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**Harvesting Rainwater - The Relevance of Hydrometeorological  
Factors on Rainwater Quality and Demonstration of the Mitigation  
Approach Using Green Roofs and Adsorption Materials**



**UNIVERSIDADE DO ALGARVE**

**Faculty of Science and Technology**

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**Erasmus Mundus Joint Master in Applied Ecohydrology (MAEH)**

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## **Declaration of authorship of work**

I declare I am the author of this work, which is original and unpublished. The sources consulted have been duly cited in the text and included in the list of references.

Date: 06.09.2024

Signature:

## **Acknowledgements**

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## **Abstract**

Water pollution is one of the main challenges facing the world at present. As water is a vital resource, it is essential that it meets minimum quality standards in order to be used as drinking water, as well as for the ecosystem health. Rainwater harvesting has received attention in recent years due to its potential use as a water source, and important as climate-adaptation strategy. However, rainwater often contains pollutants that can impact negatively on human health and aquatic ecosystems. In response to these challenges, Nature-based Solutions (NbS) have emerged as innovative approach that mimic natural processes to enhance ecosystem services, such as water quality improvement. Examples of NbS for rainwater management include green roofs, bioswales, and raingardens, which help improving rainwater quality before it infiltrates or drains to water bodies, protecting rivers, reservoirs and lakes from contamination. To further enhance the effectiveness of NbS in rainwater treatment, the use of natural and innovative sorbent materials like dolomite and biochar have demonstrated good potential.

In this way, the project aimed to assess the influence of hydrometeorological factors such as rainfall intensity (RI), antecedent dry period (ADP), and first flush on rainwater quality in the urban catchment (Łódź City, Poland) and to evaluate the efficiency of green roof technology in terms of rainwater retention and rainwater quality. Finally it aimed to identify and compare the potential enhancement of rainwater treatment through the use of innovative sorbent materials. The results demonstrated significant differences in rainwater quality between the two sites studied, particularly concerning pollutants like total phosphorous, indicating spatial impact on water quality. The research confirmed that the runoff from roofs produce elevated concentrations of pollutants including total suspended solids (TSS), total nitrogen (TN), total phosphorous (TP), and total organic carbon (TOC). A positive correlation was observed between ADP and pollutants concentration, while RI showed variable correlations across sites, suggesting that factors such as roof material, age, slope and roughness also could play a role in determining pollutant concentrations. Additionally, higher concentration of pollutants were found during the initial time of rainfall. In addition, the study identified that green roofs can significantly improve water retention and enhance rainwater quality by incorporating sorbent materials that mitigate the release of pollutants, such as phosphorus.

*Key Words: Rainwater Quality, Nature-Based Solutions, Hydrometeorology, Sorption, Climate Change, Pollutants*

## **Sumário**

A poluição da água é um dos principais desafios que o mundo enfrenta atualmente. Sendo a água um recurso vital, é essencial que cumpra os critérios mínimos de qualidade para ser utilizada como água potável, bem como para a saúde dos ecossistemas. A captação de água da chuva tem recebido atenção nos últimos anos devido ao seu uso potencial como fonte de água e à sua importância como estratégia de adaptação climática. No entanto, a água da chuva muitas vezes contém poluentes que podem afetar negativamente a saúde humana e os ecossistemas aquáticos.

Em resposta a esses desafios, as Soluções Baseadas na Natureza (SbN) surgiram como uma abordagem inovadora que imita processos naturais para melhorar os serviços dos ecossistemas, como a melhoria da qualidade da água. Exemplos de SbN para a gestão da água da chuva incluem telhados verdes, biovaletas e jardins de chuva, que ajudam a melhorar a qualidade da água da chuva antes de esta infiltrar ou entrar nos sistemas de drenagem, protegendo rios, reservatórios e lagos da contaminação. Para aumentar ainda mais a eficácia das SbN no tratamento da água da chuva, o uso de materiais sorventes naturais e inovadores, como dolomite e biochar, tem demonstrado bom potencial.

Desta forma, o objetivo do projeto foi avaliar a influência de fatores hidrometeorológicos, como a intensidade da precipitação (IP), o período seco antecedente (PSA) e o primeiro escoamento na qualidade da água da chuva; avaliar a eficiência da tecnologia de telhados verdes em termos de retenção e qualidade da água da chuva; e identificar e comparar o potencial de melhoria do tratamento da água da chuva através do uso de materiais sorventes inovadores. Os resultados demonstraram diferenças significativas na qualidade da água da chuva entre os dois locais estudados, particularmente no que diz respeito a poluentes como o fósforo total. A pesquisa confirmou que o escoamento superficial dos telhados produz concentrações elevadas de poluentes, incluindo Sólidos Suspensos Totais (SST), Azoto Total (AT), Fósforo Total (FT) e Carbono Orgânico Total (COT). Foi observada uma correlação positiva entre o PSA e a concentração de poluentes, enquanto a IP mostrou correlações variáveis entre os locais, sugerindo que fatores como

o material de telhado, a inclinação e a rugosidade também desempenham um papel na determinação das concentrações de poluentes. Além disso, foi encontrada uma concentração mais elevada de poluentes nos minutos iniciais da precipitação. Adicionalmente, o estudo identificou que os telhados verdes podem melhorar significativamente a retenção de água e a qualidade da água da chuva através da incorporação de materiais sorventes que mitigam a liberação de poluentes, como o fósforo.

