutes. The concentrations of chemical oxygen demand (COD), total organic carbon (TOC), phosphate (PO_4), nitrate (NO_3), nitrite (NO_2) ammonia (NH_3), iron (Fe), cadmium (Cd) and zinc (Zn) were obtained from the laboratory using the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2005).

3.2.3. Quantity calibration and simulation

The PCSWMM software was used to simulate the runoff quantity. Its calibration was performed with Ev.1, Ev.2 and Ev.3 with total rainfall ranging from 1.8mm to 37.8mm, and the intensity from 1.7mm / hr to 5.1mm / hr. It was validated using Ev.4, Ev.5 and Ev.7 with a variation between 6.4 mm and 18.4 mm total rainfall, with an intensity varying between 2 mm / hr and 11.5 mm / hr. Thus, the calibration was done covering a wider range of total precipitated volume, while for validation, a greater variation of rainfall intensity. Both the calibration and validation were carried out using a 1 min timestep.

The calibration was continuous, which was manually performed using the rainfall data from 25/08/2015 to 08/09/2015 including Ev.1, 2 and 3. The validation was also continuous from Ev.4 to Ev.5, but singular for Ev.7. The effectiveness of the calibration and validation was evaluated individually for each event using the Nash-Sutcliffe Efficiency (NSE), R^2 , total runoff volume and the maximum peak difference.

After the calibration and validation were completed, (03/20/2013 to 03/20/2017) rainfall data collected over 4 years were used to simulate the runoff quality and quantity in PCSWMM. The date of 20th March was chosen because it is when the autumn season starts in the southern hemisphere. Thus, 16 seasons were included in this period and Table 3.2 shows their characteristics. As it covers a long period, a 5 min timestep for the simulation was used, rather than 1 minute for quality and quantity calibration and validation. In São Carlos, there are only two well defined seasons, which are summer and winter. Autumn and spring were analyzed as post wet and dry seasons, respectively.

Table 3.2: Rainfall characteristics in each considered season

| Seasons | Rainfall (mm) | | | |
|--|--------------------|--------------------|--------------------|--------------------|
| | Year 1 (2013-2014) | Year 2 (2014-2015) | Year 3 (2015-2016) | Year 4 (2016-2017) |
| Autumn (March 20th to June 21st) | 194.4 | 107.0 | 182.0 | 277.8 |
| Winter (June 21st to September 22nd) | 92.2 | 88.8 | 168.6 | 5.2 |
| Spring (September 22nd to December 21st) | 329.4 | 364.6 | 200.4 | 543.6 |
| Summer (December 21st to March 20th) | 345.4 | 592.6 | 527.4 | 624.8 |
| Year Total | 961.4 | 1153.0 | 1078.4 | 1451.4 |

3.2.4. Quality calibration and simulation

Quantity simulations were done using buildup/washoff model, which is described below. Its calibration was performed using Ev.2 and Ev.3, while the validation was carried out using Ev.1 and Ev.6. The predicted discharge obtained from the quantity simulation was used for a continuous calibration and validation with 6 months of warm-up. To avoid propagating errors from the quantity prediction to the quality calibration, the observed discharge was used for Ev.2 and Ev.3. Validation was carried out using the predicted discharge and Ev.1 was used only to compare the simulated mean concentrations with the one found in the composite sample, and also to verify if their magnitudes corresponded.

The quality calibration was performed according to two methodologies: one calibrating the pollutant load and the other calibrating their concentration. The load-based calibration aimed to maximize the NSE of the load pollutograph, given by Equation (1) (Nash, & Sutcliffe, 1970), while the concentration-based calibration was done by maximizing the Volumetric Efficiency (VE) of the concentration, proposed by Criss & Winston (2008) and shown in Equation (2). VE was used, rather than the sum of the square difference, for an equal weight in the events as the simple sum of the square difference would generate larger results for the events with larger concentrations. This equation was also preferred to the difference between the means of the simulated and observed concentrations, because this can mark a difference between instantaneous concentrations in different periods. Furthermore, the NSE was not used for concentration-based calibration as some concentrations tended to be constant and steady observed values may result in large negative values, not necessarily representing a very poor result (Criss & Winston, 2008). The buildup and washoff parameters were adjusted until the observed and simulated values were closed, then the EXCEL solver tool (non-linear GRG) was used to refine their values.

The difference of the mean concentrations and of total income mass, VE, NSE and R^2 were used to evaluate the quality model. Concentration outliers were identified and not considered during the model evaluation.

$$NSE = 1 - \frac{\sum (C_{obs(t)} - C_{sim(t)})^2}{\sum (C_{obs(t)} - \bar{C}_{obs})^2} \quad (1)$$

$$VE_{(x)} = 1 - \frac{\sum |C_{sim(t)} - C_{obs(t)}|}{\sum C_{obs(t)}} \quad (2)$$

where, $NSE_{(x)}$ is the Nash-Sutcliffe efficiency for pollutant x , $C_{obs(t)}$ is the t -th observed concentration, $C_{sim(t)}$ is the simulated concentration in t -th and $\overline{C_{obs}}$ is the average of observed concentrations.

To simulate the runoff quality, the same exponential buildup and washoff equations used in SWMM (Rossman, 2010) were chosen and adapted for this study. Equation (3) describes the washoff exponential equation.

$$W_{(t)} = \frac{w1 \cdot q^{w2} \cdot B_{(t)} \cdot A}{60} \quad (3)$$

where $W_{(t)}$ is the t -th washoff [kg/min], $w1$ is the washoff coefficient, $w2$ is the washoff exponent, q is the runoff rate [mm/h], $B_{(t)}$ is the buildup in the t -th time [kg/ha] and A is the catchment area [ha].

However, if the result of Equation (3) is higher than the disposal buildup, the washoff would be given by Equation (4):

$$W_t = B_{(t)} \cdot A \quad (4)$$

The buildup equation depends if the washoff has occurred or not, as follows:

$$B_{(t)} = \begin{cases} B_{(t-1)} - \frac{W_{(t-1)}}{A} & \text{if } W_{(t-1)} > 0 \\ b1 \left(1 - e^{-\frac{b2}{1440} T_{(t)}} \right) & \text{if } W_{(t-1)} = 0 \end{cases} \quad (5)$$

where $b1$ is the maximum buildup [kg/ha], $b2$ is buildup exponent [1/days] and $T_{(t)}$ is the previous dry period [min]. Each buildup/washoff parameters physical meaning are better described in the sensitivity analysis (section 3.3.2).

The previous dry period also considers the washoff. If the washoff occurred, time $T_{(t)}$ will be the number of previous dry days corresponding to the remaining buildup.

$$T_{(t)} = \begin{cases} \frac{\ln\left(1 - \frac{B_{(t)}}{b1}\right)}{b2} & \text{if } W_{(t-1)} > 0 \\ T_{(t)} = T_{(t-1)} + 1 & \text{if } W_{(t-1)} = 0 \end{cases} \quad (6)$$

Finally, the simulated concentration in minute t is given by Equation (7):

$$C_{(t)} = \frac{W_{(t)}}{Q_{(t)} \cdot 60} \quad (7)$$

where $Q_{(t)}$ is the discharge [L/s].

3.2.5. Quality sensitivity analysis

The influence of warming up the model on the initial buildup was analyzed. Therefore, antecedent warm up periods (T_w) of 1, 2 and 6 months were used to compare the buildup at the beginning of Ev.1 and Ev.6. For this analysis, 3 different $b2$ were used (0.1, 0.05 and 0.01 days⁻¹) with 3 different $w1$ (0.5, 0.07, 0.01). Table 3.3 presents the simulation periods and their considered initial buildup.

Table 3.3: Warm up periods before Ev.1 and Ev.6.

| | T_w (months) | Warm up period | *T (dry days) | Accumulated rainfall depth in the period (mm) |
|-------------|--------------------------------------|-------------------------|----------------------|--|
| Ev.1 | 6 | 02/25/2015 - 08/25/2015 | 30.0 | 626 |
| | 2 | 06/25/2015 - 08/25/2015 | 6.0 | 94 |
| | 1 | 07/25/2015 - 08/25/2015 | 14.0 | 1 |
| | 0 | 0 | 29.0 | - |
| Ev.6 | 6 | 16/11/2015 - 16/05/2014 | 6.0 | 801 |
| | 2 | 16/03/2016 - 16/05/2015 | 0.0 | 41 |
| | 1 | 16/04/2016 - 16/05/2016 | 16.0 | 9 |
| | 0 | 0 | 0.5 | - |

Note: *T represents the dry period at the beginning of the warm up period

Before the quality calibration, a sensitivity analysis of the buildup and washoff parameters was also performed by varying the w_1 , w_2 , b_1 and b_2 , to verify their influence on the concentration.

3.3. Results and discussion

3.3.1. Quantity calibration and validation

Table 3.4 presents the calibrated catchment parameters and the typical values for its soil type.

Table 3.4: Catchment parameters after quantity calibration.

| PARAMETER | Used | Typical Values | Obs |
|-------------------------|-------|------------------------|--|
| Width (m) | 130 | NA | GIS assisted |
| Slope (%) | 3.5 | NA | GIS assisted |
| Imperv. (%) | 22 | NA | GIS assisted |
| N Imperv | 0.017 | 0.011 - 0.024 | Smooth asphalt - Cement rubble surfaces (McCuen, 1996) |
| N Perv | 0.2 | 0.15 | Short grass (McCuen, 1996) |
| Dstore Imperv (mm) | 0.85 | 1.27 - 2.54 | Impervious surfaces (ASCE, 1992) |
| Dstore Perv (mm) | 3.0 | 2.54-5.08 | Lawns (ASCE, 1992) |
| Suction Head (cm) | 15.0 | 5.57-141.5 / 1.8-41.85 | Sandy Clay Loam / Sandy Loam (Rawls, 1982) |
| Conductivity (mm/hr) | 6.0 | 1.5/10.9 | Sandy Clay Loam / Sandy Loam (Rawls, 1982) |
| Initial Deficit (frac.) | 0.143 | 0.143 / 0.246 | Difference between soil porosity and field capacity (Rossman, 2010). Values for Sandy Clay Loam / Sandy Loam |

Note: NA = not applicable.

The quantity calibration and validation results can be observed in Table 3.5. The simulated and observed discharges in the calibration and validation are shown in Figure 3.2.

The total predicted volume for Ev.4 presented the highest variation when compared to the observed one. It was 21.20% lower, while Ev.7 was the most precise with -1.02% in the total predicted volume. The simulated peak in Ev.3 was 93.03% higher than that observed, but this event has a total predicted volume difference of only 2.96% and a satisfactory NSE value of 0.74.

Table 3.5: Quantity calibration and validation results.

| | Events | NSE | R ² | *Total observed depth (mm) | *Total predicted depth (mm) | Total volume difference (%) | Max. observed Peak (L/s) | Max. predicted peak (L/s) | Max. peak difference (%) |
|--------------------|-------------|------|----------------|-------------------------------------|--------------------------------------|-----------------------------------|-----------------------------------|------------------------------------|--------------------------------|
| Calibration | Ev.1 | 0.95 | 0.96 | 0.54 | 0.61 | 13.21 | 22.41 | 22.97 | 2.50 |
| | Ev.2 | 0.75 | 0.78 | 0.28 | 0.29 | 5.45 | 5.00 | 5.23 | 4.58 |
| | Ev.3 | 0.74 | 0.89 | 13.96 | 13.55 | -2.96 | 98.38 | 189.90 | 93.03 |
| Validation | Ev.4 | 0.80 | 0.81 | 1.51 | 1.19 | -21.20 | 39.12 | 37.63 | -3.81 |
| | Ev.5 | 0.73 | 0.75 | 1.43 | 1.33 | -6.75 | 11.62 | 12.55 | 8.01 |
| | Ev.7 | 0.78 | 0.78 | 3.83 | 3.79 | -1.02 | 38.98 | ** 32.77 | -15.93 |

Note: *Volume normalized by the catchment (2.37ha) ** The maximum peak in Ev.7 was 36.81 L/s, at 11:13am. However, the peak shown in the table was registered at 14:25pm, which is correspondent to the maximum observed peak (see Figure 3.2). The observed peak at 11:12am was 36.66 L/s (0.39% lower compared to the correspondent observed peak).

The predicted runoff discharge, as shown in Figure 3.2, is more unstable than that observed with perturbations corresponding to the precipitation occurrence. The rain gauge precision may be the reason, which registers only 0.2mm when the bucket tips, after catching the corresponding volume. In Ev.2, for example, the rainfall was light and constant, not intermittent as was used for the simulations. It generates small runoff peaks, similar to the ones observed in Ev.1 after 10:19 and is more significant for smaller events.

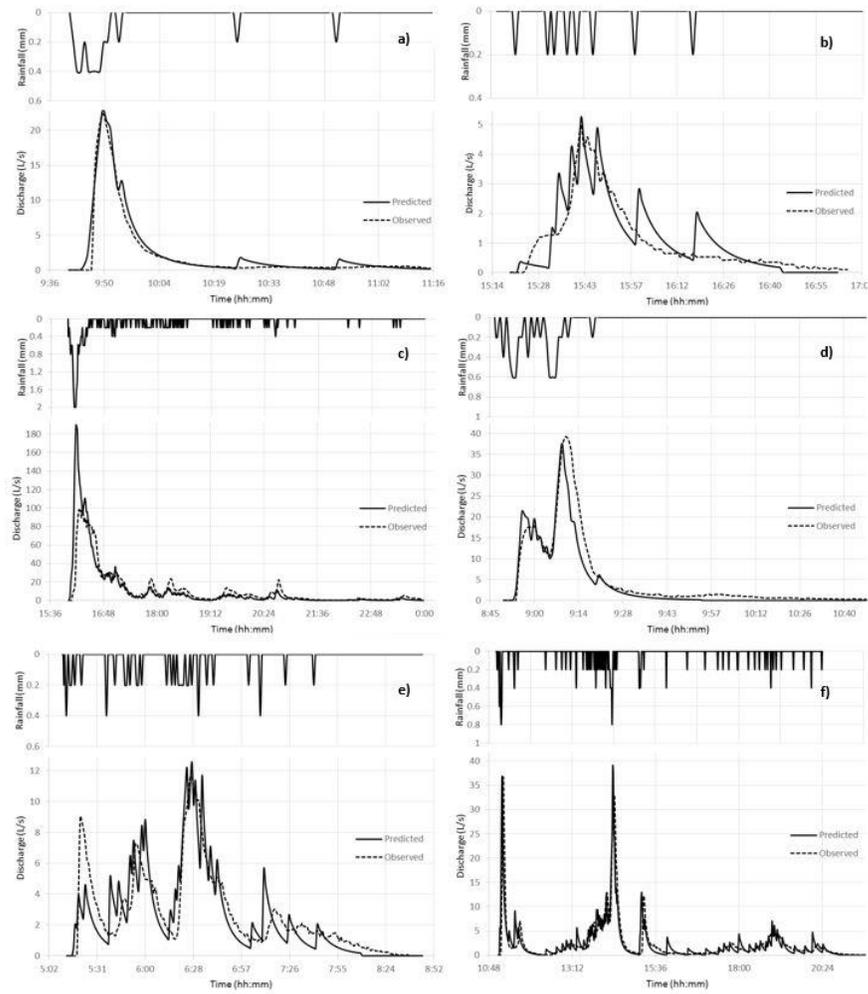


Figure 3.2: Observed and predicted runoff for: Ev.1 (a); Ev.2 (b); Ev.3 (c); Ev.4 (d); Ev.5 (e) and Ev.7

(f)

The events with qualitative monitoring are shown in Figure 3.3 and the difference between the simulated and observed runoff discharge values during the quality sampling time is visible. At 15:29, in Ev2 for example, the observed discharge was about 5 times higher, while at 16:10 in Ev.3, approximately 6 times lower. Since the discharge is crucial for representative quality modelling, the observed discharge was used for quality calibration to avoid the quantity simulation errors.

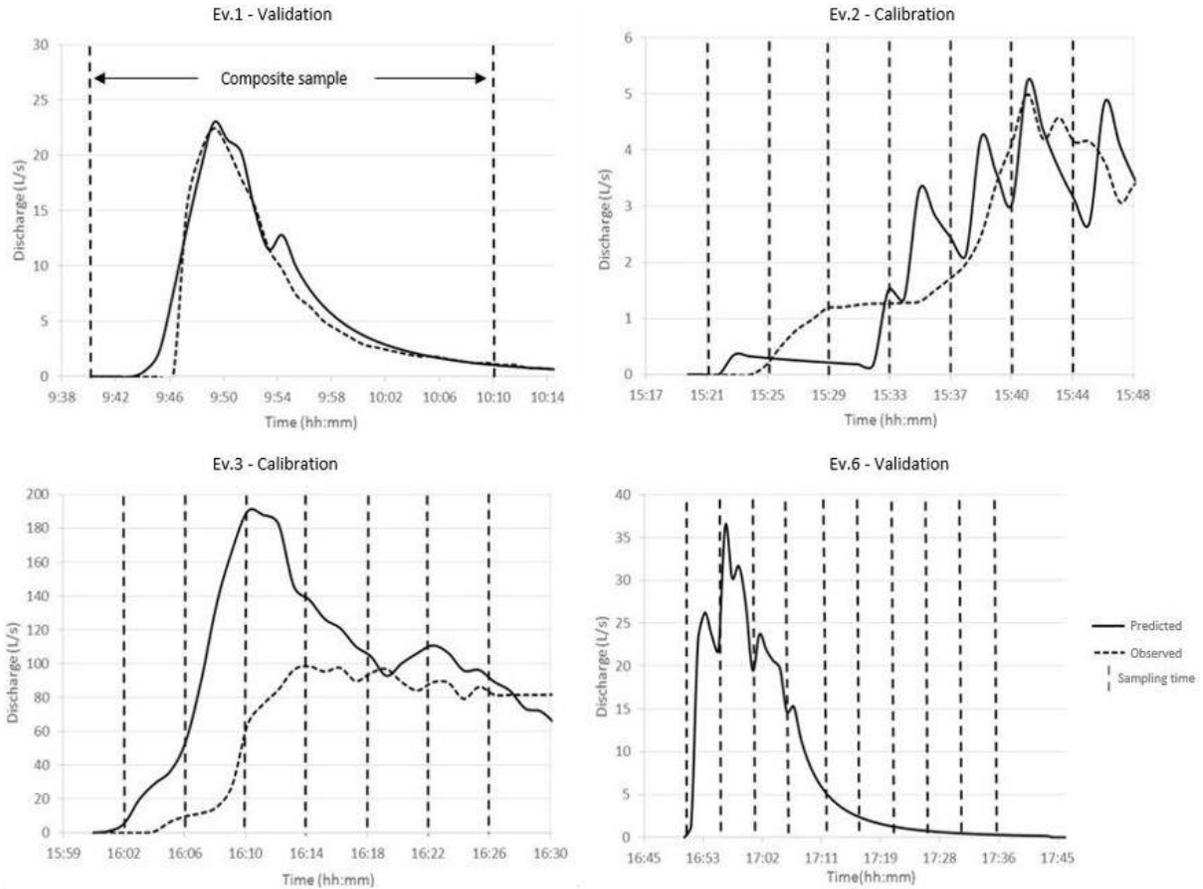


Figure 3.3: Quality monitoring events and the sampling time

3.3.2. Sensitivity analysis of the model warm up

First, the influence of the simulation period on the initial buildup was verified. Table 3.6 presents the buildup difference at the beginning of Ev.1 and Ev. 6, compared to 6 months of warm up.

Table 3.6: Buildup difference (%) relative to 6 months of warm up with sensitivity analysis of parameters $w1$ and $b2$.

| | T_w (month) | Ev.1 $b2(1/day)$ | | | Ev.6 $b2(1/day)$ | | |
|-----------|---------------|---------------------|-------|------|---------------------|-------|-------|
| | | 0.01 | 0.05 | 0.1 | 0.01 | 0.05 | 0.1 |
| $w1=0.5$ | 0 | -29.6 | -14.1 | -4.5 | -93.4 | -88.3 | -82.8 |
| | 1 | -2.0 | 0.0 | 0.0 | -10.1 | -2.3 | -0.3 |
| | 2 | -0.0 | 0.0 | 0.0 | -0.2 | -0.0 | 0.0 |
| $w1=0.07$ | 0 | -49.5 | -18.6 | -4.9 | -89.4 | -94.5 | -94.9 |
| | 1 | -44.8 | -4.9 | -3.4 | -27.3 | -6.3 | -0.8 |
| | 2 | -15.7 | -1.3 | -0.1 | -12.0 | -1.5 | -0.1 |
| $w1=0.01$ | 0 | -66.6 | -22.5 | -5.4 | -93.9 | -95.7 | -95.8 |
| | 1 | -52.0 | -18.9 | -3.9 | -47.1 | -9.1 | -1.0 |
| | 2 | -37.2 | -3.1 | -0.1 | -35.0 | -3.9 | -0.2 |

The difference from 6 months tends to be higher for lower buildup accumulation ($b2$) and higher washoff rates ($w1$). For a $w1 = 0.01$ and $b2 = 0.1 \text{ days}^{-1}$, the buildup can be subestimated in 99.38% in Ev.6 if $T_w=0$, while for $T_w=1$ and $T_w=2$ previous months, the error drops to 51.93% and 31.19% in Ev.1 and to 65.32% and 34.97% in Ev.6, respectively. Using the previous simulation time is more effective for Ev.6 that only has 10.8 hours of previous dry days. With a $w1=0.07$ and $b2=0.05 \text{ days}^{-1}$, for example, by using $T_w=2$, the error drops from 97.23% to 1.54%.