***Palavras-chave:** Qualidade da Água da Chuva, Soluções Baseadas na Natureza, Hidrometeorologia, Sorção, Alterações Climáticas, Poluentes.*

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## LIST OF ABBREVIATIONS

Abbreviation	Definition
NbS	Nature-based Solutions
CEC	Contaminants of emerging concern
PPCP	Pharmaceuticals and personal care products
TWP	Tire wear particles
PFAS	Per- and polyfluorinated alkyl substances
RI	Rainfall intensity
D	Duration of rainfall
ADP	Antecedent dry period
LID	Low impact development
BGI	Blue green infrastructure
GI	Green infrastructure
ERCE	European Regional Centre for Ecohydrology
RS1	Rain (wet and dry deposition) Site 1
RS2	Rain (wet and dry deposition) Site 2
RWS1	Rainwater (runoff from roof) Site 1
RWS2	Rainwater (runoff from roof) Site 2
V	Volume
W	Weight
ExR1	Experimental roof #1
ExR2	Experimental roof #2
ExR3	Experimental roof #3
ExR4	Experimental roof #4
ExR5	Experimental roof #5

# 1 Introduction

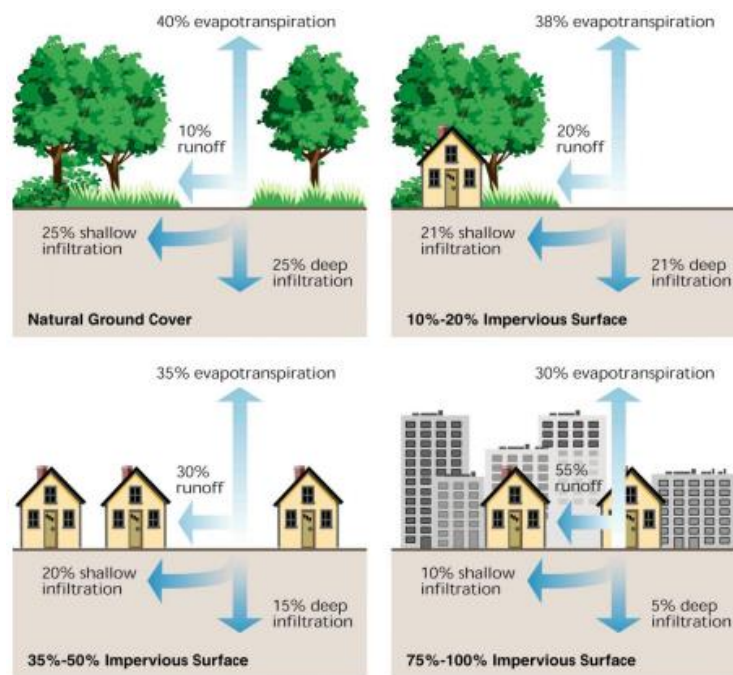
## 1.1 General background

According to the world water development report, by 2050, five billion people will suffer from water scarcity, and the number could be exacerbated due to the climate change, the increased water demand and water pollution (UNESCO, 2018). This has led to the identification of rainwater harvesting as a potential alternative. Although harvested rainwater is used as a drinking water source in many arid and semi-arid regions, numerous studies have warned about its use as a potable source since the quality is not really assure to be safe as a drinking water source (Chubaka et al. 2018; Gwenzi et al. 2015). Despite this, rainwater harvesting is one of the best methods available for establishing sustainable water cycles in urban developments (Kim et al. 2005). The necessity to look for alternatives to supply water has been the result of many processes as population growth, urbanisation, and climate change. All of this has contributed to reduce the availability of drinking water in numerous cities around the world and this has caused the exploration of alternative water sources such as rainwater (Zhang et al. 2014). Furthermore, the wide use of grey infrastructure combined with high density development, and climate change, are generally observed as being responsible for such environmental concerns as urban drought, the heat island effect (Gunawardena et al. 2017), hydraulic stress (Leitner et al. 2017) and intensified pollution transfer in urban areas (Zhang et al., 2015).

## 1.2 The role of water in urbanised areas

One of the processes that has driven the impact on water resources around the world is urbanisation. Currently, more than half of the world population lives in urban areas, a number expected to increase to about 70% by 2050 (United Nations, Department of Economic and Social Affairs, 2019). Although the cities occupy only 2% of continental surface, they are home for more than half of the population, which traduce in the consumption of up to three-quarters of the natural fossil and renewable resources and energy production, and the contribution of three-quarters of greenhouse gas emissions (UNEP, 2011). This rapid and extensive urbanisation has led to significant changes in land cover, replacing natural landscapes into impervious surfaces, thereby disrupting the hydrological cycle. This disruption reduces infiltration, and impacts at the same time biological and ecological processes within urban catchments (Kong et al. 2021). In urban catchments, sewer

infrastructure often includes combined sewers overflow (CSO) systems, which discharge stormwater directly into water bodies such as streams, lakes or reservoirs, during heavy rainfall events. These systems are designed to manage excess water without any treatment, which can exacerbate water quality issues by introducing elevated levels of nutrients, suspended matter and faecal coliforms into the environment (Carpenter et al. 2016). Figure 1.1 illustrates the process of urbanisation and disruption of hydrological cycle, which contributes to increased urban flooding in many regions around the world. In addition, disruption of the urban water cycle leads to further degradation of water and water-related ecosystems, through hydraulic stress, habitat degradation and physical and chemical pollution of water bodies, lowering their health and ecological status (Wagner & Zalewski, 2009).



*Figure 1.1.* Changes in land cover due to urbanisation. Adapted from "Stream Corridor Restoration Principles, Processes and Practices" by Federal Interagency Stream Restoration Working Group, 1998, Item No. 0120, pp. 3-23.

Nowadays, increasing urbanisation and the harmful effects of climate change have influenced the water balance, resulting in unfavourable events such as severe flooding, droughts, and heat stress (Kasprzyk et al. 2022). Therefore, the negative impact of urban hydrology modification is even more visible recently due to climate change (Flörke et al. 2018; Miller & Hutchins, 2017). Moreover, the lack of access to adequate water sources is particularly pronounced in regions such

as Africa, Asia and Latin America, making effective and adequate water management a critical factor in order to address these challenges. In addition to the extreme events and the problems regarding access to water sources, the loss of the ecosystems services in urban areas due to the alterations on land covers is also an important point to take into account as it could impact even the health of people. For instance, the decrease in air humidity in the dry period can increase at the same time air pollution, which in turn promotes allergic diseases of the respiratory system such as allergic rhinitis and atopic bronchial asthma (Kupryś-Lipińska et al. 2009). Another example is the loss of cultural ecosystem services such as recreation, as the poor quality of water bodies that receive discharges of urban stormwater impact the use of those areas for sport or recreational activities.