Configuring only with previous dry days ($T_w=0$), it is assumed that the last rainfall event washed all the pollutant, which does not necessarily occur. The longer the warm up time, the more precise the initial buildup is. Thus, to ensure better accuracy, Ev.1, Ev.2, Ev.3 and Ev.6 were simulated continuously for the quality calibration and validation, using 6 months to warm the model up.

3.3.3. Washoff and buildup sensitivity analysis

A sensitivity analysis of a general pollutant was performed, according to their buildup and washoff characteristics. The maximum buildup ($b1$) sensitivity analysis was performed

(appendix A1), and the results showed that it is directly proportional to the concentrations. A $b_1=0.1$ kg/ha for example, generates concentrations 10 times higher than those with a $b_1=0.01$ kg/ha. Thus, this coefficient can be used to adjust the pollutant magnitude. This kind of adjustment is an advantage of the washoff exponential equation, which considers the buildup when compared to the rating curve. Washoff predictions for small catchments are reliable (Sage et al., 2015), however buildup determination is a major problem (Obropta & Kardos, 2007), and this kind of adjustment also helps calibrate the buildup more effectively.

Concerning the washoff, the w_1 and w_2 were also verified and are shown in Figure 3.4. Lower values of w_2 result in higher concentrations for lower discharge. For Ev.2 and w_2 equal to 0.7, for example, there was a peak of concentration when the runoff was minimum, and the opposite occurred when w_2 was equal to 1.3. When w_2 is equal to 1, the discharge does not influence the concentration. It only decreases due to the buildup consumption, otherwise it would be constant (see appendix A2).

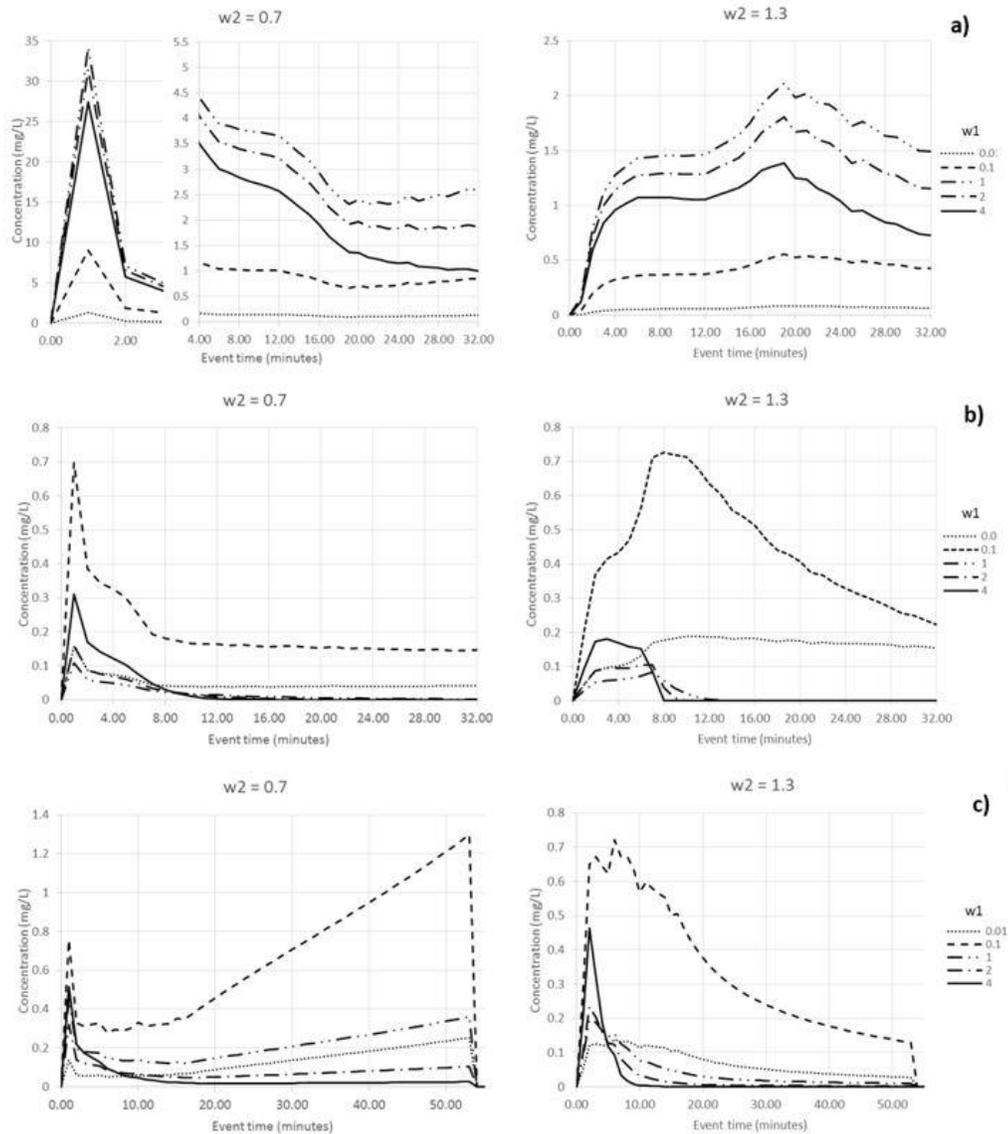


Figure 3.4: Washoff sensitivity analysis for Ev.2 (a), Ev.3 (b) and Ev.6(c). In this case, $b_1=0.1$ kg/ha and $b_2=0.02$ days⁻¹.

A higher w_1 results in higher washoff values and, consequently, higher concentrations. However, the buildup decreases more rapidly and may affect the concentration as lower buildup results in lower concentrations, as previously explained. In Ev.2, the concentration increased with the w_1 until it was equal to 1, while for Ev.3 and 4, it was until 0.1. This can be explained by the

previous rainfall events, which were less intense for Ev.2, when the highest values for w_1 had less impact on the buildup.

For a certain value of w_1 , a previous rainfall event completely washes the pollutant off and the buildup is the same for next event, for any higher w_1 . In Ev.3 with $w_2=1.3$, for instance, the initial buildup is the same for a w_1 higher than 1. The same accumulated pollutant is washed off faster with a w_1 equal to 4, with a higher concentration in a shorter period when compared to a w_1 equal to 1 and 2.

This behavior concerning the w_1 coefficient can be used to better adjustment. If the predicted concentration is too low in Ev.2 and too high in Ev.3 for example, it may become closer to the observed concentration in both events by simply raising the w_1 coefficient. As high intensity rainfalls are common in the tropics, this kind of adjustment may be common and has to be considered when calibrating. It also highlights the importance of warming the model up.

Figure 3.5 shows how w_1 influences the buildup. For lower w_1 , such as 0.01, the buildup tends to be more constant, while for a value equal to 2, the buildup ends more easily. At the beginning of Ev.3 and Ev.6, the disposal buildup is nearly null with a $w_1=1$ and 2, illustrating why the concentration is lower in these events with higher w_1 values.

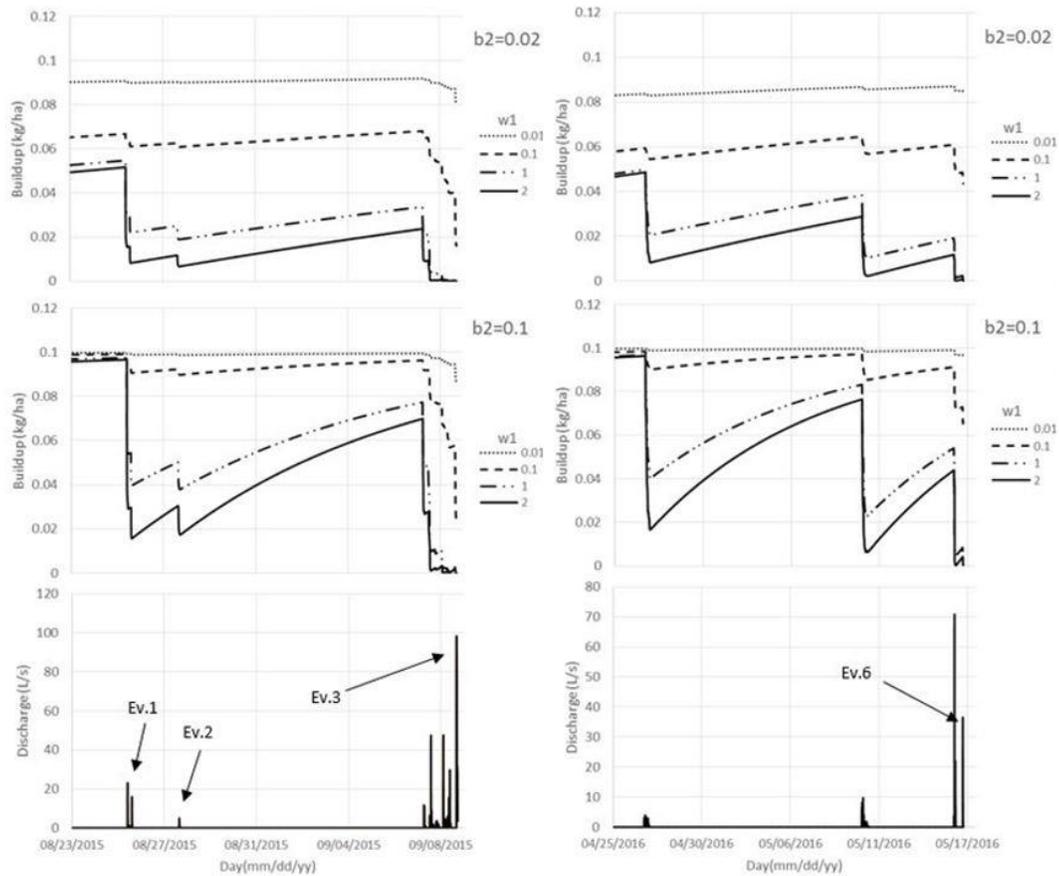


Figure 3.5: Disposal buildup decrease with runoff occurrence (influenced by w_1) and increase (influenced by the b_2). In this case, $b_1=0.1$ kg/ha.

The influence of the buildup accumulation rate is also shown in Figure 3.5. The lower the rainfall volume prior to the event, the more influence this coefficient has on the concentrations. It can be observed in the figure that for Ev.2 with $w_1 = 1$ for example, it has an initial buildup of approximately 0.25 kg/ha for b_2 equal to 0.02 days⁻¹, and around 0.5 kg / ha when b_2 is 0.1 days⁻¹, an increase of 100%. Regarding Ev.3, the buildup is approximately 0.006 and 0.028 kg / ha for b_2 equal to 0.02 and 0.1 days⁻¹ respectively, representing an increase of 330%.

3.3.4. Quality calibration and validation

The buildup and washoff parameters after the concentration and load-based calibration are presented in Table 3.7.

Table 3.7: Calibrated buildup and washoff

| | Concentration calibration | | | | Load-based calibration | | | |
|-----------------------|---------------------------|------|---------------|----------------|------------------------|------|---------------|----------------|
| | Washoff | | Buildup | | Washoff | | Buildup | |
| | w1 | w2 | b1 (kg/ha) | b2 (1/days) | w1 | w2 | b1 (kg/ha) | b2 (1/days) |
| Cd | 0.023 | 1.3 | 0.031 | 0.012 | 0.017 | 1.31 | 0.023 | 0.089 |
| COD | 0.17 | 0.88 | 8.6 | 0.0058 | 0.018 | 0.69 | 11 | 0.027 |
| Fe | 0.42 | 0.89 | 0.36 | 0.086 | 0.36 | 0.67 | 0.36 | 0.029 |
| NH₄ | 0.10 | 0.93 | 0.15 | 0.017 | 0.0025 | 0.79 | 2.7 | 0.014 |
| NO₃ | 0.29 | 0.92 | 0.10 | 0.024 | 0.011 | 0.45 | 0.82 | 0.0078 |
| NO₂ | 0.043 | 0.92 | 0.020 | 0.0014 | 0.0012 | 0.86 | 0.080 | 0.024 |
| TOC | 0.062 | 0.92 | 5.9 | 0.0043 | 0.051 | 0.91 | 5.5 | 0.0046 |
| PO₄ | 0.088 | 1.0 | 0.019 | 0.039 | 0.12 | 1.07 | 0.012 | 0.033 |
| Zn | 0.11 | 1.0 | 0.021 | 0.029 | 0.098 | 1.04 | 0.021 | 0.029 |

Table 3.8 compares the predicted and observed results for the calibration (Ev.2 and Ev.3) and validation (Ev.6). The concentration-based calibration, as expected, resulted in predicted concentrations close to those observed, except for Fe in Ev.3 with a variation of 193% in the mean concentrations. NH₃, Cd, COD and Fe did not have the same proximity in the concentrations for Ev.6 with a variation of 164, 574, 193, 226%, respectively. In Ev.1, the highest variation was determined for Fe, when the predicted concentration was 45.9% higher, indicating that this calibration was suitable in this event.

The load-based calibration generally resulted in a higher variation in the mean concentration, such as NO₃ in Ev.2 with a 214% variation against 16.4% when calibrating the concentration. However, this method more accurately predicted the total pollutant mass, and consequently the event mean concentration (EMC) since the runoff volume is constant. Even with a 214% variation in NO₃ mean concentration, the predicted total mass was only 1.9% lower, while the predicted mass, using the concentration-based calibration, was 52% higher. The

validation with Ev.1 presented good results, except for Fe with 80% variation. The mass variation was also low in Ev.6, indicating a good fit of the calibrated buildup and washoff parameters.

Table 3.8: Calibration methods comparison.

| | | Concentration-based calibration | | Load-based calibration | |
|-----------------------|------|--------------------------------------|----------------------------------|--------------------------------------|----------------------------------|
| | | Difference of mean concentration (%) | Difference of EMC/total mass (%) | Difference of mean concentration (%) | Difference of EMC/total mass (%) |
| Cd | Ev.1 | 38.39 | - | 13.00 | - |
| | Ev.2 | -5.13 | 10.09 | -22.72 | -10.31 |
| | Ev.3 | 3.46 | 11.88 | -14.56 | -7.34 |
| | Ev.6 | 573.73 | 775.20 | 510.72 | 691.86 |
| COD | Ev.1 | 4.51 | - | -35.14 | - |
| | Ev.2 | 17.27 | 37.09 | 7.20 | -11.35 |
| | Ev.3 | -15.79 | -10.42 | -21.54 | -23.74 |
| | Ev.6 | 192.69 | 128.99 | 238.84 | 63.57 |
| Fe | Ev.1 | 45.92 | - | 80.28 | - |
| | Ev.2 | -10.29 | 8.33 | 8.95 | -15.09 |
| | Ev.3 | 192.68 | 101.17 | 62.79 | -1.49 |
| | Ev.6 | 226.39 | 49.56 | 199.85 | -19.75 |
| NH₄ | Ev.1 | -29.29 | - | -29.29 | - |
| | Ev.2 | 4.23 | 21.13 | -109.48 | -9.71 |
| | Ev.3 | -5.60 | -7.02 | 109.53 | -19.21 |
| | Ev.6 | 163.78 | 126.60 | -45.33 | 86.09 |
| NO₃ | Ev.1 | 17.45 | - | 1.92 | - |
| | Ev.2 | 16.40 | 51.62 | 214.27 | -1.88 |
| | Ev.3 | 2.66 | 18.50 | 13.47 | -10.02 |
| | Ev.6 | 28.19 | 26.71 | 171.53 | -19.92 |
| NO₂ | Ev.1 | 24.29 | - | 24.29 | - |
| | Ev.2 | -15.32 | -1.69 | -14.79 | -7.41 |
| | Ev.3 | -4.61 | -0.29 | -8.14 | -5.95 |
| | Ev.6 | -10.17 | -59.90 | 15.27 | -8.80 |
| TOC | Ev.1 | 0.90 | - | 12.36 | - |
| | Ev.2 | -10.57 | -2.13 | -14.91 | -7.82 |
| | Ev.3 | -10.67 | -1.22 | -12.93 | -3.86 |
| | Ev.6 | 9.18 | 20.55 | 4.99 | 13.36 |
| PO₄ | Ev.1 | -2.31 | - | 4.55 | - |
| | Ev.2 | 7.99 | 11.72 | -7.24 | -1.24 |
| | Ev.3 | 3.50 | 18.69 | -19.69 | -7.86 |
| | Ev.6 | 14.08 | 12.08 | -11.24 | -4.36 |
| Zn | Ev.1 | 12.41 | - | 12.84 | - |
| | Ev.2 | 0.27 | 1.38 | -7.61 | -5.39 |
| | Ev.3 | -4.71 | -6.44 | -2.34 | -2.99 |
| | Ev.6 | 16.59 | 0.45 | 11.48 | -1.04 |

The only pollutants with high mass variation were NH₃, Cd, and COD, in which the observed concentrations were too low. Other attempts to adjust the predicted concentrations to

the observed ones in this event were made, such as a higher w_1 coefficient for a lower initial buildup in this event or a lower b_1 . However, the good fit in Ev. 2 and/or Ev. 3 were lost, suggesting that this model was not good for these pollutants prediction.

Figure 3.6 shows the calibration methods for PO_4 in Ev.3. By optimizing the NSE of the load pollutograph, the fit of concentrations in higher runoff discharges is prioritized. The first two samples pull the calibration upwards when the concentration is calibrated. By calibrating the load, these two samples tend to be ignored for a closer approximation of the following samples, when the discharge is considerably higher. The calibration and validation of the other pollutants can be observed in the appendix (appendix Figures A4-A12).

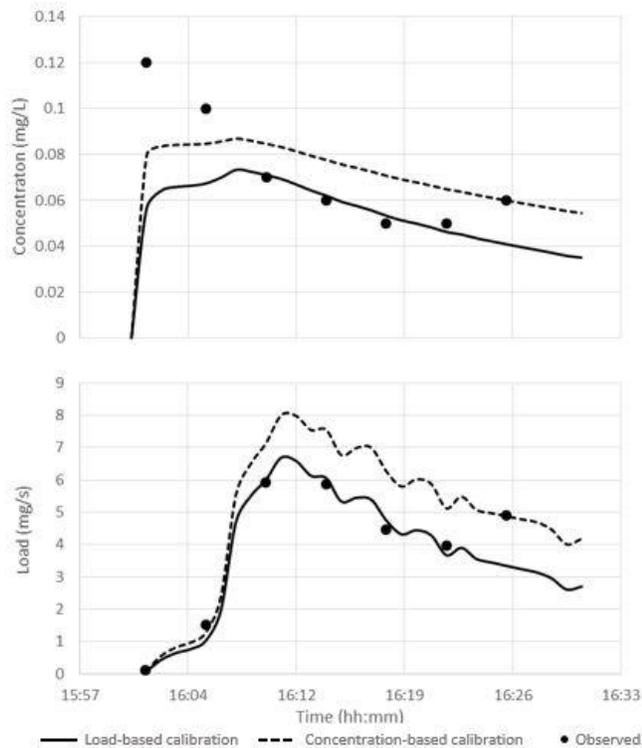


Figure 3.6: PO_4 calibration in Ev.3

As this study aims to estimate the total mass of pollutants and their EMCs into the bioretention, and not to analyze the distribution of concentrations over time as first flush studies, the load-based calibration method was used for the simulations. Since NH_4 , Cd, and COD could not be validated with Ev.6, they were not included in the simulations to characterize the runoff in this study. However for the other pollutants, this kind of calibration also generated satisfactory values of VE, NSE and R^2 for their load pollutograph (appendix Table A3), in addition to the predicted mass proximity.

3.3.5. Runoff characterization

First, rainfall events were separated by duration or, for those without runoff, by the basin time of concentration of 20 minutes. A total of 1,520 events occurred in the period, of which 628 (41%) did not generate runoff with a total rainfall varying from 0.2mm and 0.8mm. Every event with 1mm or higher generated runoff.

Table 3.9 presents the predicted runoff volume and the total mass of Fe, NO_3 , NO_2 , PO_4 , TOC and Zn. Over 4 years, approximately 1223mm (or 29.000m³) of runoff was generated. This runoff washed approximately 9659g/ha, 3818.2g/ha, 93.8g/ha, 306.9g/ha, 29731g/ha, 475.5g/ha of Fe, NO_3 , NO_2 , PO_4 , TOC and Zn, respectively, per hectare of catchment.