Climate change models do not provide optimistic projections, so the disruption of the water cycle is expected to further increase the challenges. Prolonged droughts and more intense precipitations will directly impact the cities increasing the intensity of floods and droughts. At the same time, higher temperatures will intensify the urban heat islands. The consequent microclimate change and poor air quality will further compromise the environmental security, health and quality of life of cities inhabitants, that on the last decades have already caused thousands of premature deaths in Europe (European Environment Agency, 2012; Wagner & Breil, 2013).

### 1.3 Rainwater quality

As urban areas are facing rapid changes in land cover, it is important to identify the different types of impervious surfaces present on an urban scale in order to distinguish the sources of runoff: roof runoff, road runoff, and runoff from surfaces such as parking lots, open spaces etc. These sources often combine into a final stream, known as urban stormwater (De Buyck et al. 2021). Depending on the type of runoff, the quality of the water could differ, influencing the type of pollutants as well as their concentrations or loads. With the accelerated rate of urbanisation, the increase in terms of volume and velocity of stormwater runoff have mobilized more pollutants from watersheds to receiving water bodies, ultimately affecting the quality of rivers, lakes or any other final recipient of stormwater (Pamuru et al. 2022).

The enrichment of many pollutants takes place in the water when it washes over impervious surfaces (Davis et al. 2001), however, the pollutants present in runoff are consequence of specific phases of pollution:

- 1) Wet deposition, which involves the wash off of atmospheric pollutants and the scavenging of contaminants from aerosols, gases and volatile particles (Sánchez et al. 2015).
- 2) Dry deposition, which is mostly influenced by the dry period preceding the precipitation events resulting in the accumulation of pollutants on surfaces such as roofs, roads, park lots etc. This process is not influenced by precipitation but rather by wind and air humidity, which can affect the variation of dry deposition in different areas (Sánchez et al. 2015).
- 3) Leaching, where pollutants may leach (or dissolve) from the materials of surfaces (e.g., the leaching of organic pollutants from concrete roof), adding more pollutants to the rainwater (De Buyck et al. 2021; Sánchez et al. 2015).

Figure 1.2 represents a graphical abstract of the sources of runoff contamination that commonly occur in urban areas.

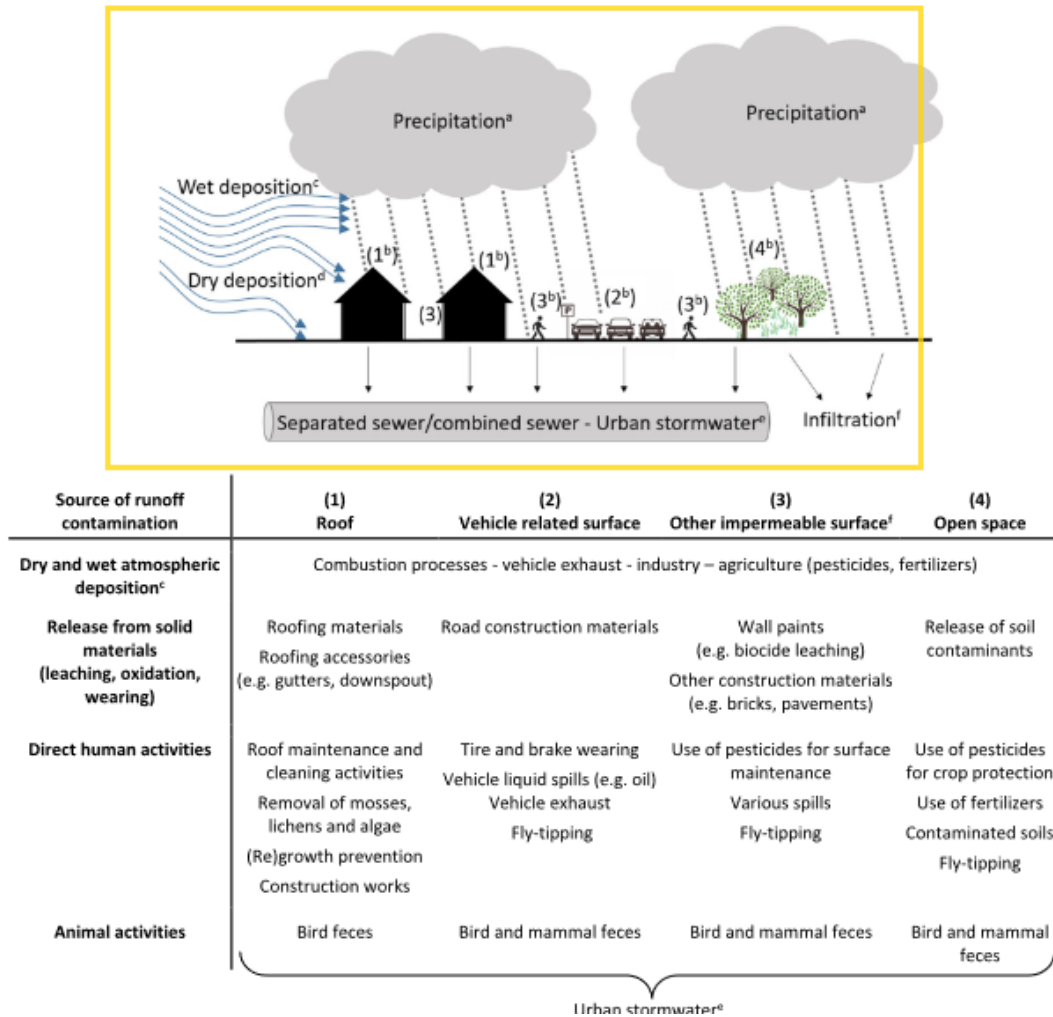


Figure 1.2. Sources of runoff contamination on urban areas. Adapted from De Buyck et al. 2021

As it was mentioned before, rainwater goes through different stages of contaminant wash-off, and it is important to distinguish between them. At first, regarding the atmospheric deposition, Duncan (1995) considered that total nitrogen concentration in urban rainfall is between 1 and 2 mg/L. Furthermore, the presence of some ions in rainfall such as nitrate and ammonium, originated from anthropogenic activities, are recurrent in urban areas like Sao Paulo metropolitan region (Sánchez et al. 2015). In addition to wet and dry deposition, bird faeces and lichens on roofs are significant sources of ammonium and phosphorous in roof runoff.

Despite the different pollutants that can be encountered in rainwater and the variations between regions or sites, some pollutants are of major concern due to their negative impacts on aquatic ecosystems. Nutrients such as nitrogen and phosphorous are washed from various urban surfaces

during rainfall events. These nutrients can accumulate downstream, leading to eutrophication in recipient water bodies, which negatively impacts ecosystem quality and can stimulate harmful algae blooms. In the same way, some metals like copper (Cu), lead (Pb) and Zinc (Zn) can be washed and transported by rainwater, as these elements are present in tire wear and building materials like roofs (Pamuru et al. 2022). It is important to notice that the type and level of pollution are also determined by the type of surface and the materials that come into contact with rainwater. For instance, Nicholson et al. (2010) and Olaoye & Olaniyan (2012), found that the type and material of the catchment's surface can significantly influence the contamination of runoff.

Apart from nutrients and heavy metals, contaminants of emerging concern (CEC) have appeared as another group that will require more attention in future due to the importance and the significant amounts of these compounds that rainwater or stormwater could potentially contain. As Saifur & Gardner (2021) mentioned, “stormwater runoff remains a significant driver of environmental pollution and is a major source of several new CEC such as pharmaceuticals and personal care products (PPCP), tire wear particle (TWP) compounds, and per- and polyfluorinated alkyl substances (PFASs)”. These kind of contaminants become a challenge in order to be treated since many CEC contain unique physiochemical properties that may make them more difficult to remove (Bodus et al., 2024). Management of CEC is also essential due to the toxicity and ability to bioaccumulate which means a serious threat to living organisms (Kasprzyk et al. 2022). Most of the studies regarding CEC are addressed in the stormwater, however some studies have also identified the emerging pollutants on atmospheric deposition, and also in the leaching from surfaces. For instance, Newton et al. (2014) identified five emerging chemicals: two pesticides (trifluralin and chlorothalonil), and non-BDE flame retardants: 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), and Dechlorane Plus (DP) on atmospheric deposition. In the case of the roof runoff, Müller et al. (2023) investigated the releases of metals and several groups of CEC: alkylphenols, alkylphenol ethoxylates, and phthalates. The study used commercially available materials commonly used on buildings and urban surfaces.

The presence and concentration of different pollutants in rainwater, including the CEC, can vary depending on several factors, including the characteristics of the area (e.g whether is urbanised and

is surrounded by industries) and the prevailing hydrometeorological conditions. A thorough understanding of these factors is fundamental for the rainwater management.

#### 1.4 Influence of hydrometeorology factor on rainwater quality

As it is mentioned by Zalewski et al. (2021), one of the most important challenges in the 21<sup>st</sup> century is understanding the causal relationships between abiotic factors (such as hydrological cycle), biotic factors (for instance ecological aspects), and the dynamic of society regarding the prevention of disasters (floods and droughts), environmental degradation and the sustainable provision of ecosystems services. The importance of hydrological cycle becomes even more visible in the case of urban areas that are characterized by large sealed areas (roofs, roads, car parks), and, the importance of these areas in terms of climate change impacts. In the case of rainwater, previous studies and research on rainwater quality have correlated hydrological parameters with the pollutants studied in order to determine possible relationships between them. Parameters such as rainfall intensity (RI), duration of rainfall (D) and antecedent dry period (ADP) have been the primary focus (Esfandiar et al. 2024; Wang et al. 2013; Zhang et al. 2014). RI and D have been showed negative correlation regarding the level of pollutants, while for ADP a positive correlation with pollutants concentration has been determined by many authors (DeBusk & Hunt, 2014; Wang et al. 2013; Zhang et al. 2014). Further on, “first flush” is another crucial factor for rain water quality. The first flush refers to the initial portion of the precipitation event that contains the highest concentration of pollutants. This happens during the initial minutes of the event (5 – 10 minutes) when accumulated particles on surfaces and in the atmosphere are washed off. The concept of “first-flush” is proposed to describe the first period of rainfall event, based on considering the cumulative pollutant load versus cumulative runoff volume for a single event (Bertrand-Krajewski et al. 1998; Kim et al. 2005; Nason et al. 2012).

Sánchez et al.(2015), mentions that “the washout of the air above the cities occurs rapidly and in the initial stage of a storm event, so this process is almost independent of RI and rainfall volume”. Despite this generalised concept, different criteria have been used to identify the first-flush, depending on the ratio of the percentage load of pollutants to the percentage of runoff volume. On the other hand, other authors point out that it is important to relate the first flush with other hydrological factors such as RI, ADP and runoff depth (Perera et al. 2021) which impact the water quality of that first flush.

For the purpose of this research and from now on, the term of rain will be referred as direct wet and dry deposition, rainwater will refer to water produced by roof runoff and stormwater will refer to the combination of runoff produced by roofs, roads and other impervious surfaces.

## 1.5 Nature Based Solutions

In response to the growing pressure on water resources, the concept of Nature-based Solutions (NbS) has emerged as a sustainable alternative to traditional grey infrastructure. Also known as low impact development (LID) facilities, Blue-Green Infrastructure (BGI) or green infrastructures (GI), NbS endeavours to emulate natural processes. These type of solutions help to preserve ecosystem services such as reduction of runoff and flood protection, groundwater pollution prevention, biodiversity conservation and microclimate control (Kasprzyk et al. 2022). Examples of BGI include green roofs, bioretention cells, bioswales, permeable pavement, and infiltration basins and trenches (Dietz & Clausen, 2006). This type of NbS has demonstrated benefits such as increasing retention capacity in a catchment, mitigating the events and consequences of flooding and improving the quality of runoff that is eventually discharged into rivers or lakes.

In urban areas, NbS have been mostly implemented to manage stormwater. For instance, Gdansk (Poland) was one of the cities that implemented rain gardens across different areas such as parks, the city centre, main crossroads and car parks (Kasprzyk et al. 2022). The use of vegetated swales has also been implemented and documented in many sites. Wu & Allan (2018), for example, investigated the effect of vegetated swales constructed in a section of a road surface in North Carolina, United States.