The proportion of washed pollutants was also observed in the seasons. As expected, summer is the season when the highest mass of pollutants is washed, followed by spring, autumn and winter, a result influenced mainly by the total volume of rainfall. The only exception is TOC, which was more washed in spring than summer, and more in winter than autumn, influenced maybe by the leaves falling during the winter. The proportions of NO_2 throughout the seasons are the most similar to the proportions of runoff, suggesting that this pollutant washing is more dependent on the runoff.

Table 3.9: Predicted runoff quality and quantity for the simulated period (March, 2013- March, 2017)

| | Rainfall | Runoff | Fe | NO3 | NO2 | PO4 | TOC | Zn |
|----------------------|-----------------------|---------------------|--------------------|--------------------|---------------------|---------------------|---------------------|----------------------|
| | Absolute values | | | | | | | |
| | (mm) | (mm) | (g/ha) | (g/ha) | (g/ha) | (g/ha) | (g/ha) | (g/ha) |
| Total accumul | 4644.2 | 1223 | 9659 | 3818.2 | 93.8 | 306.9 | 29731 | 475.5 |
| Year averag | 1161 (± 208) | 305.8 (± 9.5) | 5723 (± 687) | 2262 (± 271) | 55.5 (± 13.9) | 181.8 (± 8.8) | 17615 (± 757) | 281.6 (± 10.5) |
| | Seasonal fraction (%) | | | | | | | |
| Autumn | 16.39% | 14.60% | 19.95% | 15.59% | 14.89% | 18.76% | 17.83% | 18.73% |
| Winter | 7.64% | 7.75% | 16.93% | 10.11% | 7.95% | 14.94% | 19.06% | 15.21% |
| Spring | 30.96% | 31.95% | 30.70% | 35.58% | 32.15% | 31.46% | 35.20% | 31.71% |
| Summer | 45.01% | 45.70% | 32.42% | 38.73% | 45.01% | 34.84% | 27.91% | 34.36% |

A relation between the total runoff volume and pollutant mass generated in an event was observed and is shown in Figure 3.7. It can be observed that for lower w_1 , the relation between the runoff volume and pollutant mass was more linear as it had a lower impact on the total buildup, as can be seen in the section on washoff and buildup sensitivity analysis. This explains the similarity in runoff and NO_2 proportion in the seasons. This influence of the w_1 on relation between total pollutant mass and total runoff volume is expected to be more significant in the tropical zone, due to higher frequency of intense rainfalls.

For Zn, PO_4 and Fe, the event that generated the highest mass was a 29.6mm rainfall depth that generated 171.3m³ of runoff. It was the first rainfall event with runoff in the spring of 2016, after a winter with only 5.2mm of rainfall.

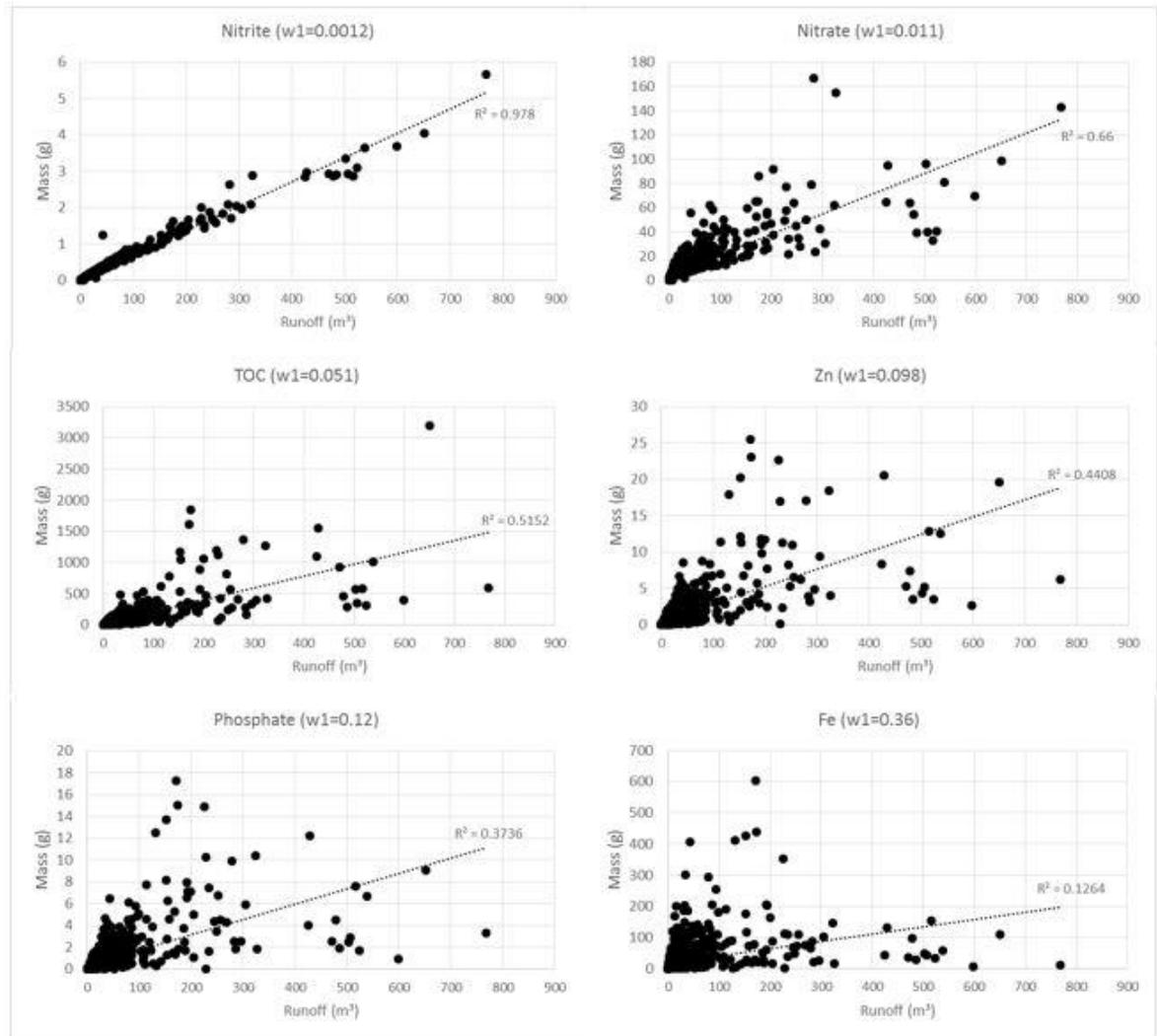


Figure 3.7: Runoff volume and pollutant mass relation

The EMC for each of these events was calculated and their mean for each one was determined, shown in Table 3.10. In general, the highest EMCs were found during the winter, followed by autumn, spring and summer, except for NO_3 that has an EMC in spring higher than in autumn. It occurs due to longer accumulation periods and lower runoff volumes during the winter, facilitating the buildup increase. Winter is also the season when water bodies have lower discharges and higher concentrations of pollutants in the runoff can be more harmful.

Table 3.10: Predicted EMC of the pollutants

| | Fe (mg/L) | NO₃ (mg/L) | NO₂ (mg/L) | PO₄ (mg/L) | TOC (mg/L) | Zn (mg/L) |
|---------------------|------------------|------------------------------|------------------------------|------------------------------|-------------------|------------------|
| Autumn | 2.84 (±3.57) | 1.09 (±0.81) | 0.011 (±0.0026) | 0.036 (±0.029) | 3.65 (±2.33) | 0.055 (±0.042) |
| Winter | 6.05 (±6.17) | 1.53 (±0.84) | 0.012 (±0.0020) | 0.059 (±0.037) | 7.25 (±2.79) | 0.092(±0.051) |
| Spring | 2.25 (±2.41) | 1.32 (±0.94) | 0.011 (±0.0023) | 0.031 (±0.0023) | 3.43 (± 2.15) | 0.048 (±0.033) |
| Summer | 1.70 (±2.01) | 0.98 (±0.73) | 0.011 (±0.0032) | 0.026 (±0.019) | 2.36 (±1.42) | 0.040 (±0.027) |
| Total period | 2.46 (±3.27) | 1.15 (±0.83) | 0.011 (±0.0028) | 0.032 (±0.026) | 3.34 (±2.40) | 0.050 (±0.038) |

The predicted EMCs found in this study are relatively low when compared to other runoff EMCs found in literature (Table 12), which indicates that the studied catchment presents low contaminant content. The average EMC of Nitrite, phosphate, TOC and Zn lower than any of those presented in table 12, while Fe was higher when compared to the one found by Bäckström et.al (2003) and nitrate when comparing to Wang et. al (2013), Zhang et.al (2012) and Barrett et.al (1998). The pollutants concentration in the runoff vary from each study presented in the table, and those with the same catchment type have also different EMCs. The reason may be other influencing factors such as soil type and pollution sources at the surroundings.

This studied catchment is surrounded by an environmental conservation area, which may prevent higher pollutants buildup in the area. Another possible reason to low EMC is the fact of including all the events in the entire period, even the ones after other events when the buildup is relatively lower.

Table 3.11: Average EMC in other studies

| | | EMC (mg/L) | | | | | | |
|----------|-------------------|------------|-----------------|-----------------|-----------------|------|------|------------------------|
| Location | Catchment type | Fe | NO ₃ | NO ₂ | PO ₄ | TOC | Zn | Reference |
| China | University Campus | 11.8 | 1 | - | - | - | 0.69 | Wang et.al (2013) |
| China | Farmland | - | 4.18 | - | 0.32 | - | - | Lang et.al (2013) |
| | Forestland | - | 0.6 | - | - | 10.3 | - | |
| China | Farmland | - | 5.09 | - | - | 19.7 | - | Zhang et.al (2012) |
| | Village | - | 9.9 | - | - | 10.8 | - | |
| USA | Parking lot | - | 0.39 | 0.025 | 0.075 | 12 | - | Brown & Borst (2015) |
| USA | Highway | 2.8 | 1.07 | - | - | 46 | 0.22 | Barrett et.al (1998) |
| Sweden | Highway | 0.33 | 2.87 | - | - | 11.8 | 0.13 | Bäckström et.al (2003) |
| USA | Highway | - | 2.7 | 0.3 | 0.2 | - | 0.5 | Han et.al (2006) |
| Italy | Highway | 3.1 | 4.8 | 0.7 | - | - | 1.7 | Mangani et.al (2005) |
| Germany | Roof | - | - | - | - | 4.3 | 6.8 | Schriewer et.al (2008) |

3.4. Conclusions

This paper discussed the steps to estimate the quantity and quality of runoff drained in the past 4 years in a subtropical catchment. Firstly, a sensitivity analysis elucidated how the buildup and washoff parameters influence the predicted concentration: (i) buildup estimation can be easier when using washoff exponential equation, rather than the rating curve; (ii) the magnitude of concentration can be also adjusted with the w_1 , when combined to previous rainfall characteristics; (iii) the calibration reliability of events were highly dependent upon the model warm-up period.

Concerning the model calibration and validation, the following can be summarized: (i) the overall calibration and validation of the quantity was satisfactory. The higher difference in peak flows was for Ev.3, in which the predicted peak was 93% higher. Ev.4 presented the highest difference in the total runoff volume, and the simulated one was approximately 20% lower. (ii) the quality load-based calibration presented a greater proximity of the total mass and the EMC, however with a higher difference in the mean concentrations. Even with lower precision for the smallest discharge, the load-based calibration was chosen for the simulations; (iii) load-based

calibration generated satisfactory predicted pollutant mass for all pollutants with a major difference for NH₃ in Ev.3 when the predicted pollutant mass was 19% lower. However, NH₃, Cd and COD could not be validated, which suggests that the quality model used in this paper was not suitable for these pollutants.

After quality and quantity calibration and validation, the runoff could be finally characterized: (i) in 4 years, it is estimated that 9659g/ha, 3818.2g/ha, 93.8g/ha, 306.9g/ha, 29731g/ha, 475.5g/ha of Fe, NO₃, NO₂, PO₄, TOC and Zn were respectively washed by approximately 1223 mm (or 29,000m³) of runoff; (ii) the lower the w_1 coefficient, the more linear the relation between the total pollutant mass generated and the total runoff; (iii) except for TOC, most of the pollutant mass was generated during the summer (wet season). Winter (dry season) presented the highest EMCs, followed by Autumn (post dry season), due to longer accumulation periods.

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4. EFFECTS OF CLIMATE CHANGE ON LOW IMPACT DEVELOPMENT (LID) PERFORMANCE - A CASE STUDY IN SÃO CARLOS, BRAZIL.

A modified version of this chapter will be submitted as: César Ambrogi Ferreira do LAGO et al., Effects of Climate Change on Low Impact Development (LID) Performance - a Case Study in Sao Carlos, Brazil.

Abstract

Urbanization increases runoff volume and velocity, resulting in higher risks of flooding and a higher amount of pollutants carried by stormwater. To mitigate these impacts, Low Impact Development practices (LID), such as bioretention have been used to treat stormwater runoff enhancing the sustainability of urban drainage systems. However, climate change is expected to alter the rainfall regime and, consequently, the efficiency of LID controls, and its impacts need to be better evaluated. In addition, there are few studies analyzing LID performance under a subtropical climate, which has different rainfall regimes and a runoff generation process when compared to temperate climates. This study, in particular, estimated the efficiency of a bioretention in São Carlos, Brazil in a subtropical region for 4 different future periods (2020-2039, 2040-2059, 2060-2079 and 2080-2099) with an estimated rainfall for 2 RCP scenarios (4.5 and 8.5), forced by the HADGEM2-ES global model. These scenarios were based on the ETA Regional Climate model and downscaled to São Carlos by the Brazilian National Institute for Space Research and compared to the period of 1980-1999. The PCSWMM software was used to determine the income of runoff and pollutants and a specific model for the outflow was used to better represent the characteristics of the studied bioretention. In 100 years, the precipitated volume will decrease by 13% and 29% if RCP 4.5 or RCP 8.5 occur, respectively. Climate change, however has little effect on the quantity efficiency, which is approximately 80% for both scenarios and all analyzed periods. Climate change improves the EMC reduction by the bioretention, minimizing the EMC increase by the phenomenon. Results show that pollutants with higher w_1 washoff coefficient will have higher EMC reduction over the years. The bioretention efficiencies tend to maintain over the years. On the other hand, the EMC reduction tends to increase.

Keywords: Climate changes, Bioretention, Quali-quantity efficiencies.

4.1.Introduction

According to IBGE (2016), approximately 185 million Brazilians live in urbanized areas. One of the main consequences of urban development is the change in the hydrologic cycle as it generates soil imperviousness, resulting in an increase in the runoff volume (Lucas & Sample 2015, Guan, Sillanpää, & Koivusalo, 2015), and consequently in higher risks of floods (Sun, Tong & Yang 2016, Sun et al. 2017) and the amount of pollutants carried (Fletcher, Andrieu & Hamel, 2013), affecting the quality of urban rivers. Thus, poorly planned urbanization tends to increase qualitative and quantitative water insecurity. To mitigate these impacts, Low impact Developments (LID), such as bioretention cells are being used to treat not only quantitative but also qualitative rainwater for a more sustainable urban drainage system (Macedo, 2017).

In addition to the influence of urbanization, different climates generate different hydrological responses that may interfere with the performance of these LID practices. In tropical climates for example, high intensity rainfalls result in a faster response in the runoff (Piro & Carbone, 2014), where the pollutants are washed faster. However, few studies evaluate LID response to the rainfall regime in these regions (Macedo et al, Submitted).

According to Marengo & Ambrizzi (2014), climate change can also aggravate water insecurity in Brazil, through greater occurrences of floods and droughts, generating various negative impacts such as the increase of food and energy insecurity. Chou et al. (2014-a) verified the impacts of climate change in South America through two Representative Concentration Pathway (RCP) scenarios of 4.5 and 8.5, forced by two global models (HadGEM2-ES and the MIROC5). They estimate that during the summer there will be a decrease in rainfall volume in the central region of Brazil and an increase in the southeast region. In the austral winter, a decrease is expected in both regions. They also suggest that intense rainfall will be more frequent

in the south-central region of the country, there will be more consecutive dry days in the northeast region, which already suffers from severe droughts, and the humid Amazon region will have fewer consecutive wet days. Lyra et al (2017) evaluated the impacts of climate change on the metropolitan areas of São Paulo, Rio de Janeiro and Santos, which are of vital economic importance to Brazil. It is estimated that there will be an average increase of 9°C by the end of the century, if scenario RCP 8.5 prevails, with a reduction of 50%, 45% and 40% in rainfall volumes for the metropolitan region of Rio de Janeiro, Santos and São Paulo, respectively. The RCP 8.5 and 4.5 scenarios are projections of radiative forcing levels reaching respectively 8.5 and 4.5 W/m² by the end of the century based on greenhouse gas emissions (Van Vuuren, 2011).

The present study aims to evaluate the impacts of climate change on a bioretention located in the city of São Carlos, in the southeastern region of Brazil with a subtropical climate. The RCP 4.5 and 8.5 scenarios were analyzed, with downscaling based on the Eta Regional Climate Model forced by the global HadGEM2-ES model. The data were acquired with a spatial scale of 5km and a 3-hour time scale, which was later reduced to 5min through a modified Bartlett-Lewis rectangular pulse model, and therefore the generation of runoff and pollutants into the bioretention could be simulated. For the bioretention outflow, a specific model was used for greater accuracy on depth accumulation on its surface.

4.2.Methodology

4.2.1.Study area and data collection

The bioretention has 60m² area. It has a 0.5m top layer composed by soil, and 2.7m for storage composed by gravel (0.7m) and sand (2m). This LID has undergone thorough maintenance which has increased its efficiency (Macedo et al., 1017) and will be its performance after this maintenance that will be evaluated.

The studied bioretention is located on Campus 2 at the University of São Paulo (USP), São Carlos, Brazil, with a Cfa classification according to Köppen and Geiger. It receives runoff from an area of 2.3 hectares with 22% of imperviousness. The local soil has 20% clay, 10% silt and 70% sand composition and is classified between sandy clay loam and sandy loam soils (USDA, 2017). Its average slope is 3.5%, obtained through Digital Elevation Model (DEM). The campus is currently under occupation and the impervious area is expected to grow, reaching 50% by 2025 and 80% by 2100 (Rosa, 2016).

Data from seven monitored events were used to calibrate the quantity and quality of the inlet runoff, however only three have quantity data after the maintenance. The outlet calibration and validation were also done with seven monitored events, with three events after the maintenance and four more recent ones. Rainfall data was obtained using a 0.2mm precision rain gauge, installed around 400m far from the bioretention. A water level sensor (HOBO Water Level U201-02) was used to measure the water level every minute, which was then used to calculate the discharge. The following pollutants were analysed: total organic carbon (TOC), phosphate (PO₄), nitrate (NO₃), nitrite (NO₂), iron (Fe) and zinc (Zn).

4.2.2. Bioretention outflow model

The maximum storage observed during all the monitored events was 1.7m from the 2.7m possible inside the bioretention (63% of its capacity). Thus, infiltration in the upper soil layer is the only determinant factor for the bioretention quantity efficiency. The water balance in this layer is shown in Equation (1):

$$\Delta H = \left(\frac{(Q_{in} - Q_{out}) \cdot t}{A \cdot \phi_a} + P - f \cdot t - E \right) \cdot 1000 \quad (1)$$

where ΔH (m) is the variation of the level at the surface of the bioretention, t (s) is the timestep, Q_{in} ($L.s^{-1}$) is the inflow, Q_{out} ($L.s^{-1}$) surface exit flow, A (m^2) is the surface area of the bioretention, ϕ_a is the fraction of the unoccupied surface area, f ($mm.s^{-1}$) is the infiltration rate, P (mm) is the precipitation and E (mm) is the evaporation in t seconds. The outflow is given by the equation of a triangular weir as a function of the surface ponding depth (Porto, 2006). If the berm height is exceeded, there will be no more ponding on the bioretention surface and the excedance is then instantly transformed into flow. The cases for the outflow of the bioretention are given by (2):

$$\begin{cases} Q_{out} = 0 & \text{if } H \leq h \\ Q_{out} = 1.427(H - h)^{2.5} & \text{if } H > h \\ Q_{out} = 1.427hb^{2.5} + A.\phi_a.(H - hb) & \text{if } H > hb \end{cases} \quad (2)$$

for a ponding depth H (m), a height h (m) of the weir e and a hb (m) berm height.

The infiltration rate f was calculated by the Green-Ampt method (Green & Ampt, 1911), in Equation (3)

$$f = k_s \frac{(\Psi + L + H)}{L} \quad (3)$$

where k_s is the saturated hydraulic conductivity (mm/s), Ψ (mm) is the suction head and L (mm) is the depth of the saturated layer, given by (4). Since below the soil is a layer of gravel and a layer of sand, with a much higher hydraulic conductivity, they will not be saturated and L will always be equal to or lower than the soil layer depth L_s (mm).

$$L = \frac{F}{\theta_d} \quad (4)$$

$$\theta_d = (\Phi - \theta_i) \quad (5)$$

$$0 < L \leq L_s \quad (6)$$

where F (mm) is the total infiltrated depth, θ_d is the moisture deficit, Φ is the soil porosity and θ_i is the initial moisture below the wetting front, given by (4).