In the case of rainwater, there are fewer studies or applications of NbS compared to stormwater. In spite of this, green roofs, are a common solution that has increased the rate of implementation across many cities. The implementation of intensive or extensive green roofs in countries as Japan or Sweden has helped to minimize flooding problems, and improve the rainwater quality (Berndtsson et al. 2009). In Recife, Brazil, Santana et al. (2022) carried out a study that characterize the water quality flowing from a green roof in order to evaluate the potential of non-potable uses of this water. In the same way, the authors Carpenter et al. (2016) examine the quality and the quantity of discharge related to precipitation events over an annual cycle from a green roof in Syracuse, NY. In Australia, the approach of water sensitive urban design has been associated with

the implementation of measures such as green roofs, raingardens or infiltration systems. Raingardens are often implemented in domestic, commercial and industrial buildings, where there is potential for a very significant impact on runoff management at the source, commonly the runoff from the roofs (Department of Planning and Local Government, 2010).

Although many of these cases have been implemented successfully, some concerns have been exposed due to the release of some nutrients or compounds from these kind of solutions. This is the case of phosphorous, which has been found by some authors as problematic. Berndtsson et al. (2006) claimed that “green roofs runoff can impair quality of receiving waters by contributing substantial amounts of phosphate phosphorus to the runoff”. Additionally, some authors (Berndtsson, 2010; Mitchell et al. 2017; Rowe, 2011) have claimed that specially the young green roofs can contribute very high levels of phosphate via runoff to local waterways, so the roof age and other factors like type of soil, fertilization routine among others have a significant effect on the amount of phosphorous that can be released. The same has been found for bioretention systems. For instance, Paus et al. (2014) suggested that the phosphorous release from bioretention media during storm water infiltration is a concern, remarking also that “particulate phosphorous captured by the media could slowly dissolve over time and become a source of phosphorous release”.

The common processes in rainwater treatment of NbS include filtration, sorption, precipitation, ion exchange among others. Filtration is the simplest process, involving the entrapment of particles of considerable size into the interstitial spaces. Precipitation provides the removal of phosphorous and heavy metals through the formation of metal-ligands and subsequent settling of these particles. Ion exchange is also important for the removal of heavy metals due to the potential capacity to exchange cation or anions. Nevertheless, one of the most important processes and the focus of this research, is the sorption process, because as mentioned before, one of the main concerns about implementation of NbS is the release of some nutrients or pollutants. This process enables the removal of dissolved pollutants such as phosphates or heavy metals through direct bonding, both physical and chemical (Ali and Pickering, 2023). The use of different amendment materials has been studied in order to identify novel materials with the potential to increase the removal rates of pollutants. For example, studies have investigated the effectiveness of biochar, zeolite, and other materials in enhancing the sorption capacity for phosphorus and heavy metals (Ekanayake et al.

2021; Reddy et al. 2014b; Xiong et al. 2022). These materials have shown promising results in increasing pollutant removal efficiency in NbS systems.

## 1.6 Aim of the study and hypothesis

The aim of the present study was to:

- 1) Determine the influence of hydrometeorological factors such as rainfall intensity, antecedent dry period, and first flush on rainwater quality.
- 2) Verify the efficiency of green roof technology as a type of NbS in terms of runoff quantity and quality.
- 3) Identify and compare the potential enhancement of rainwater treatment through the inclusion of innovative sorption materials.

### **Hypothesis:**

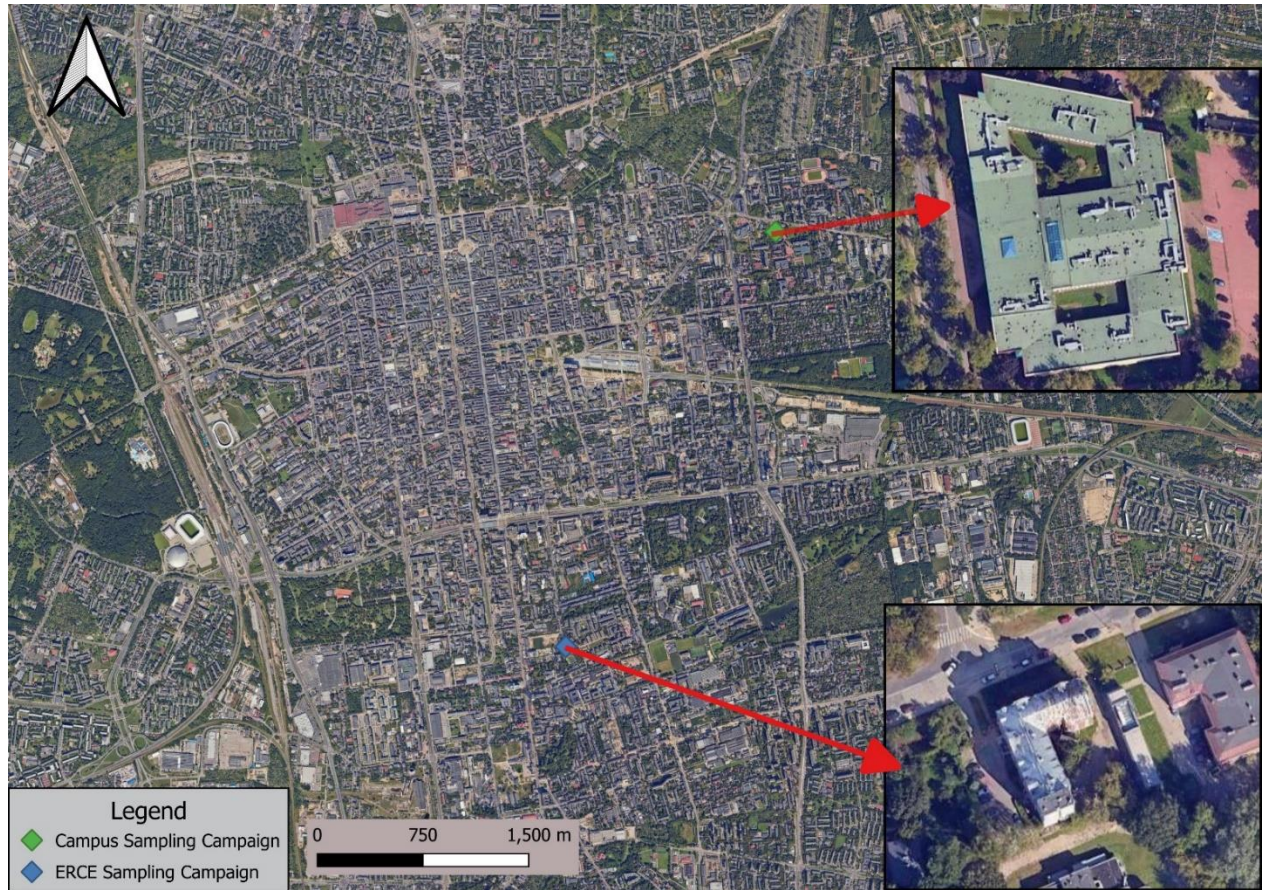
- 1) There is an impact on wet and dry deposition and rainwater quality in urban areas influenced by the spatial and temporal distribution.
- 2) The pollutants concentration in rainwater are significantly correlated with antecedent dry period and rainfall intensity.
- 3) The first flush of the rainfall events represent significantly higher concentrations of pollutants.
- 4) The green roofs have a significant reduction of water runoff volume and provide an enhancement of the rainwater quality through the inclusion of innovative sorption materials.