For values of $L \rightarrow 0$ at the beginning of the infiltration process, $f \rightarrow \infty$. To prevent the possibility of an infinite infiltration value, the maximum depth (f_{max}) to be infiltrated in a time, correspondent to the minimum timestep, was obtained. Therefore, the maximum infiltrated depth at an event beginning must be equal to the infiltration rate:

$$f_{max} = k_s \frac{\left(\psi + \frac{f_{max}}{\theta_d} + H \right)}{\left(\frac{f_{max}}{\theta_d} \right)} \quad (7)$$

During the phase there will be no ponding, then $H=0$. After working equation (7), f_{max} is given by Equation (8):

$$f_{max} = \frac{k_s \theta_d}{2} \left(\theta_d^{-1} + \sqrt{\theta_d^{-2} + \frac{4\psi}{k_s \theta_d}} \right) \quad (8)$$

The value of θ_i , to calculate θ_d , depends on the water depth (LW) contained in the soil, by Equation (6). The maximum depth in the soil occurs when the whole layer is saturated and, to maintain the bioretention plants healthy, soil moisture will always be equal to or greater than the wilting point (WP).

$$\theta_i = \frac{LW}{L_s} \quad (9)$$

$$L_s WP \leq LW \leq L_s \Phi \quad (10)$$

The water variation in the soil varies as shown in Equation (11). If there has been infiltration, it will be added to the previous water content depth, considering that the infiltrated volume is equally distributed in the whole layer, and subtracting the evapotranspiration loss. For an amount of water greater than field capacity (FC), when the influence of the gravitational force occurs, the equation adapted from Rossman (2010) was used to decrease the water in the soil. Below the field capacity, the water decrease occurs only by evapotranspiration.

$$\left\{ \begin{array}{l} Lw \leftarrow Lw + F - ET \quad \text{if } f > 0 \\ Lw \leftarrow Lw - \frac{Ls\sqrt{k_s}(\Phi - WP)\Delta t}{75} \quad \text{if } Lw \geq L_sFC \\ Lw \leftarrow Lw - ET \quad \text{if } Lw < L_sFC \end{array} \right. \quad (11)$$

The daily reference evapotranspiration was used for calibrating this model, which was calculated by the Penman-Monteith method at a station 6.7 km far from the bioretention, obtained from the Embrapa (Brazilian Agricultural Research Company) website. Diurnal and nocturnal evapotranspiration were considered separately, with nocturnal evapotranspiration corresponding to 14% of the daily total (Malek, 1992; De Dios et al, 2015).

4.2.3. Climate Change Scenarios

Four different future periods (2020-2039, 2040-2059, 2060-2079 and 2080-2099) were analyzed for 2 RCP scenarios (4.5 and 8.5), forced by the HADGEM2-ES global model. These scenarios were based on the ETA Regional Climate model and downscaled to São Carlos by the Brazilian National Institute for Space Research and is available at projeta.cptec.inpe.br (Chou et al., 2014-a; Chou et al, 2014-b; Lyra et al, 2017). The 1980-1999 period was used for comparison and this historical data was also acquired from the same website.

Moreover, 5km^2 and 3 hour spatial and temporal resolution data of rainfall, evapotranspiration and temperature were acquired. As the concentration time of the studied basin is 20 min, the rainfall data had to be desegregated to a 5min timestep. Therefore, the Modified Bartlett-Lewis Rectangular Pulse Stochastic Rainfall Model was used for desegregation.

Modified Bartlett-Lewis Rectangular Pulse Stochastic Rainfall Model basically consists of 4 steps: (1) a storm starts according to the Poisson process (t,λ) ; (2) A random number η , with a gamma distribution of mean α/v and variance α/v^2 , is specified to each event; (3) Each rainfall has one or more cells; the secondary cells will start with the Poisson process $(t,\eta k)$, and no more cells will start after an exponentially distributed average time $(1/\eta\Phi)$; (4) each cell is a rectangular pulse with an exponentially distributed height with mean μ_x , and duration also exponentially distributed with mean $1/\eta$. Then the storm will be given by the sum of all cells, which has the frequency and characteristics determined by 6 parameters (λ , α , v , k , μ_x and Φ). (Back et al., 2011; Rodriguez et al., 1987; Rodriguez et al., 1988)

Four years were used to calibrate the Bartlett-Lewis modified model parameters. To do this, the historical rainfall regime of a 5min timestep was aggregated to a 3 hour timestep and then desegregated. The calibration was done to approximate the observed and desegregated number of wet cells, variance, total rainfall and percentage of cells with a precipitation depth lower than 0.4mm, a depth between 0.4mm and 1mm, 1mm and 2mm, 2mm and 4mm, 4mm and 10mm, and those higher than 10mm. The model parameters were calibrated for each month individually, and therefore 12 calibrations were performed with 4 months each.

4.3.Results

4.3.1. Outflow calibration and validation

Table 4.1 shows the calibrated parameters. The local soil is classified between Sandy Clay Loam and Sandy Loam, (USDA, 2017), thus the reference values for these two types are shown. Two parameters in the table can be highlighted: the ponding area of 50% and the conductivity of 770mm/hr.

The percentage of 50% for the ponding area is justified by the berm that covers part of the bioretention surface area, and the surface area loss is due to the increase in the containment barrier at its back, one of the actions performed during maintenance in the technique (Macedo et al., 2017).

The difference between the conductivity measured in the soil and the effective conductivity in the bioretention is explained by the semi-direct injection measure, also performed during maintenance, which consists of holes in the soil layer and filled with sand. This calibration shows that the semi-direct injection was responsible for an increase in approximately 13,000% in the top layer hydraulic conductivity. Considering a conductivity of 3,600,000 mm/hr for sand, it is estimated that the injections correspond to 21% of the bioretention surface area.

Table 4.1: Calibrated bioretention parameters

| Parameter | Used | Typical Values | Obs |
|----------------------------------|------|-------------------------------|--|
| Area (m ²) | 60 | - | Sized |
| Ponding area (%) | 50 | - | Sized and maintenance measures |
| Berm height (mm) | 30 | - | Sized |
| Surface slope (%) | 0 | - | Sized |
| Weir height (m) | 0 | - | Sized |
| Soil Thickness (mm) | 500 | - | Sized |
| Porosity (volume fraction) | 0.4 | a)0.332-0.464 b) 0.351-0.555 | a) Sandy Clay Loam b) Sandy Loam (Rawls, 1982) |
| Field capacity (volume fraction) | 0.25 | a) 0.186-0.324 b) 0.126-0.288 | a) Sandy Clay Loam b) Sandy Loam (Rawls, 1982) |
| Wilting point (volume fraction) | 0.13 | a) 0.85-0.211 b) 0.031-0.159 | a) Sandy Clay Loam b) Sandy Loam (Rawls, 1982) |
| Conductivity (mm/hr) | 770 | 5.8 | Measured |
| Suction Head (cm) | 60 | a)5.57-141.5 b) 1.8-41.85 | a) Sandy Clay Loam b) Sandy Loam (Rawls, 1982) |

Table 4.2 compares the simulated and observed bioretention outflows. The NSE and R2 values were satisfactory, except in event 7 with 0.32 and 0.56, respectively. Simulated and observed quantity efficiencies are close in both calibration and validation. The largest difference in efficiency is observed for event 11, despite the high values of NSE and R2. The simulated peak reduction also represents that observed well. Event 5 has the largest difference between the percentages of peak reduction, underestimating the peak reduction by approximately 17%, even this event presenting the best approximation between the quantitative efficiencies. The simulated and observed hygrograms also have similar behaviors, which can be observed in Appendix A13 and A14.

Table 4.2: Outflow calibration.

| | | Efficiency | | Peak reduction | | | |
|--------------------|--------------|------------|----------------|----------------|----------|-----------|----------|
| | | NSE | R ² | Predicted | Observed | Predicted | Observed |
| Calibration | Ev 4 | 0.76 | 0.69 | 64.4% | 76.6% | 32.6% | 35.0% |
| | Ev 5 | 0.84 | 0.97 | 95.3% | 93.6% | 76.8% | 59.1% |
| | Ev 6 | 0.88 | 0.91 | 77.2% | 64.6% | 29.4% | 15.6% |
| | Ev 7 | 0.32 | 0.56 | 81.7% | 85.3% | 71.7% | 73.6% |
| Validation | Ev 8 | - | - | 98.4% | 100.0% | 96.5% | 100.0% |
| | Ev 10 | 0.9 | 0.91 | 95.4% | 94.4% | 77.5% | 73.1% |
| | Ev 11 | 0.94 | 0.97 | 47.6% | 34.2% | 12.2% | 0.3% |

4.3.2. The bioretention performance

The bioretention performance was evaluated with rainfall between 2013 to 2017, covering period of data collection in the LID practice. Table 4.3 shows the inflow and outflow of pollutants. It is estimated that 1091mm of surface flow has entered the bioretention and 539mm left, representing a retention 50.6%.

Table 4.3: Bioretention performance.

| | Runoff (mm) | Fe (g/ha) | NO3(g/ha) | NO2(g/ha) | PO4 (g/ha) | TOC (g/ha) | Zn (g/ha) |
|--------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Inlet | 1091.7 | 9270.7 | 3650.6 | 84.2 | 294.5 | 30747.6 | 455.5 |
| Outlet | 539.0 | 2528.1 | 993.7 | 36.8 | 119.2 | 13362.9 | 191.3 |
| Period Efficiency | 50.6% | 72.7% | 72.8% | 56.3% | 59.5% | 56.5% | 58.0% |
| Average efficiency of events * | 76.6% ($\pm 26.4\%$) | 78.0% ($\pm 25.0\%$) | 76.9% ($\pm 25.4\%$) | 76.7% ($\pm 26.1\%$) | 77.8% ($\pm 25.5\%$) | 76.9% ($\pm 26.0\%$) | 77.5% ($\pm 25.7\%$) |

Note: *Disregarding the events with 100% efficiency.

TOC and Fe, also in Table 4.3, were the pollutants with a greater mass input, with approximately 30 and 9 kg/ha, while NO₂ had the lowest amount washed into the bioretention with 84.2 g/ha. All pollutants have a removal efficiency greater than the quantity efficiency. Fe has the highest removal efficiency (72.7%) and the lowest NO₂ with 56.3%. If the efficiency is analyzed through the average of all the events, the qualitative efficiencies of the pollutants are closer. This suggests that the pollutants present greater efficiencies for larger events, since events with higher rainfall volumes are less frequent and weigh less on average.

The quantity efficiency of the events was related to the average discharge, shown in Figure 4.1-a. The average discharge and quantitative efficiency appears to have an inverse exponential function relation. For average discharges below 1.8L/s, the quantitative efficiency was 100%. The event with the lowest quantitative efficiency of approximately 10% had an average flow rate of 102L/s. Figure 4.1-b shows the peak reduction in each event. The peak reduction percentage falls as they grow, until the peak events reach approximately 150 L/s. Events with a peak higher than that tend to have a reduction below 10%. Events with a peak lower than 6L/s tend to have a quantity efficiency of 100%, and hence, 100% peak reduction.

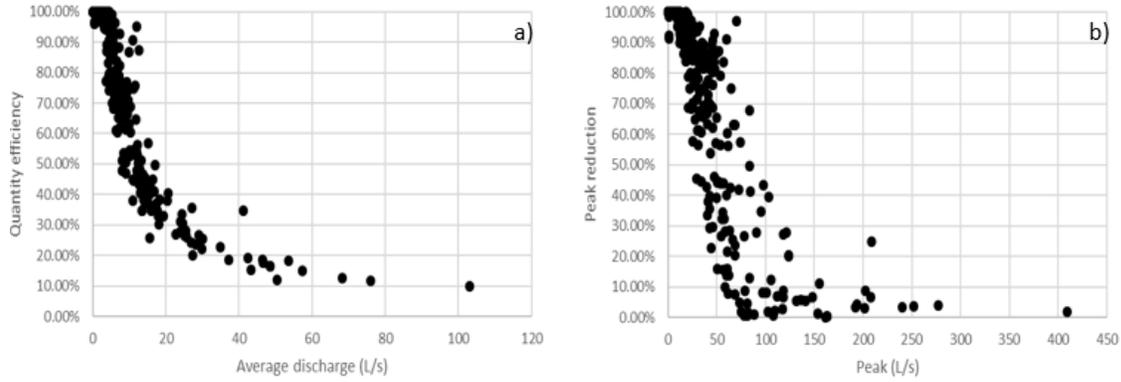


Figure 4.1: Quantity efficiency and peak reduction.

The influence of w_1 and w_2 of the washoff on the removal efficiency of pollutants was verified. Figure 4.2 shows that highest w_1 results in the average efficiency, and the closer to 1 the value of w_2 is, the more linear the relation between the qualitative and quantitative efficiency.

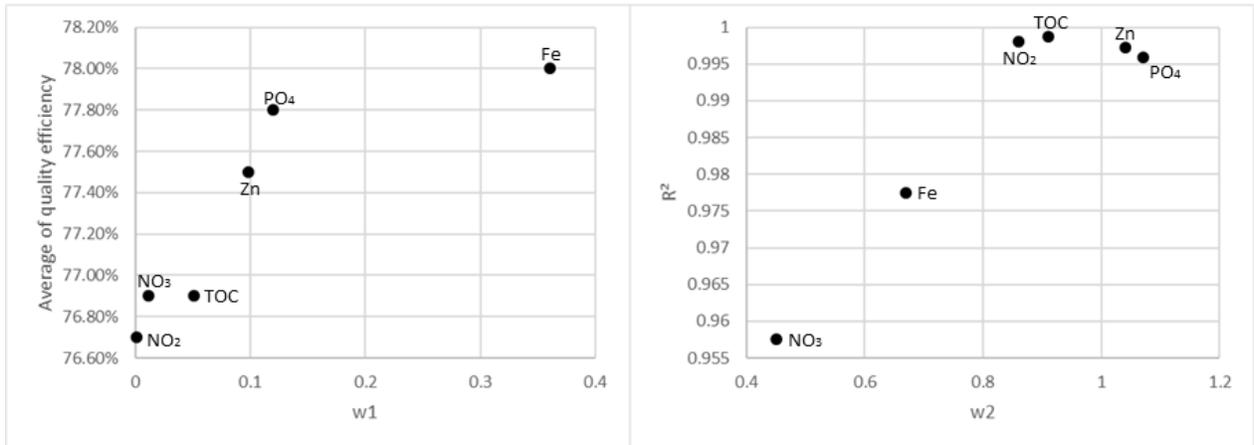


Figure 4.2: Influence of washoff parameters.

The event with the greatest difference between quantity efficiency and Fe removal, which has a higher w_1 , is shown in Figure 4.3 to explain why pollutants with higher w_1 are better retained.

This event started with low buildup available due to previous events. The initial buildup is depleted by small discharge at the beginning of the event, as shown by the drop in concentration over the event. When Fe concentration is high, the inflow is sufficiently low for a total absorption into the bioretention, thus retaining a larger portion of the pollutant. When the inflow increases, the bioretention is not able to retain most of it, reducing the quantity efficiency. It occurs when the Fe concentration is already low, minimizing the output of the pollutant mass.

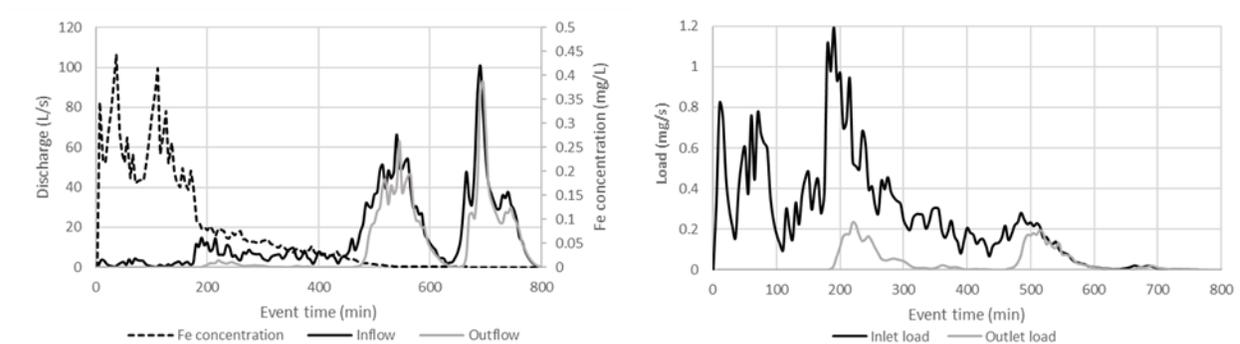


Figure 4.3: Events with the highest difference in quantity and Fe removal efficiencies.

Figure 4.4 shows the relation between quantitative and qualitative efficiency of the events for NO_3 with higher w_2 and TOC with lower w_2 . It can be observed that the removal efficiency of TOC is more linearly dependent on the quantitative efficiency, while nitrate has a greater variation. To illustrate this, two events with the greatest difference between quantitative and NO_3 removal efficiencies were separated (Figure 4.5).

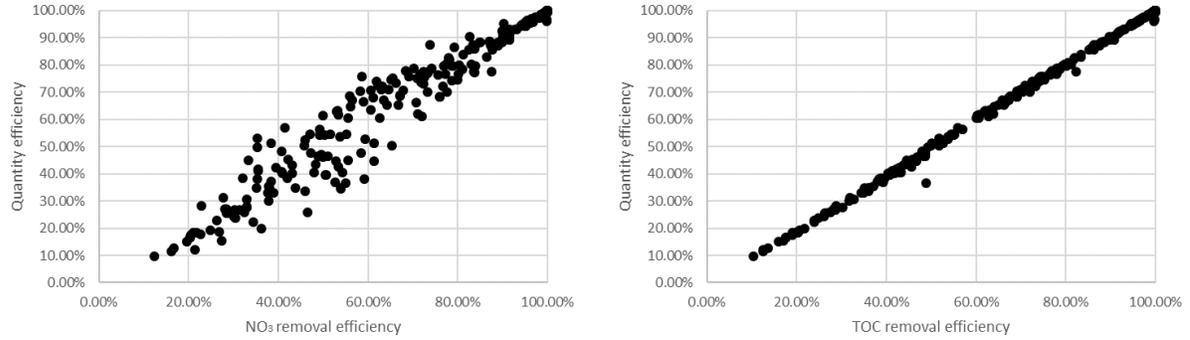


Figure 4.4: Influence of w_2 on the relationship between quantitative and qualitative efficiency

For smaller values of w_2 , higher concentrations are found in lower flows. In Figure 4.5-a, the event with NO_3 removal efficiency is lower than quantitative, the runoff portion with higher flow is absorbed at the beginning, when the water content in the soil layer is low and infiltration capacity is high. When the outflow begins, NO_3 concentration is high resulting in a higher mass output.

Figure 4.5-b shows the event with the highest removal efficiency. In this event, higher inflows surpass the bioretention capacity, when outflow with low NO_3 concentration occurs. When the outflow ceases with lower discharges, NO_3 concentration is much higher and most of its mass is retained.

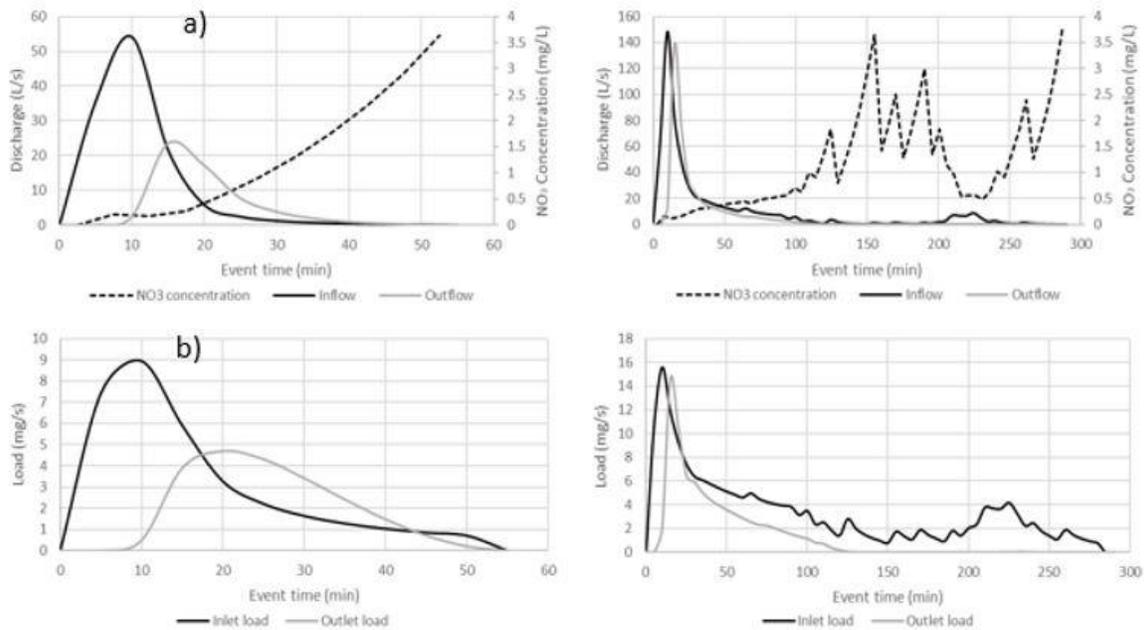


Figure 4.5: Examples of NO₃ removal

4.3.3. Rainfall desegregation and climate changes in Sao Carlos

Table 4.4 shows the disaggregation performance by the modified Bartlett-Lewis method. The number of wet cells, rainfall depth and the variance in each month present close values. The total disaggregated precipitation in the period was 4352.3mm, 2.8% greater than the observed. The number of wet cells in the disaggregated series was 6865, number 3.5% lower than that observed, of 7116. R^2 values between observed and simulated wet cells, ordered by the largest depths, were also satisfactory. The graphs showing this relationship, for each month, can be found in Appendix A15 and A16. Table 4.5 shows the difference of the total rainfall volume between the raw future scenarios and their disaggregated series. The largest difference can be observed from 1980 to 1999 with a 3% lower volume used in the simulations.