## 2 Materials and methodology

### 2.1 Study area

This research, that is part of the project Water4All, will be implemented in the city of Łódź, specifically in the Campus of University of Łódź, as an exemplary area of blue-green infrastructure, in order to minimize the uncertainty of water resources in urban space related to climate change.

The city of Łódź is located in central Poland. Is inhabited by about 711000 people and occupies an area of 293 km<sup>2</sup> (Sakson et al. 2018). The city has a temperate climate, with a mean annual temperature of 8°C, and an annual mean rainfall of 572 mm (Zawilski et al. 2014). The city area is also the source of 18 streams that convey water towards its outskirts. The development of the city has led to reduced ability of the landscape to retain water and has created some challenges. Increased flooding, creation of a heat island, low humidity and high concentration of dust and air pollutants during dry weather, and decreased quality of water for human health, recreational use, aesthetical values and good ecological status are some of them (Wagner & Zalewski, 2009). Rainwater management in Łódź is based on grey infrastructure, as usual in European cities. Rainwater is collected from all sealed surfaces and moves to the city centre, where it is primarily transported to the Group Wastewater Treatment Plant (GWWT). However, to avoid overcapacity of the wastewater treatment plant, during intense storms the greater portion of stormwater is released directly into urban rivers. In the new city districts rainwater is collected by a separate sewerage system and flows directly into urban rivers and is rarely treated prior to the release (Zawilski et al. 2014). Regarding the rain and rainwater sampling, two areas were identified for the purpose of the study. The first place (defined as Site 1) was the building of European Regional Centre for Ecohydrology (ERCE), located in the centre of the city. The second place (defined as Site 2) was the Campus of the Faculty of Biology and Environmental Protection University of Łódź located at the north east part of the city. In Figure 2.1 the map of Łódź is shown along with the locations of the sampling points. The abbreviation for the different type of samples will be: Rainwater from Titanium-Zinc roof Site 1 (RWS1) & Rainwater from Tar roof Site 2 (RWS2), Rain site 1: ERCE (RS1), Rain site 2: Campus (RS2).



*Figure 2.1. Location of Sampling Points of Rain and Rainwater*

In the next sections, 2.1.1 and 2.1.2, the sampling campaigns are described with more detail.

### 2.1.1 Sampling campaign Site 1

The European Regional Centre for Ecohydrology (ERCE) is located in the centre of the city, coordinates 51°45'05.79" N and 19°27'54.54"E. The area is surrounded by house buildings and located in front of the street Henryka Sienkewicza that pass through the centre of the city.

The sampling of rainwater was carried out from middle of March 2024 until the end of June 2024. In these 4 months 13 events of rainfall were sampled (n=13). Three containers of plastic of 20 litres were disposed in three places close to the parking area of ERCE in order to quantify the precipitation volume and measure the quality of direct rain (wet and dry deposition). It is important to mention that in some events (specially March and April) the containers were receiving vegetation material from the surrounding area due to the fall of vegetation and strong wind, and it was decided after few weeks to put a net at the top of the containers that prevent the entrance of some animals

and vegetation to the containers, however the containers were not completely closed before the rainfall events, so dry deposition was always present during the sampling campaign. Figure 2.2 shows one of the containers located in the institute and the net that was added to the containers to prevent the entrance of animals and vegetation.



*Figure 2.2.* Container located in the institute to sample rain (left) and the addition of a net to the containers to prevent the entrance of animals and vegetation.

For the rainwater sampling it was used one of the pipes connected to one of the gutters from the building roof. The area that was used to collect the water from this roof is shown in Figure 2.1. This area corresponds to 44 m<sup>2</sup> according to a calculation made through Google Earth and the material of the roof is zinc-titanium. For the collection of rainwater it was conducted manually when the rain event occurred during the weekdays. In the case of some of the weekends that was forecasted a rainfall event a container of 1 litre was disposed to collect just the initial time of the event. The events of sampling are described with more detail in Table A- 1 of APPENDIX. This table contains the main data of the events: start date and hour, end date and hour, antecedent dry period, volume of the samples collected in the containers (if was collected), information about if was or not collected rainwater, and some observations during the event. Some events are separated into two, for example, event number 7 that is divided into 7.1 and 7.2 due to the difference on the start hour, however it was considered the same event.

### 2.1.2 Sampling campaign Site 2

The Faculty of Biology and Environmental Protection of University of Łódź is located in the north-east of the city, coordinates 51°46'39.59" N and 19°29'11.26"E. The place is surrounded mostly by residential buildings and other campus from the university. As this area is not exactly in the centre of the city, it has also green places around the campus, which makes this place more a suburban area than the first sampling point. The sampling campaign of rainwater was carried out from beginning of April 2024 until end of June 2024. In these 3 months a total of 12 events of rain were sampled (n=12). For the sampling of rainwater were used two of the pipes connected to two gutters from the building roof. One of the pipes corresponds to the shown in Figure 2.3.