Table 4.4: Desegregated and observed rainfall

| | Number of wet cells | | Precipitation (mm) | | Variance | | R ² |
|--------------|---------------------|----------|--------------------|----------|--------------|----------|----------------|
| | Desegregated | Observed | Desegregated | Observed | Desegregated | Observed | |
| Jan | 1317 | 1420 | 810.69 | 815.80 | 0.038 | 0.041 | 0.959 |
| Fev | 725 | 714 | 565.43 | 539.00 | 0.056 | 0.052 | 0.979 |
| Mar | 916 | 858 | 562.89 | 530.40 | 0.034 | 0.029 | 0.968 |
| Apr | 259 | 240 | 135.90 | 129.40 | 0.0070 | 0.0064 | 0.988 |
| May | 684 | 713 | 375.48 | 351.60 | 0.016 | 0.013 | 0.949 |
| Jun | 366 | 344 | 209.20 | 192.20 | 0.011 | 0.011 | 0.951 |
| Jul | 206 | 192 | 89.24 | 82.60 | 0.0036 | 0.0036 | 0.957 |
| Aug | 37 | 35 | 16.01 | 17.00 | 0.00040 | 0.00059 | 0.958 |
| Sep | 420 | 448 | 245.93 | 240.60 | 0.014 | 0.012 | 0.987 |
| Out | 317 | 430 | 307.55 | 319.40 | 0.028 | 0.022 | 0.979 |
| Nov | 422 | 448 | 240.21 | 240.60 | 0.012 | 0.012 | 0.981 |
| Dec | 1196 | 1274 | 793.73 | 773.40 | 0.050 | 0.042 | 0.987 |
| Total | 6865 | 7116 | 4352.26 | 4232.00 | | | |

Table 4.5 shows the climate change impacts on temperature and precipitation in the city of São Carlos, as the data acquired from INPE suggest (Chou et al., 2014-a; Chou et al, 2014-b; Lyra et al, 2017).

Table 4.5: Climate changes impacts on temperature and precipitation

| | 1980-1999 | 2020-2039 | | 2040-2059 | | 2060-2079 | | 2080-2099 | | Difference in 1 century | |
|--------------------------|-----------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|-------------------------|-----------------|
| | | 4.5 | 8.5 | 4.5 | 8.5 | 4.5 | 8.5 | 4.5 | 8.5 | 4.5 | 8.5 |
| Average Temperature (°C) | 21.35 | 24.46 | 25.40 | 24.39 | 25.65 | 25.79 | 27.42 | 26.01 | 29.43 | 4.66 | 8.08 |
| Total Precipitation (mm) | 38926 | 23394 | 20093 | 27548 | 26649 | 23938 | 23061 | 23031 | 18771 | -41% | -51% |
| Desegregation difference | -3.0% | 2.6% | 1.8% | -0.2% | -1.4% | -0.4% | -0.3% | -0.1% | 0.3% | Average | 0.0%±0.2 |

For the less optimistic scenario, RCP 8.5, an increase of approximately 8°C in the average air temperature and a fall of almost 30% in the rainfall volume are expected. If the RCP scenario 4.5 occurs, it is estimated that the impacts will be milder, with an increase of almost 5°C in the air temperature and a fall of 13% in the precipitation.

Table 4.6 shows the climate change impacts on the quantity and quality of runoff. The analysis was made disregarding the initial 6 months of warm-up for a better precision of the quality data.

Table 4.6: Estimated climate change impact on precipitation, runoff and pollutant washoff.

| | 1980-1999 | 2020-2039 | | 2040-2059 | | 2060-2079 | | 2080-2099 | | Difference in 1 century | |
|-------------|-----------|-----------|---------|-----------|---------|-----------|---------|-----------|---------|-------------------------|--------|
| | | 4.5 | 8.5 | 4.5 | 8.5 | 4.5 | 8.5 | 4.5 | 8.5 | 4.5 | 8.5 |
| Runoff (mm) | 7393.2 | 4296.5 | 3512.0 | 5267.9 | 4971.6 | 4551.3 | 4408.0 | 4153.4 | 3486.9 | -43.8% | -52.8% |
| Fe (g/ha) | 5425.1 | 5209.7 | 5060.8 | 5161.7 | 5216.6 | 4983.4 | 4964.3 | 5056.5 | 4948.7 | -6.8% | -8.8% |
| NO3 (g/ha) | 2473.3 | 2181.4 | 2015.8 | 2210.6 | 2187.2 | 2076.0 | 2032.0 | 2092.3 | 1911.1 | -15.4% | -22.7% |
| NO2 (g/ha) | 64.7 | 39.7 | 33.0 | 46.8 | 44.4 | 40.7 | 39.3 | 37.8 | 31.8 | -41.6% | -50.8% |
| PO4 (g/ha) | 172.9 | 152.6 | 141.6 | 154.5 | 156.6 | 144.0 | 145.0 | 148.0 | 140.2 | -14.4% | -18.9% |
| TOC (g/ha) | 14178.4 | 14271.7 | 13768.3 | 13891.7 | 14046.5 | 13687.7 | 13685.2 | 13858.0 | 13855.5 | -2.3% | -2.3% |
| Zn (g/ha) | 264.1 | 232.7 | 216.1 | 236.4 | 239.6 | 220.3 | 222.0 | 211.2 | 213.6 | -20.0% | -19.1% |

The input depth in the period between 1980 and 1999 is higher than all future periods for both scenarios, it falls to the 2020-2039 scenario, has an increment for the next period and continuously falls until 2080-2099. In 100 years, the drop in surface runoff is greater than the pollutant fall. The pollutant with the highest decrease was NO² with low coefficient w₁, tending to follow the decrease in the inlet runoff volume. Fe with the highest w₁ was the pollutant with the second lowest percentage drop. TOC, with lower exponent buildup, had a drop of only 2.3% in 100 years in both scenarios.

4.3.4. Climate change impacts on bioretention performance

Table 4.7 shows the outlet runoff depth and pollutant mass for each analyzed period for the two RCP scenarios.

Table 4.7: The climate change impacts on bioretention performance

| | 1980-1999 | 2020-2039 | | 2040-2059 | | 2060-2079 | | 2080-2099 | |
|---------------------|-----------|-----------|--------|-----------|--------|-----------|--------|-----------|--------|
| | | 4.5 | 8.5 | 4.5 | 8.5 | 4.5 | 8.5 | 4.5 | 8.5 |
| Runoff (mm) | 1356.5 | 685.5 | 513.1 | 1079.3 | 1026.9 | 936.3 | 935.0 | 770.7 | 653.5 |
| Quantity efficiency | 81.7% | 84.0% | 85.4% | 79.5% | 79.3% | 79.4% | 78.8% | 81.4% | 81.3% |
| Fe | 326.7 | 258.2 | 222.6 | 312.7 | 298.4 | 276.2 | 307.9 | 254.9 | 272.3 |
| Fe removal | 94.0% | 95.0% | 95.6% | 93.9% | 94.3% | 94.5% | 93.8% | 95.0% | 94.5% |
| NO3 | 202.7 | 147.4 | 125.7 | 179.9 | 176.9 | 166.3 | 173.7 | 155.4 | 153.7 |
| NO3 removal | 91.8% | 93.2% | 93.8% | 91.9% | 91.9% | 92.0% | 91.5% | 92.6% | 92.0% |
| NO2 | 9.8 | 5.1 | 3.9 | 7.7 | 7.4 | 6.7 | 6.7 | 5.6 | 4.9 |
| NO2 removal | 84.9% | 87.0% | 88.1% | 83.5% | 83.4% | 83.4% | 82.8% | 85.2% | 84.7% |
| PO4 | 21.6 | 16.4 | 14.4 | 19.6 | 19.9 | 17.7 | 19.7 | 17.1 | 16.7 |
| PO4 removal | 87.5% | 89.3% | 89.8% | 87.3% | 87.3% | 87.7% | 86.4% | 88.4% | 88.1% |
| TOC | 1808.9 | 1514.3 | 1366.8 | 1732.5 | 1858.1 | 1716.2 | 1956.0 | 1715.1 | 1761.5 |
| TOC removal | 87.2% | 89.4% | 90.1% | 87.5% | 86.8% | 87.5% | 85.7% | 87.6% | 87.3% |
| Zn | 34.03 | 25.57 | 22.49 | 30.84 | 31.78 | 27.95 | 31.46 | 25.20 | 26.33 |
| Zn removal | 87.1% | 89.0% | 89.6% | 87.0% | 86.7% | 87.3% | 85.8% | 88.1% | 87.7% |

Despite the decrease in the runoff volume over the years, the quantity efficiency of bioretention tends to remain constant over the years. The efficiency for scenario 8.5 is a bit lower when compared to scenario 4.5, and is only higher in the near future between 2020 and 2039. The difference between efficiencies is more significant between periods than between scenarios. The periods between 2040 and 2079 show the lowest efficiencies in both scenarios, below 80%. The explanation is due to a higher percentage of stronger events.

The cells with a 3-hour timestep, which were subsequently disaggregated, were analyzed in Figure 4.6, showing the occurrence percentage of a given cell above a given depth.

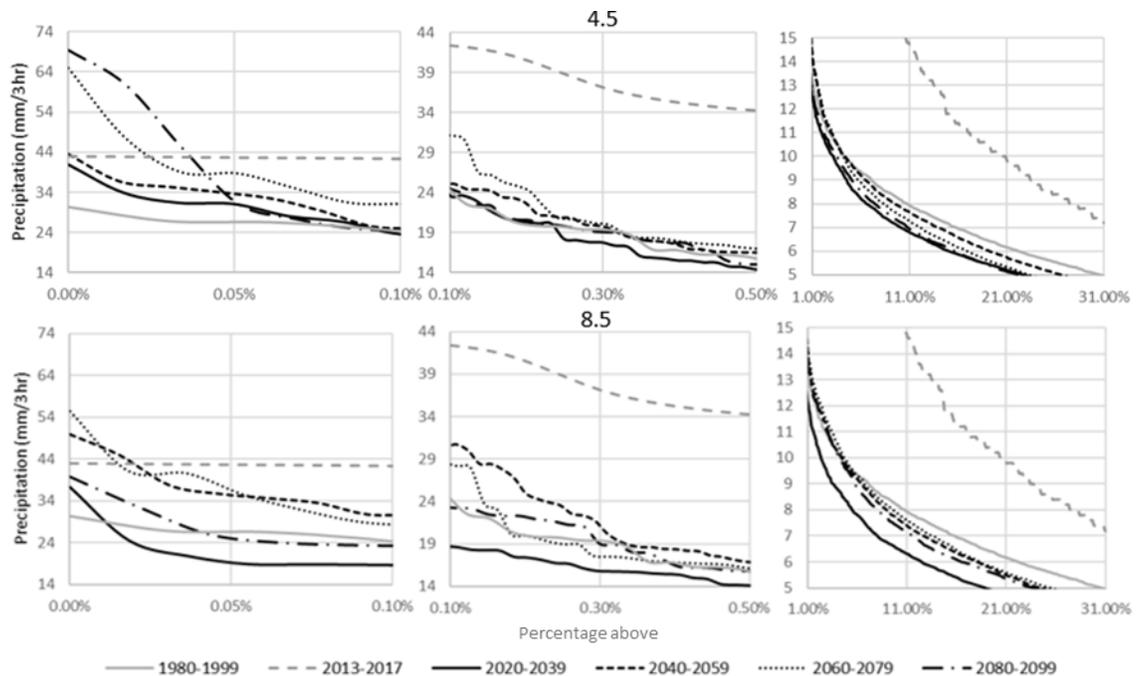


Figure 6: Rainfall regime over the years

It is observed that the periods 2040-2059 and 2060-2079 are generally more intense, explaining smaller quantitative efficiencies. The period from 2020 to 2039 presents the smallest depths, followed by the period from 2080 to 2099, periods with the highest efficiencies.

The periods 1980-1999 and 2013-2017 are in gray. For the older scenarios, it can be observed that the 0.5% more intense cells of these periods tend to be smaller than the other scenarios analyzed, only becoming greater between the 1% and 31% largest cells. The most recent period from 2013 to 2017 can be highlighted for events that are much higher than the other periods within the 1% and 31% largest events, which explains the much lower quantity and quality efficiencies. By analyzing rainfall events by the city intensity duration frequency curve (IDF), it can be observed that there were 17 rainfall events over 1 year of return time, suggesting a very atypical rainfall regime in the region during these years. An intense drought was also

recorded, which resulted in a water crisis in the region leading to rationing measures and economic losses in several sectors.

The pollutant removal efficiencies follow the trend of quantity efficiency, in which the periods 2040-2059 and 2060-2079 have lower removal percentages, as shown in Table 4.7. However, the removal efficiencies are greater than the quantity efficiency and, as observed between 2013 to 2017, the pollutants with higher washoff coefficient w_1 are the ones with the highest removal efficiency. Fe generally presents greater efficiency for the scenarios, above 93%, while NO₂ presents the lowest percentage retained, at most 88.1%.

Despite the decrease in the pollutant mass washed in 100 years, the EMC increases as shown in Table 4.8. The concentration of TOC is the most affected by climate change, while NO₂ has the lowest growth.

TOC has the lowest buildup recovery rate of b_2 , and with more frequent rainfall events from 1980 to 1999, it becomes harder to recover its maximum buildup. With climate changes, however, longer dry times allow this pollutant to reach higher buildup, also explaining the lower mass drop of this pollutant in 100 years.

Table 4.8 also shows that bioretention is able to soften the EMC growth. The bioretention efficiency is greater in the initial moments of the event, with drier surface soil and when the first flush occurs. Thus, this phenomenon with higher concentrations, is absorbed more easily, while the cleaner runoff tends to leave the bioretention more frequently. This reduction is also influenced by parameter w_1 . Fe (highest w_1) had the largest EMC reduction while NO₂ had the lowest. TOC, despite the highest EMC increase, presented the second smallest EMC reduction. This pollutant buildup reaches higher levels in future scenarios, but its fall is slower due to a low

w1. It results in a greater constancy in concentration, which decreases the bioretention capacity in reducing EMC levels.

Table 4.8: Climate change impacts on EMC and its reduction by the bioretention.

| | 4.5 | | | | | | | | | | | |
|-------------------------|--------------|---------|--------------|---------|---------------|---------|--------------|---------|--------------|---------|--------------|---------|
| | Fe | | NO3 | | NO2 | | PO4 | | TOC | | Zn | |
| | EMC in | EMC out | EMC in | EMC out | EMC in | EMC out | EMC in | EMC out | EMC in | EMC out | EMC in | EMC out |
| 1980-1999 | 0.7 | 0.24 | 0.33 | 0.15 | 0.0088 | 0.0072 | 0.023 | 0.016 | 1.92 | 1.3 | 0.036 | 0.025 |
| 2020-2039 | 1.21 | 0.38 | 0.51 | 0.22 | 0.0092 | 0.0075 | 0.036 | 0.024 | 3.32 | 2.2 | 0.054 | 0.037 |
| 2040-2059 | 0.98 | 0.29 | 0.42 | 0.17 | 0.0089 | 0.0072 | 0.029 | 0.018 | 2.64 | 1.6 | 0.045 | 0.029 |
| 2060-2079 | 1.1 | 0.29 | 0.46 | 0.18 | 0.0089 | 0.0072 | 0.032 | 0.019 | 3.01 | 1.8 | 0.048 | 0.030 |
| 2080-2099 | 1.22 | 0.33 | 0.50 | 0.20 | 0.0091 | 0.0073 | 0.036 | 0.022 | 3.34 | 2.2 | 0.051 | 0.033 |
| Difference in 100 years | 65.91% | 37.31% | 50.58% | 34.92% | 3.95% | 0.75% | 52.35% | 39.60% | 73.98% | 66.88% | 42.35% | 30.31% |
| Average EMC reduction | 70.5% (±2.3) | | 58.9% (±2.1) | | 19.1% (±0.85) | | 36.1% (±3.2) | | 35.1% (±3.4) | | 34.3% (±3.3) | |
| | 8.5 | | | | | | | | | | | |
| | Fe | | NO3 | | NO2 | | PO4 | | TOC | | Zn | |
| | EMC in | EMC out | EMC in | EMC out | EMC in | EMC out | EMC in | EMC out | EMC in | EMC out | EMC in | EMC out |
| 1980-1999 | 0.73 | 0.24 | 0.33 | 0.15 | 0.0088 | 0.0072 | 0.023 | 0.016 | 1.9 | 1.33 | 0.036 | 0.025 |
| 2020-2039 | 1.2 | 0.32 | 0.47 | 0.18 | 0.0077 | 0.0057 | 0.033 | 0.021 | 3.2 | 1.99 | 0.050 | 0.033 |
| 2040-2059 | 1.0 | 0.28 | 0.42 | 0.16 | 0.0084 | 0.0068 | 0.030 | 0.018 | 2.7 | 1.72 | 0.045 | 0.029 |
| 2060-2079 | 1.1 | 0.33 | 0.45 | 0.19 | 0.0086 | 0.0072 | 0.032 | 0.021 | 3.0 | 2.09 | 0.049 | 0.034 |
| 2080-2099 | 1.2 | 0.35 | 0.46 | 0.20 | 0.0091 | 0.0075 | 0.034 | 0.022 | 3.3 | 2.29 | 0.051 | 0.034 |
| Difference in 100 years | 62.37% | 46.73% | 37.54% | 33.49% | 3.41% | 4.10% | 44.41% | 36.48% | 73.95% | 71.40% | 43.96% | 36.17% |
| Average EMC reduction | 70.4% (±1.9) | | 58.4% (±2.2) | | 19.2% (±3.26) | | 35.1% (±2.1) | | 33.1% (±3.0) | | 32.9% (±2.1) | |

4.4. Conclusions

Using a specific model, this study verified the performance of a bioretention located in a subtropical climate. It analyzed the quantity efficiency, the relation between the peak flow and its reduction, and the removal efficiency of Fe, NO₃, NO₂, PO₄, TOC and Zn separately according to their washoff/buildup parameters.

The climate change impacts were also estimated in the city of São Carlos for RCP 4.5 and 8.5. Both scenarios point to a reduction in rainfall volume in the city by 13% and 29%

respectively. However, the mass of the pollutants washed varies according to their specific washing characteristic.

However, climate change does not affect quantity efficiency, and therefore bioretention continues to contribute in retaining runoff volume. The results also show that the bioretention, even considering only the outflow without the treatment within its filtering media, contributes to reducing the pollutant concentration. The results of this paper show that LIDs can be incorporated into traditional drainage systems to mitigate not only the impacts of urbanization but also from climate changes.

Only the effects of climate change on LID performance were analyzed in this study. However, the bioretention is located in an area where urbanization is expected to grow, from approximately 20% today to 80% in 2100 (Rosa, 2016). Therefore, it is recommended to assess the climate change and urbanization impacts combined in the catchment to more accurately verify the bioretention performance by the end of the century.

4.5. References

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5. GENERAL CONCLUSIONS

In Chapter 3, the runoff quantity and quality were characterized. In this chapter, a sensitivity analysis clarified how the buildup and washoff parameters influence the predicted inputs of pollutants. This Chapter also presented the washoff exponential equation chosen in the simulations and the correct warm-up period. Concerning the results in this chapter, the quality load-based calibration presented a greater proximity of the total mass and the EMC, between predicted and observed loads, even with a higher difference in the mean concentrations. This Chapter also seasonally estimated the runoff quality draining into an existing LID/bioretention technique. These seasons corresponded to drier periods ("subtropical winter"), wetter ("subtropical summer"), post-wet ("subtropical fall") and post-dry ("subtropical spring") periods. Therefore, the results in Chapter 3 help to achieve the first specific objective. *“Characterize the urban runoff in a subtropical catchment, in terms of volume, flow and water quality, elucidating the runoff generation and pollutants wash-off processing, using a stepwise flowchart including calibration, validation and sensitivity analysis.”*

The specific purpose 2 *“Analyze the impacts of climate changes on a subtropical urban drainage.”* was investigated in Chapter 3. The RCP 4.5 and 8.5 for four future periods were compared to the current one. The results compared the temperature, total rainfall volumes, rainfall intensity, runoff volume, total pollutants mass and EMC. For both scenarios, the average temperature tends to increase while rainfall and runoff volumes decrease. Pollutant mass tends to decrease less than runoff, while the concentration increases. The variation of pollutant concentration throughout the scenarios depends on each buildup/washoff parameter, as was investigated in the first specific objective.

The general purpose “*To elucidate how runoff generation and pollutant wash-off processes respond to upstream factors of an experimental LID technique and, evaluate how this practice would perform as a local adaptation strategy considering rainfall-runoff scenarios under climate change.*” was also investigated in Chapter 3 and could be reached after the specific purposes. Quantity efficiency slightly varies around 80% over the years for both scenarios and climate change seems to have little impact on it. However, quality efficiency and EMC reduction varies from pollutants according to their buildup/washoff parameters and the possible reasons could be explained after investigating the specific purposes in Chapters 3 and 4. Besides the fact that quantity efficiency has been maintained, the EMC reduction tends to be improved with climate changes. These results showed that the hypothesis” (*... decreasing stormwater retention and pollutant removal performance of LID practices*” was not confirmed.

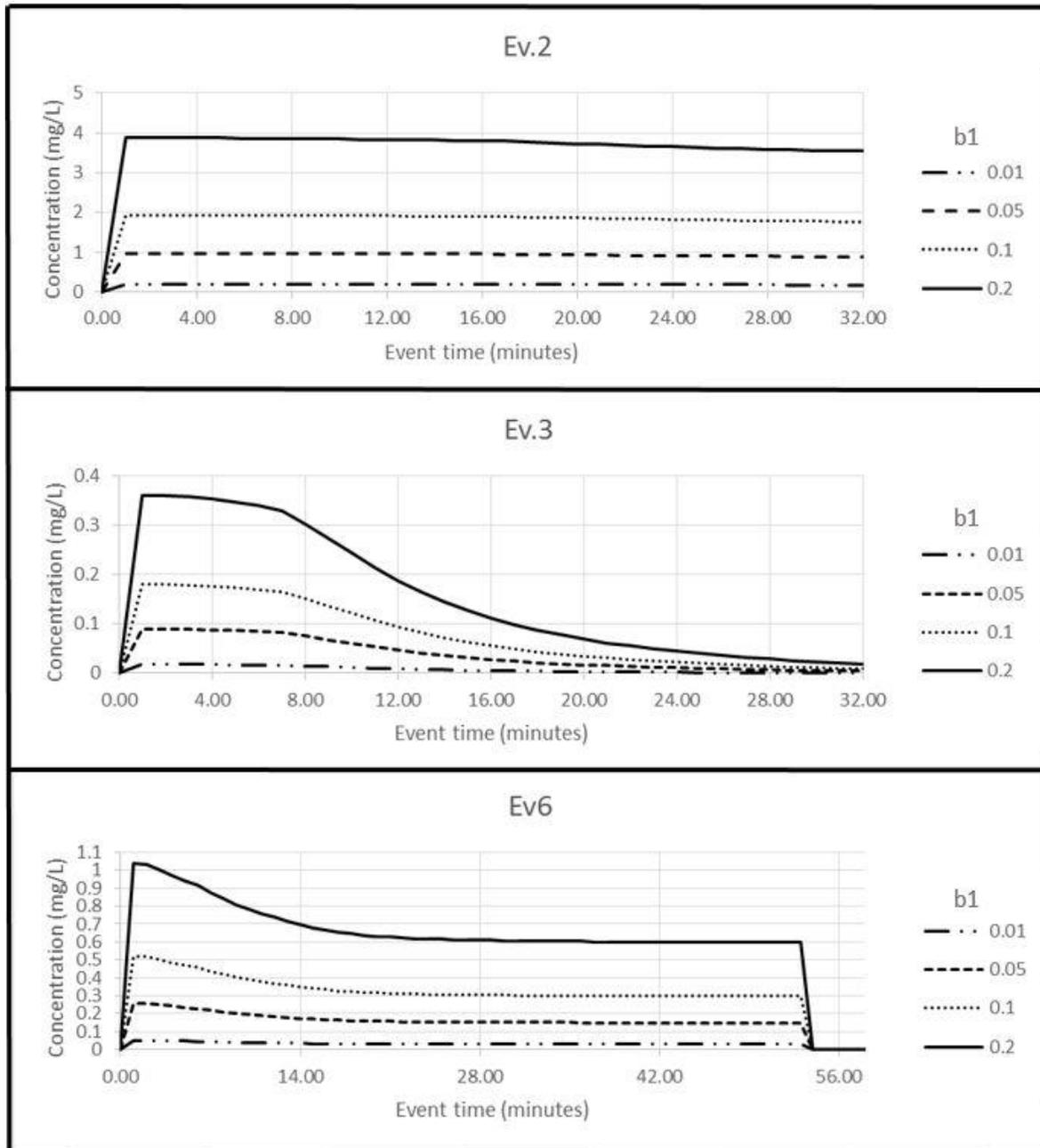
Recommendations for future research

- 1- Quality simulations using buildup/washoff were studied in this dissertation, however NH₃, Cd and COD could not be validated suggesting that this model was not satisfactory for these pollutants. Therefore, other quality models have to be investigated in a subtropical climate to verify which one better represents the hydrological processes involved in this climate.
- 2- A single bioretention performance was analyzed in the microdrainage. Further studies are required to better evaluate the climate change impacts on the sustainable urban drainage, which comprises several units and types of LIDs.
- 3- The quality efficiency was obtained not considering physical processes on the bioretention surface. It is recommended to characterize the pollutant concentration on sediments per granulometric size, thus addressing the sedimentation process.

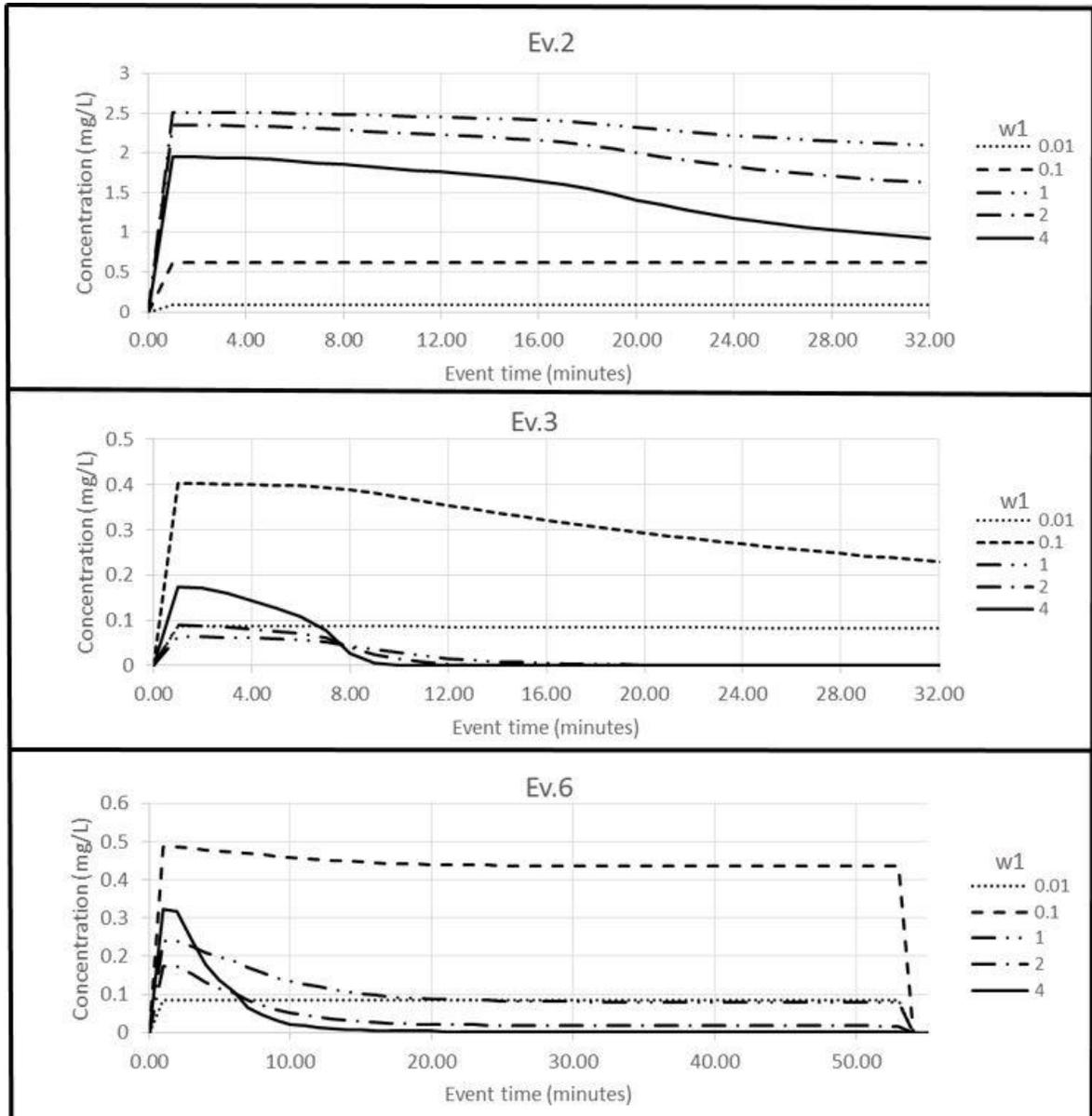
- 4- In addition, it was supposed that no chemical reaction occurred inside the bioretention, during the simulations. For a better precision in quality efficiency, these reactions need to be studied and eventually included in the mass balance.
- 5- Third generation LIDs, which aim to reuse water and nutrients, are currently being studied. This dissertation showed that climate change will alter the quantity of runoff and pollutants, and will possibly affect the resource reuse. Therefore, these impacts on third generation LIDs can also be measured.
- 6- The studied area is currently under occupation, altering the runoff quantity and quality. Then, land use and climate change combined impacts need to be quantified.

APPENDIX

A1- Sensitive analysis of the maximum buildup. In this case, $w_1=0.5$, $w_2=1$ and $b_2=0.02 \text{ days}^{-1}$.



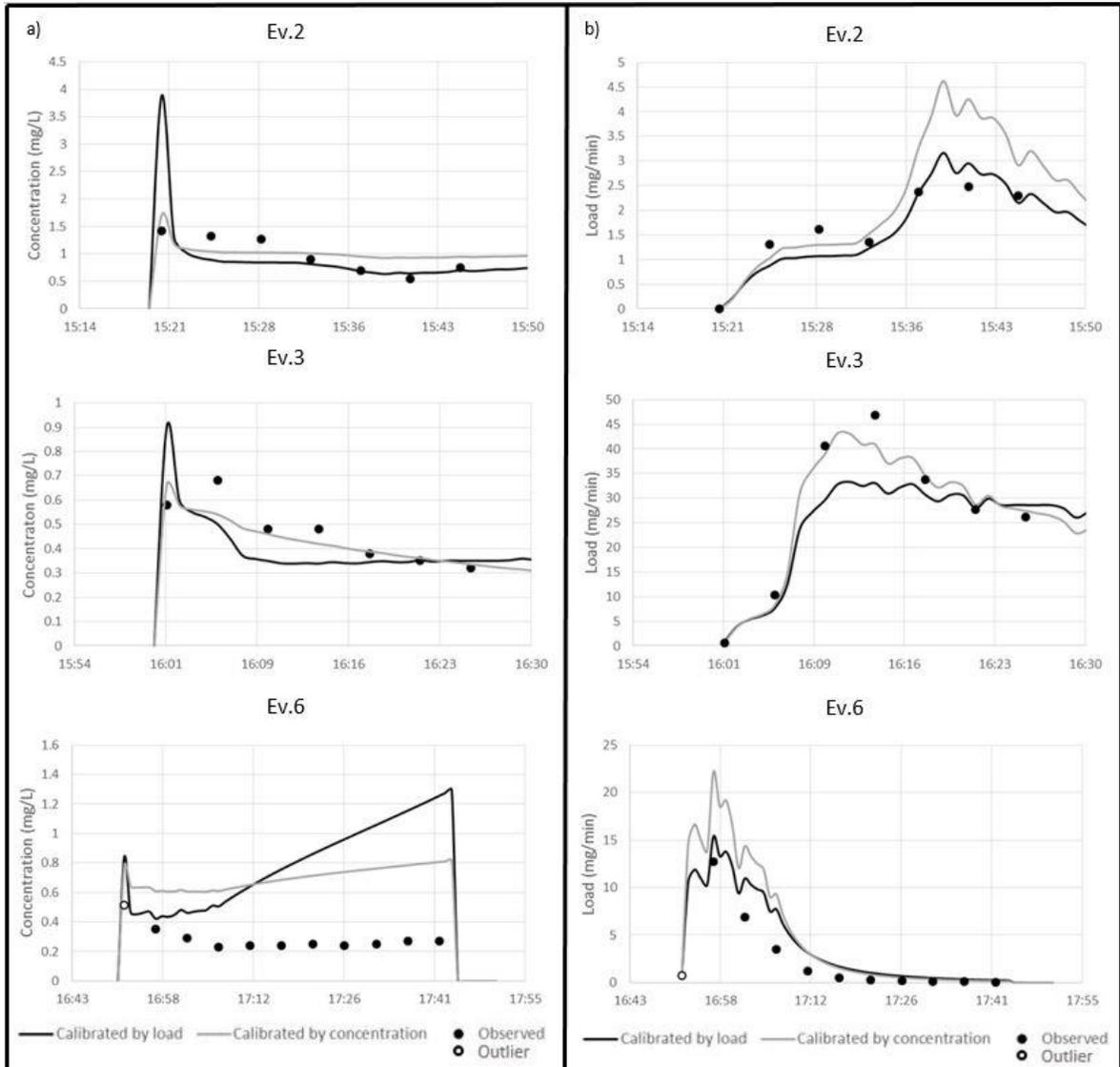
A2- Sensitive analysis of the washoff for $w_2 = 1$. In this case, $b_1 = 0.1 \text{ kg/ha}$ and $b_2 = 0.02 \text{ days}^{-1}$.



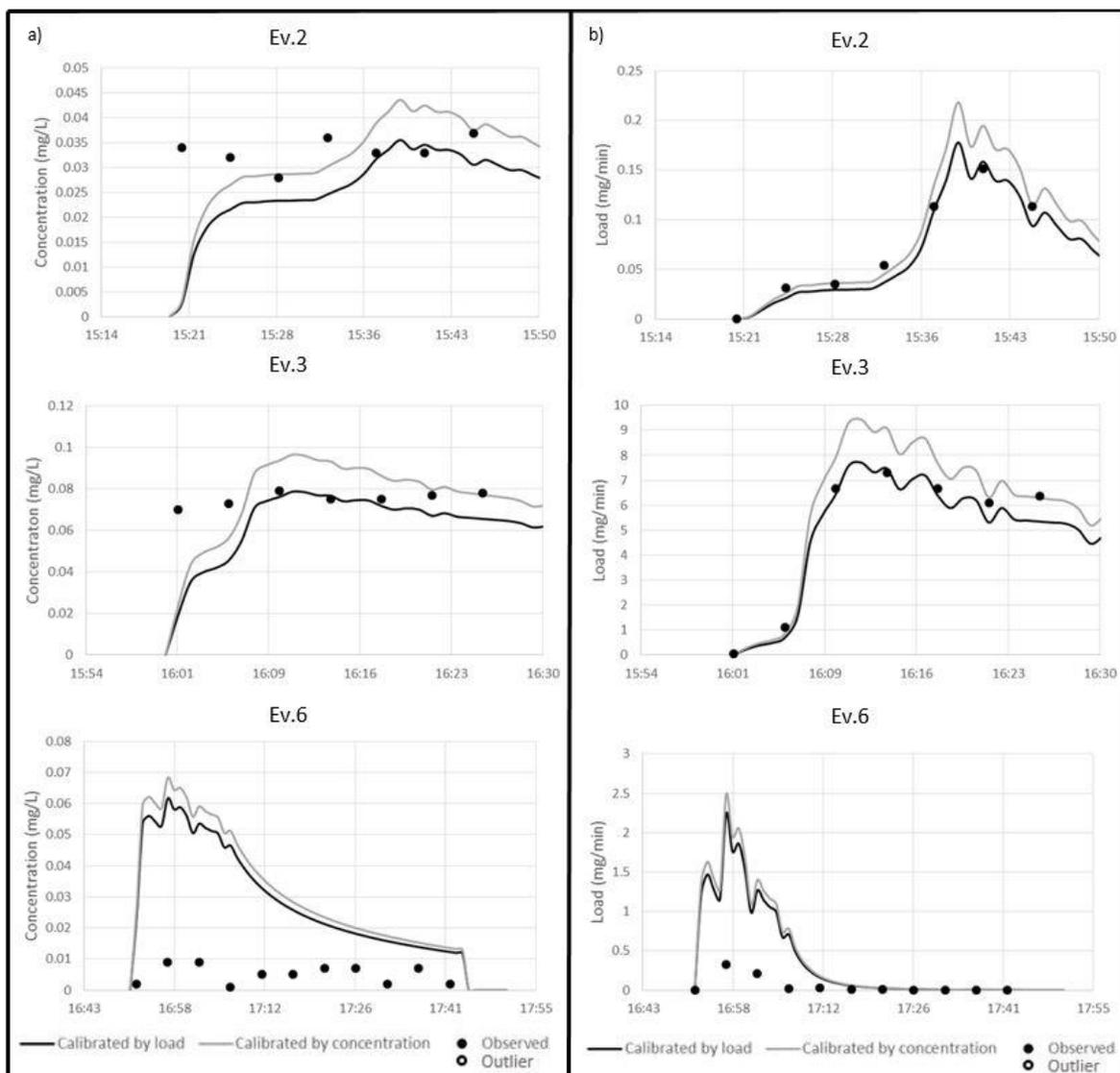
A3- Pollutograph and load calibration evaluation with NSE and VE and R².