*Figure 2.3.* Collection of rainwater from Campus of University of Łódź

The roofs that were used to collect the rainwater from this site are shown in Figure 2.4 and corresponds to 720 m<sup>2</sup> (left) and 692 m<sup>2</sup> (right). For the collection of rainwater when the rain event occurred during the weekdays in hours were the campus was opened the collection was conducted manually. In the case of the weekends or nights that was forecasted to rain, a plastic bottle of about 500-750 millilitres was disposed to collect it, however in these cases the sample just correspond to the initial time of rain.



Figure 2.4. Areas of rainwater collection in Campus of University of Łódź

## 2.2 Collection of hydrometeorological data

For the collection of hydrometeorological data, it was provided through a temporal meteorological station, located at Wojska Polskiego Street, used it as part of ATENAS project. The meteorological station provided daily data about rainfall and also temperature data(ATENAS, 2020).

The rainfall pattern history during the months of March to June, which are the ones the sampling was done, are highlighted in Figure 2.5. March is colder than April, May, and June, being June the warmest. In terms of rainfall, March and April are considered drier than May and June, when storms are more frequent and intense precipitation events may happen.

	January	February	March	April	May	June	July	August	September	October	November	December
Avg. Temperature (°C)	-2	-0.8	2.9	8.9	14	17.4	19.5	19	14.4	9.2	4.7	0.4
Min. Temperature (°C)	-4.5	-3.8	-1.1	3.7	8.8	12.4	14.8	14.4	10.3	6.1	2.3	-1.7
Max. temperature (°C)	0.2	2.1	6.9	13.6	18.5	21.7	23.7	23.4	18.6	12.7	7.1	2.4
Precipitation / Rainfall (mm)	48	44	52	51	74	72	96	66	62	48	48	51
Humidity(%)	84%	82%	76%	67%	67%	65%	68%	67%	72%	79%	85%	84%
Rainy days (d)	9	8	9	8	9	9	10	8	8	7	8	9
Sunshine hours (h)	2.7	3.6	5.5	8.6	10.1	10.9	10.9	10.3	7.4	5.0	3.3	2.5

Figure 2.5. Average monthly temperature and precipitation on the city of Łódź . Adapted from: <https://pl.climate-data.org/europa/polska/%C5%82odz-voivodeship/%C5%82odz-627/>

### 2.3 Evaluation of the green roof technology as promising NbS for rainwater management

In the campus five experimental roofs with an area of 1 m<sup>2</sup> each were located (See Figure 2.6). Two main parameters were monitored, first the runoff volume produced by the roofs, and secondly the rainwater quality. The events of sampling from these experimental roofs and the building roof described in the previous section are detailed in Table A- 2 of APPENDIX. This table contains the main data of the events: start date and hour, end date and hour, antecedent dry period, which samples were taken (roof, experimental roofs from 1 to 5), and some observations during the event and/or sampling. The description of the experimental roofs are described in the following paragraphs.



*Figure 2.6.* Experimental Roofs located at Campus of University of Łódź

Five experimental roofs were part of the research to assess the water quality for the runoff from these roofs. The experimental roofs were located on one of the gardens that is at the Faculty of Biology and Environmental Protection University of Łódź (See Figure 2.7).



*Figure 2.7.* Location of the experimental roofs that were studied

From these experimental roofs the rainwater was collected through a gutter connected to a plastic storage container as is shown in Figure 2.8. In some of the events the water was collected directly from this containers, especially when the rain events were on the weekend or during nights where there was not access to the campus, so the water was collected the next day after the rain. On other events it was possible to collect the water directly from the pipe connected to the gutter as it is shown in the right picture of Figure 2.8. It is important to state that when the water was collected from the containers, the water was mixed with water from days before, so the chemical analysis did not show on actual but rather the general status of water runoff. The description of each of the roofs is presented below.



*Figure 2.8.* Containers used for rainwater collection of experimental roofs.

- Felt roof (ExR1): This type of roof could be made by multiple layers of natural materials such as wood cellulose or synthetic materials as fiberglass or polyester. They are protected by a protective coat such as bitumen (asphalt) or tar which repels the water. See Figure 2.9.
- EPDM rubber roof (ExR2): This type of roof is made by two primary products: ethylene and propylene. Some properties of this roof are the water proof, the temperature resistance and the long duration. See Figure 2.9.



*Figure 2.9.* Felt roof (left) and EPDM rubber roof (right)

- EPDM roof with small buckets of Sedum (ExR3): The material of the roof itself is the same than the previous one, but this roof contains small buckets of the plant *Sedum Caeruleum L.* See Figure 2.10.
- EPDM roof with small buckets of Sedum and Caxit (ExR4): The roof has EPDM material, with same buckets of *Sedum Caeruleum L.* of the previous roof, but with a layer of Caxit that acts as a sorbent material that enables the removal of some pollutants such as phosphorus. See Figure 2.10.



*Figure 2.10.* EPDM roof with small buckets of Sedum (left) and EPDM roof with small buckets of Sedum and Caxit sorbent material (right).

- EPDM roof with standing water, Caxit and vegetation. This roof acts as a wetland as the water is permanently in the roof. It includes edge (*Carrex*), marigold (*Caltha palustris*), iris, and common lily (*Berula*). See Figure 2.11. Is important to mention that for this roof the samples were taken directly from the roof itself, where the water was stagnant, however this was possible just for the events on April because from May until June the water was evaporating rapidly after the event happened due to the increase of temperature, so it was not possible to sample during the events of May and June.



Figure 2.11. EPDM roof with standing water, Caxit and vegetation.