| | | Concentration-based Calibration | | | | | | Load-based Calibration | | | | | |
|------------|------|---------------------------------|---------|----------------|------------|--------|----------------|------------------------|----------|----------------|------------|--------|----------------|
| | | Concentration curve | | | Load curve | | | Concentration curve | | | Load curve | | |
| | | VE | NSE | R ² | VE | NSE | R ² | VE | NSE | R ² | VE | NSE | R ² |
| Cd | Ev.2 | 0.75 | -21.27 | 0.00 | 0.84 | 0.87 | 0.97 | 0.71 | -24.18 | 0.01 | 0.87 | 0.95 | 0.97 |
| | Ev.3 | 0.79 | -52.47 | 0.69 | 0.87 | 0.89 | 0.97 | 0.80 | -61.35 | 0.71 | 0.91 | 0.96 | 0.98 |
| | Ev.6 | -4.39 | -131.21 | 0.16 | -6.18 | -54.83 | 0.93 | -3.80 | -104.23 | 0.16 | -5.41 | -43.23 | 0.93 |
| COD | Ev.2 | 0.57 | -0.46 | 0.48 | 0.45 | -1.67 | 0.68 | -0.09 | -28.57 | 0.41 | 0.76 | 0.65 | 0.75 |
| | Ev.3 | 0.70 | 0.53 | 0.59 | 0.60 | 0.41 | 0.42 | 0.68 | 0.46 | 0.64 | 0.62 | 0.40 | 0.49 |
| | Ev.6 | -0.93 | -3.42 | 0.01 | -0.41 | -0.56 | 0.24 | -1.70 | -8.72 | 0.01 | -0.31 | 0.12 | 0.28 |
| Fe | Ev.2 | 0.79 | 0.72 | 0.72 | 0.69 | 0.32 | 0.84 | -0.18 | -33.55 | 0.63 | 0.88 | 0.85 | 0.91 |
| | Ev.3 | -1.11 | -90.62 | 0.22 | 0.04 | -3.03 | 0.40 | -0.34 | -55.73 | 0.12 | 0.64 | 0.62 | 0.62 |
| | Ev.6 | -1.41 | -4.14 | 0.34 | -0.45 | -1.36 | 0.97 | -1.45 | -6.17 | 0.01 | 0.48 | 0.84 | 0.95 |
| NH4 | Ev.2 | 0.74 | 0.33 | 0.44 | 0.64 | 0.00 | 0.86 | 0.48 | -7.77 | 0.37 | 0.85 | 0.84 | 0.90 |
| | Ev.3 | 0.90 | 0.70 | 0.71 | 0.93 | 0.97 | 0.98 | 0.74 | -0.72 | 0.34 | 0.82 | 0.79 | 0.88 |
| | Ev.6 | -0.65 | -170.97 | 0.07 | -0.06 | -0.16 | 0.98 | -1.07 | -335.66 | 0.10 | 0.37 | 0.70 | 0.95 |
| NO3 | Ev.2 | 0.57 | 0.18 | 0.42 | 0.26 | -4.85 | 0.51 | -6.89 | -1658.66 | 0.28 | 0.80 | 0.69 | 0.78 |
| | Ev.3 | 0.79 | 0.83 | 0.88 | 0.76 | 0.59 | 0.97 | 0.16 | -7.44 | 0.92 | 0.81 | 0.80 | 0.83 |
| | Ev.6 | 0.61 | -0.43 | 0.23 | 0.62 | 0.78 | 0.92 | -1.11 | -59.32 | 0.00 | 0.45 | 0.58 | 0.80 |
| NO2 | Ev.2 | 0.81 | 0.44 | 0.51 | 0.79 | 0.75 | 0.89 | 0.73 | -0.12 | 0.47 | 0.84 | 0.84 | 0.91 |
| | Ev.3 | 0.91 | 0.87 | 0.92 | 0.91 | 0.97 | 0.97 | 0.92 | 0.88 | 0.89 | 0.90 | 0.95 | 0.95 |
| | Ev.6 | 0.84 | -0.71 | 0.00 | 0.76 | 0.89 | 0.97 | 0.68 | -3.41 | 0.00 | 0.80 | 0.93 | 0.97 |
| TOC | Ev.2 | 0.82 | 0.40 | 0.47 | 0.84 | 0.88 | 0.95 | 0.82 | 0.28 | 0.47 | 0.87 | 0.91 | 0.95 |
| | Ev.3 | 0.87 | 0.69 | 0.93 | 0.93 | 0.95 | 0.97 | 0.86 | 0.67 | 0.93 | 0.92 | 0.96 | 0.97 |
| | Ev.6 | 0.16 | -0.04 | 0.01 | 0.60 | 0.82 | 0.87 | 0.18 | -0.04 | 0.01 | 0.65 | 0.85 | 0.87 |
| PO4 | Ev.2 | 0.91 | -0.47 | 0.08 | 0.87 | 0.88 | 0.98 | 0.84 | -2.31 | 0.06 | 0.89 | 0.96 | 0.97 |
| | Ev.3 | 0.76 | 0.30 | 0.36 | 0.77 | 0.69 | 0.95 | 0.75 | -0.28 | 0.15 | 0.89 | 0.90 | 0.93 |
| | Ev.6 | 0.83 | -0.29 | 0.34 | 0.84 | 0.96 | 0.98 | 0.84 | -0.31 | 0.23 | 0.89 | 0.98 | 0.98 |
| Zn | Ev.2 | 0.91 | -1.17 | 0.63 | 0.97 | 0.99 | 1.00 | 0.88 | -3.39 | 0.59 | 0.95 | 0.99 | 1.00 |
| | Ev.3 | 0.94 | 0.42 | 0.82 | 0.93 | 0.96 | 0.98 | 0.94 | 0.54 | 0.76 | 0.94 | 0.97 | 0.98 |
| | Ev.6 | 0.69 | 0.10 | 0.60 | 0.71 | 0.88 | 0.94 | 0.72 | 0.25 | 0.56 | 0.71 | 0.88 | 0.94 |

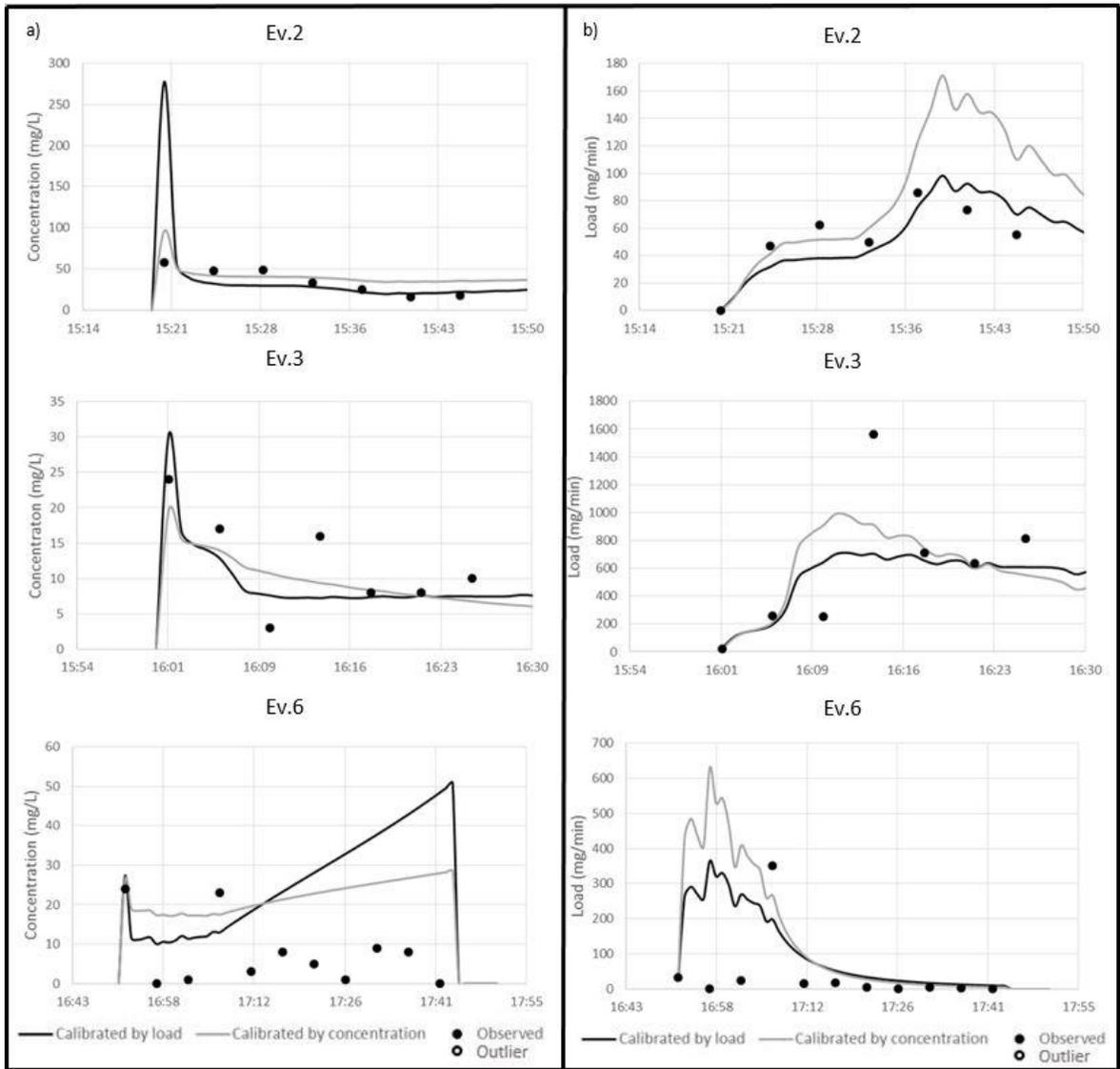
A4- Ammonia calibration and validation



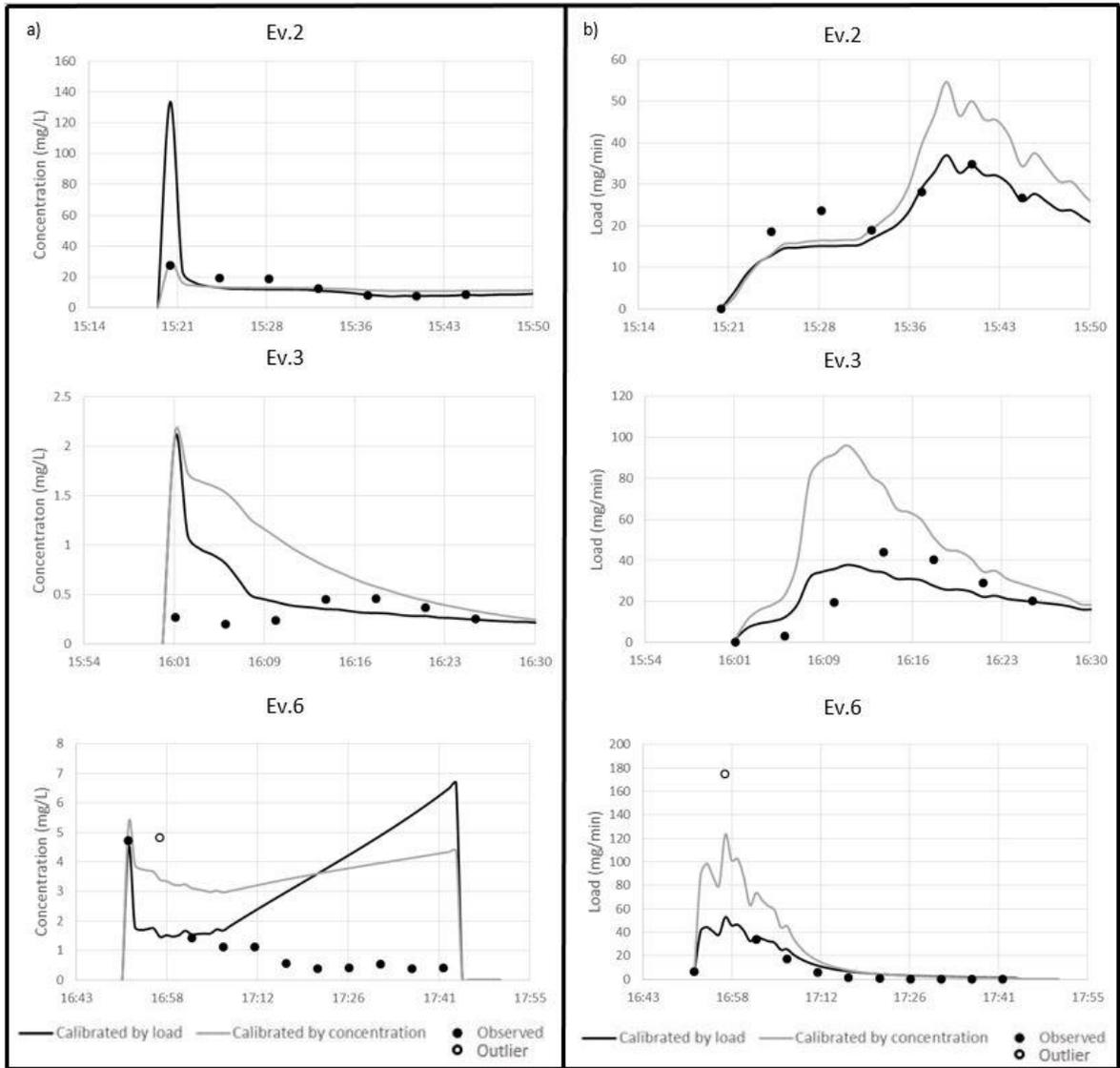
A5 – Cd calibration and validation



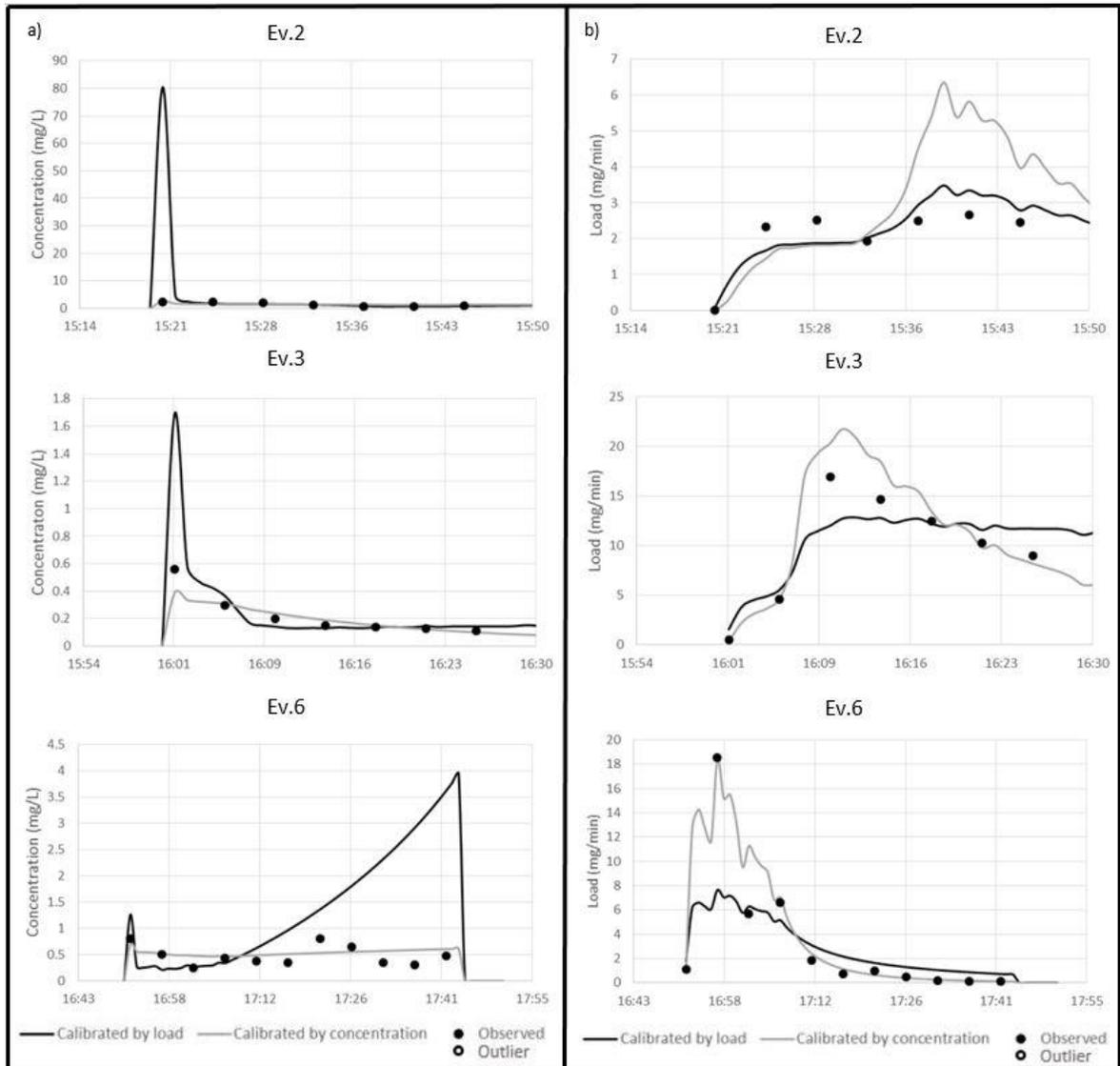
A6 – COD calibration and validation



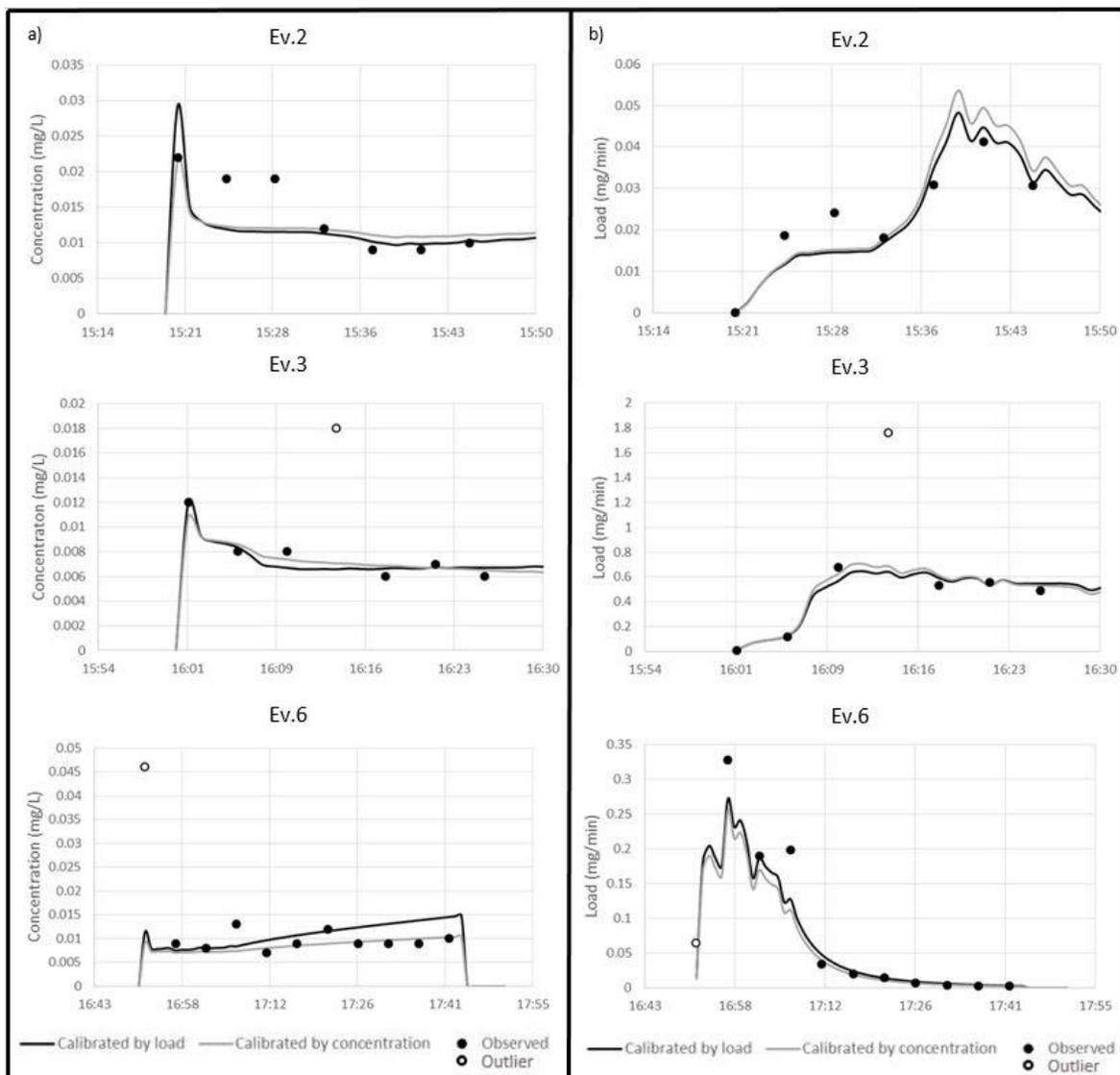
A7 – Fe calibration and validation



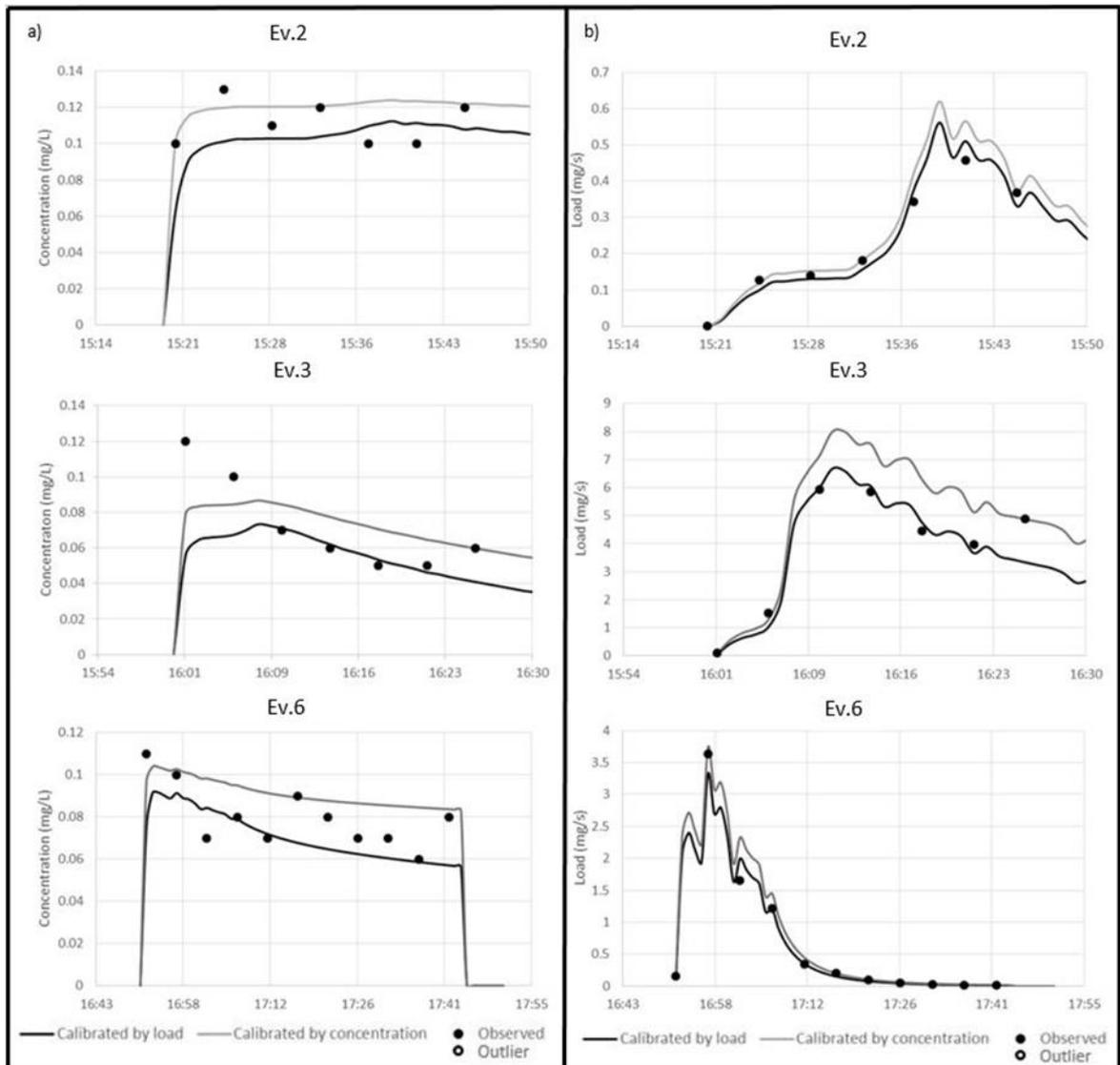
A8 – Nitrate calibration and validation



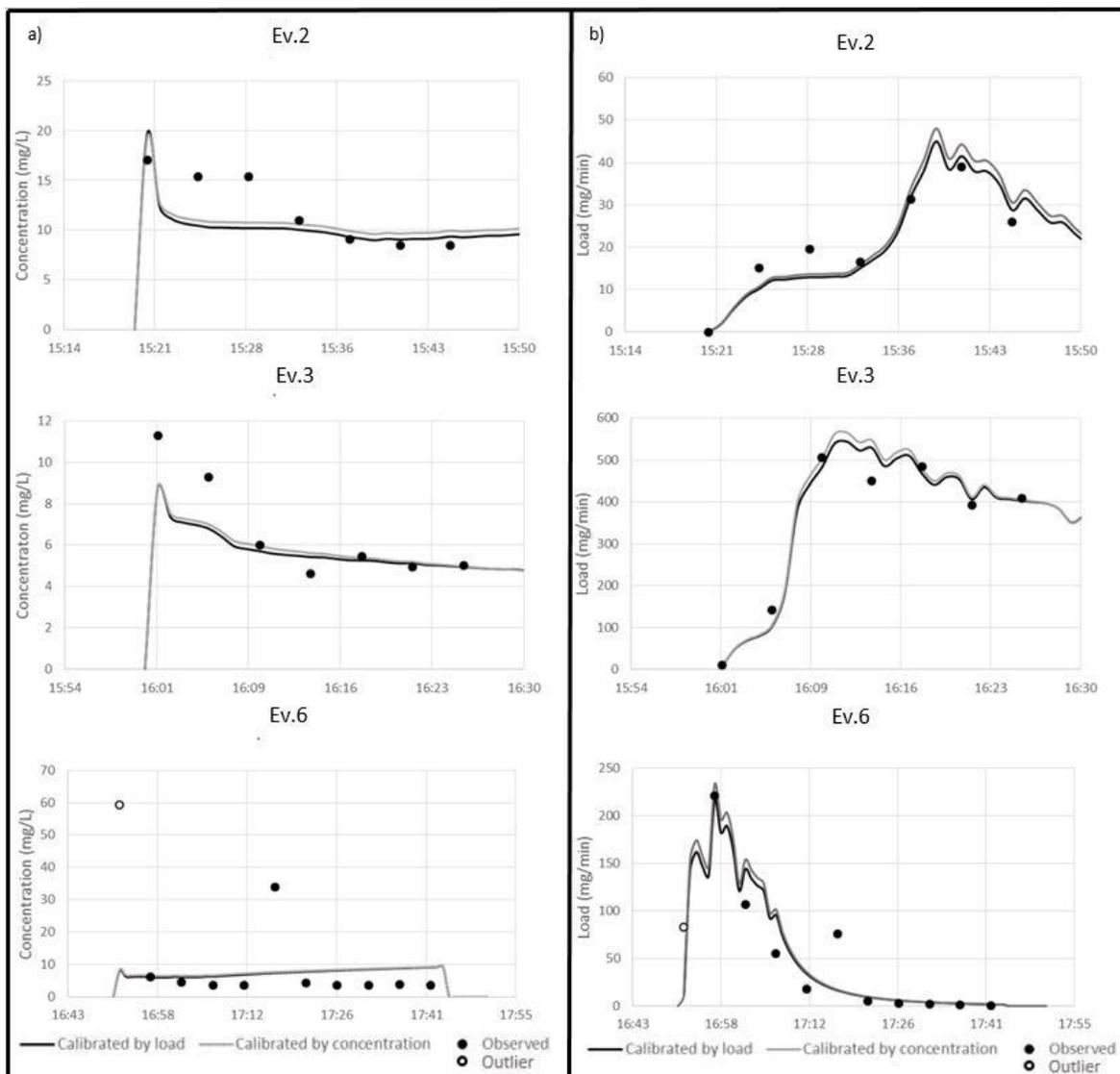
A9 – Nitrite calibration and validation



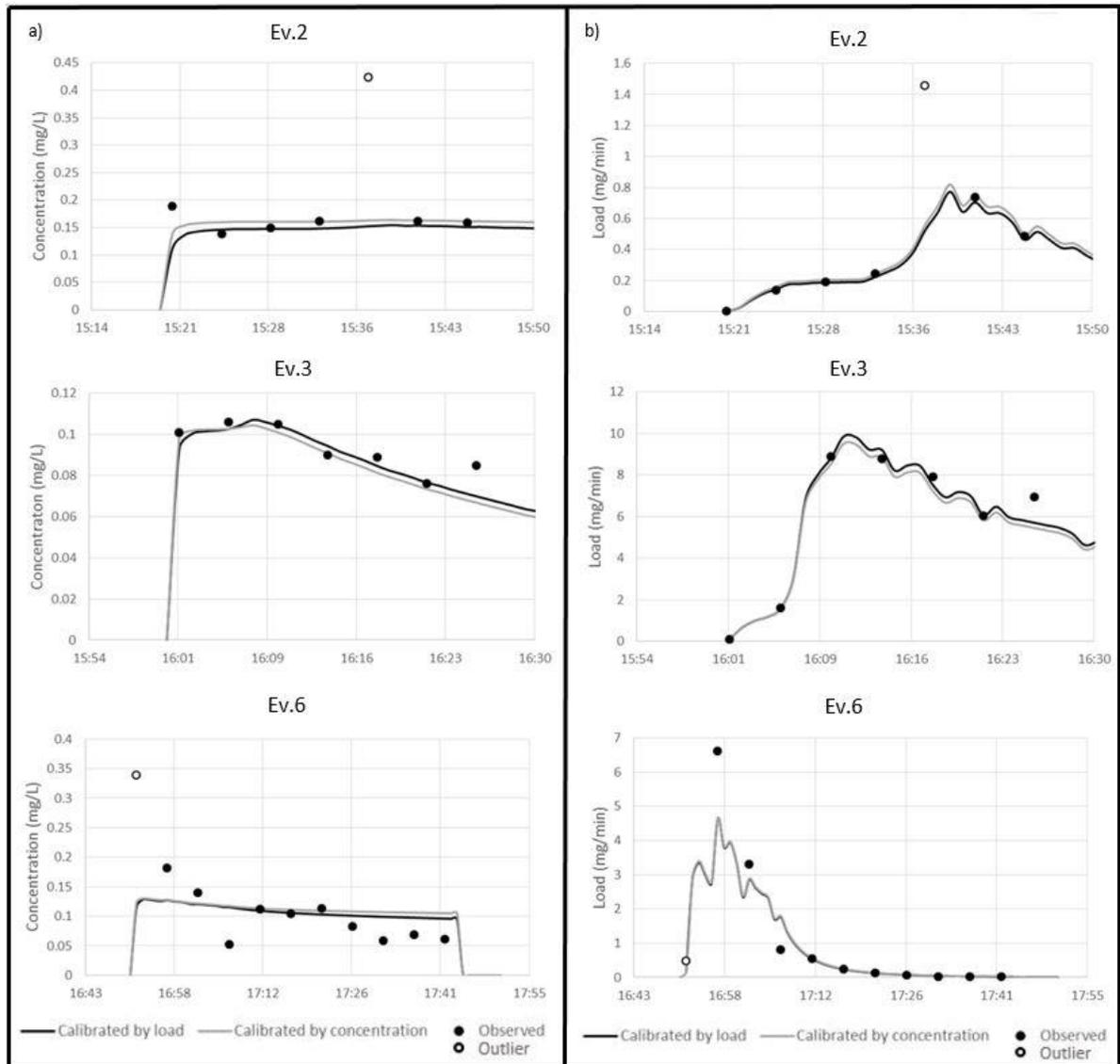
A10 – Phosphate calibration and validation

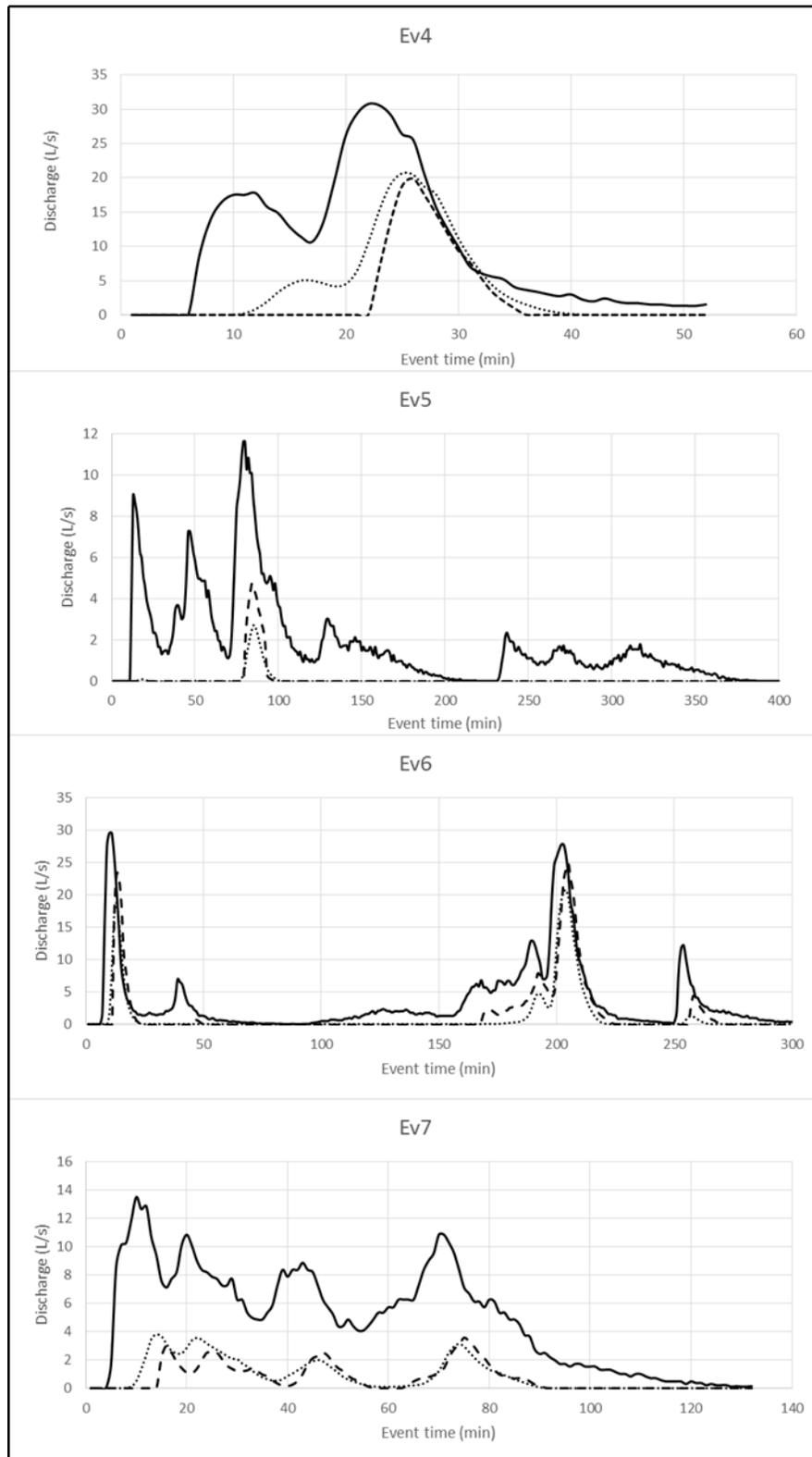


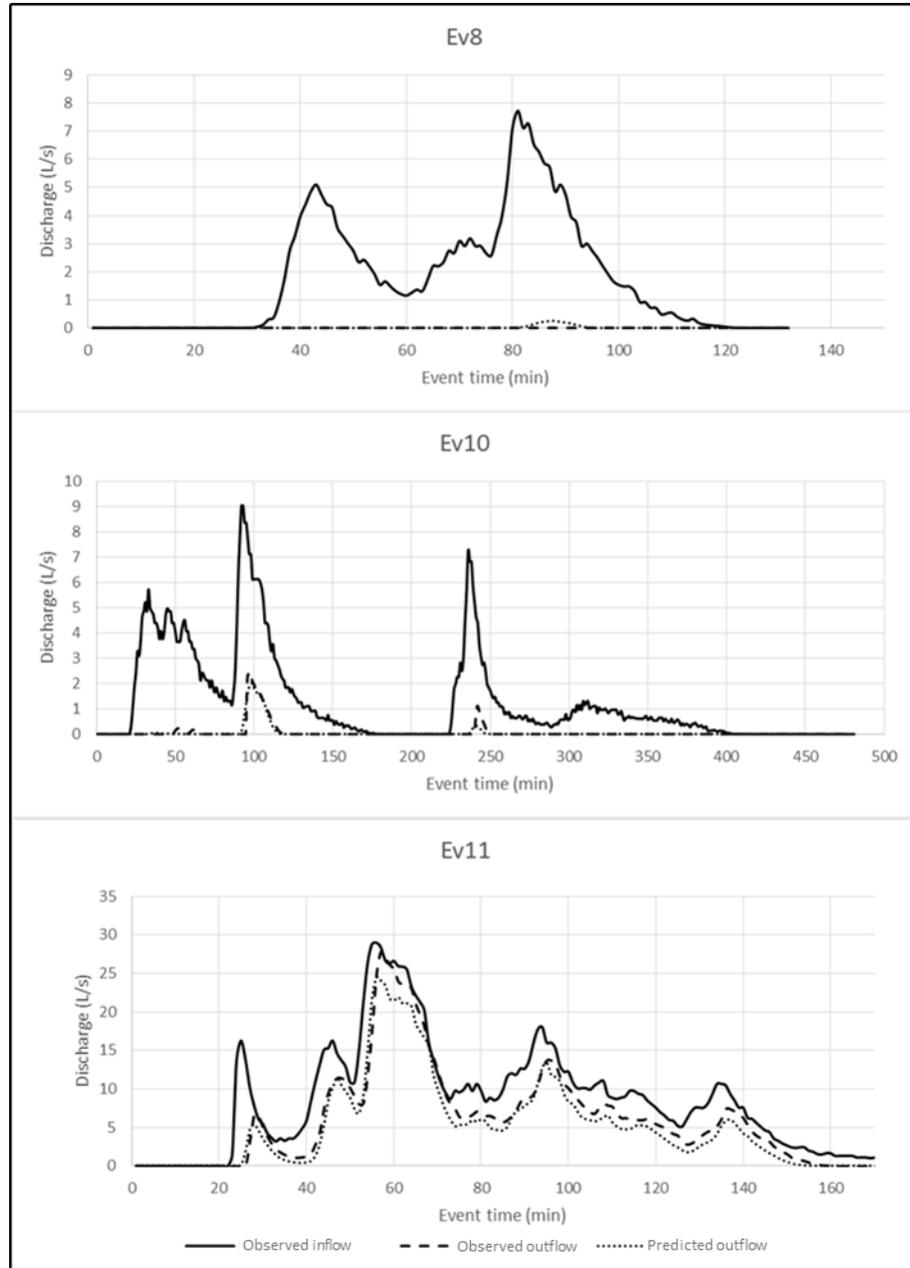
A11 – TOC calibration and validation



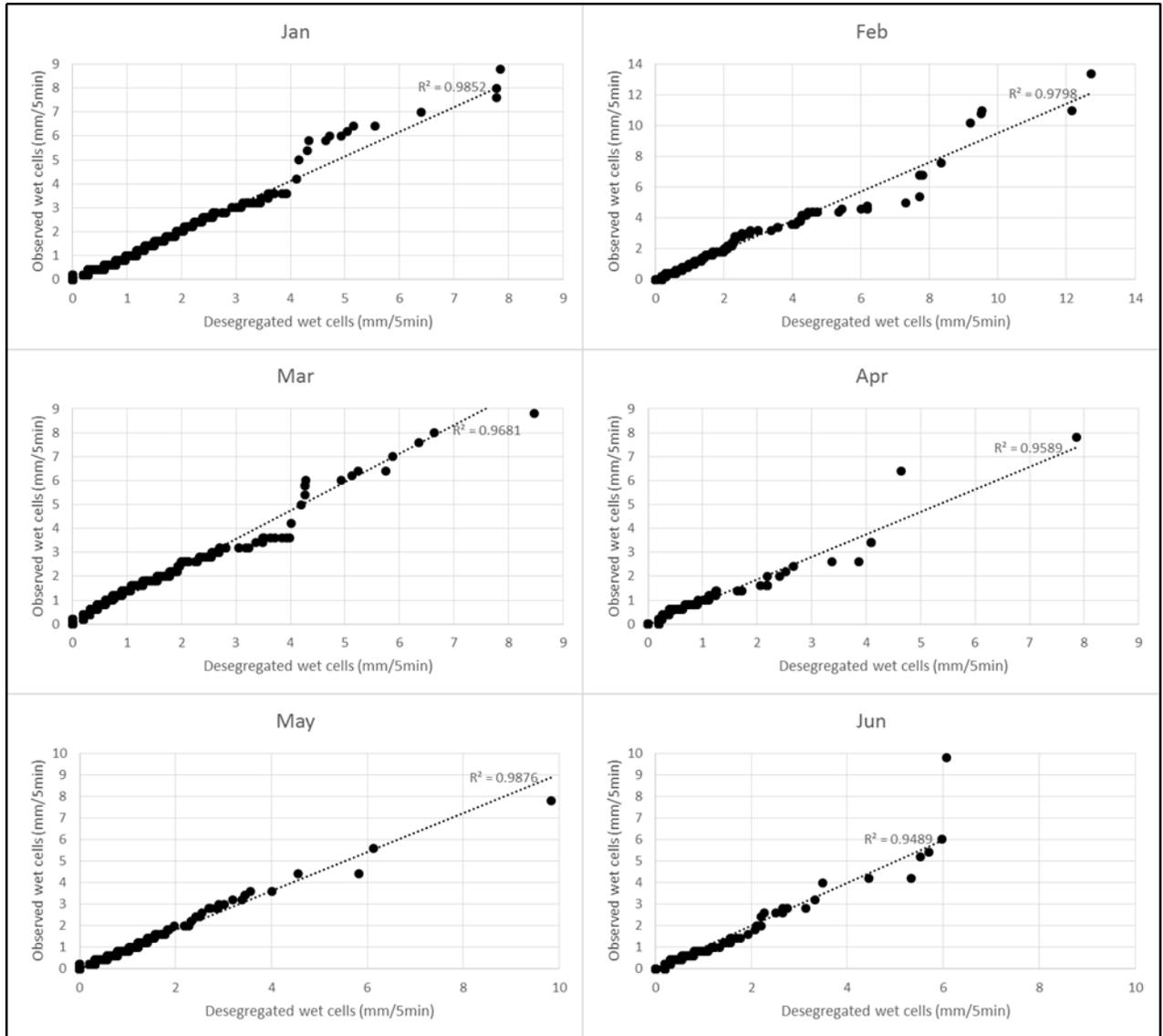
A12 – Zn calibration and validation



A13 – Bioretention outflow calibration (Ev4- Ev7)

A14 – Bioretention outflow validation (Ev8, Ev10 and Ev11)

A15 – Desegregated and observed wet cells (Jan to Jun)



A16– Desegregated and observed wet cells (Jul to Dec)