## 2.4 Chemical analysis

### 2.4.1 Total suspended solids

For the analysis of total suspended solids (TSS), the samples were filtered using a vacuum pump. Filters with a pore size of 0.45 micrometres were used for the analysis. Initially, the weight of the clean filters was recorded ( $W_1$  in mg). The filters were then assembled into the vacuum pump systems, and the samples were mixed before filtration. A measured volume ( $V$  in mL) of well mixed water was poured through the filter and the volume was recorded. After filtration, the filter was carefully removed from the system, and allowed to dry at room temperature for at least 24 hours. After the drying period, the filters were weighted again ( $W_2$  in mg). The TSS concentration was then calculated through the next equation.

$$TSS \left( \frac{mg}{L} \right) = \frac{(W_2 - W_1) * 1000}{V} \quad \text{Equation 1}$$

### 2.4.2 Total nitrogen

The analysis for Total Nitrogen (TN) was carried out through the Persulfate digestion method provided by Hach as Method 10071. This procedure consist of an alkaline persulfate digestion that converts all forms of nitrogen to nitrate. Sodium metabisulfite is added after digestion to remove

halogen oxide interferences. After that nitrate reacts with chromotropic acid under strongly acidic conditions that results in a yellow complex. After this, a spectrophotometer was used for the measurement of TN using a wavelength of 410 nm. This method generally gives 95–100% recovery on organic nitrogen standards.

### 2.4.3 Total phosphorous

For the analysis of total phosphorous (TP) it was used a procedure of mineralization from 10 millilitres of non-filtrated samples. The samples were put into digestion recipients adding the oxidizing decomposition reagent, commonly named Oxisolv. The digestion vessels were closed and digested in the laboratory microwave for 60 seconds per sample. After the digestion, 5 millilitres of the digested sample were taken to another recipient; once cool down were added 5 millilitres of deionized water. Having the 10 millilitres in total, the determination of phosphorous-phosphate content was done with the ascorbic acid method. The principle of this method consist on the reaction between three reagents (Ammonium Molybdate and antimony potassium tartrate to react in acid medium, in this case sulfuric acid). The reaction between these reagents with the orthophosphate form a phosphomolybdate complex that is then reduced to the molybdenum blue by the use of the ascorbic acid. After the reaction has taken place (15 minutes) the spectrophotometer is used in a wavelength of 690 nm to measure absorbance of the samples. Once the absorbance of the samples is read, the total phosphorous concentration is calculated based on the calibration curve that was done in this case through 5 known concentrations of P-PO<sub>4</sub>: 1, 0.5, 0.2, 0.1 and 0.05 mg/L.

### 2.4.4 Ion chromatography

For ion chromatography analysis, an Ion Chromatography Thermo Scientific Dionex Integrion system was used. Samples were initially filtered using the vacuum pump system described in section 2.4.1. If the sample volume was insufficient for this filtration method, a 0.45 micrometre membrane filter was used with a syringe for filtration. After filtering the samples, approximately 10 mL was taken and placed into the appropriate vials for analysis.

The vials were then placed into the AS-AP autosampler and the analysis protocol was set up using the associated software. The IonPac AS22-Fast-4 mm analytical column was used for anion

analysis, while the IonPac CS16-4 mm column was used for cations. The ions measured in the analysis included sodium, potassium, ammonium, lithium, calcium, magnesium, nitrite, nitrate, sulphate, phosphate, fluoride, chloride, and bromide.

#### 2.4.5 Total organic carbon

For the analysis of total organic carbon (TOC), a TOC analyser was used to determine the concentrations of organic carbon on rain and rainwater. The analyser implements the 680°C combustion catalytic oxidation technique, developed by Shimadzu. The combustion catalytic oxidation method makes it possible to oxidize not only easily-decomposed, low-molecular-weight organic compounds, but also hard-to-decompose insoluble and macromolecular organic compounds. The samples used for analysis were filtrated and non-filtrated samples, allowing the identification of TOC and dissolved organic carbon (DOC) respectively. The samples were prepared on special containers of about 45 mL, and then the programme was setup on the computer software. Once the samples are set and the analyser is running, the sample is delivered to the combustion furnace. There, it undergoes combustion through heating to 680°C with a platinum catalyst. It decomposes and is converted to CO<sub>2</sub>. The CO<sub>2</sub> generated is cooled and dehumidified, and then detected by the infrared gas analyser (NDIR). The concentration of total carbon (TC) in the sample is obtained through comparison with a calibration curve formula. Furthermore, by subjecting the oxidized sample to the sparging process, the inorganic carbon (IC) in the sample is converted to CO<sub>2</sub>, and the IC concentration is obtained by detecting this with the NDIR. The TOC concentration is then calculated by subtracting the IC concentration from the obtained TC concentration.

#### 2.4.6 Sorption test

The sorption test was carried out in order to estimate the phosphorous sorption capacity of some commercial sorbent materials that are described in the section 2.4.6.1. The materials were chosen in based to the ones that were mostly studied in previous researches such as zeolite and gravel, and also some available innovative commercial sorbent materials like Biochalix and Bioker. For the sorption test it was used KH<sub>2</sub>PO<sub>4</sub> to prepare a stock concentration and then dilutions were made to test the sorption capacity in 5 concentrations of PO<sub>4</sub>: 50, 20, 10, 5 and 1 mg/L. Additionally, the

sorption test was performed with rainwater collected from RWS1. In the next sections the materials and the procedure is described with more detail.

#### 2.4.6.1 Materials

- Gravel: This material is normally used on the bioretention cell designs to provide a drainage layer. It is found commonly on the bioretention systems implemented in many countries and also as part of the researches that study the performance of different sorbent materials.
- BioChalix: The material consist on a mix of minerals and selected batches of limestone that is used as a sorbent of phosphorous compounds. Has a porosity up to 34% that enables bacteria to decompose organic materials and what makes a perfect substrate for nitrifying bacteria.
- Zeolite: Natural zeolites are formed in basaltic lava, in specific rocks that are subjected to moderate geologic temperature and pressure (Reddy et al. 2014a). Due to their porous structure, high specific surface area, and excellent cation exchange capacity, zeolites can remove a wide range of chemical compounds via absorption (Bailey et al. 1999).
- Bioker: The material is composed of a light expanded clay aggregates coated with biopolymer with fixed components (in this case calcite for the removal of phosphates). It works as adsorbent in contact with the water (Jarosiewicz et al. 2022).

##### 2.4.6.1.1 Procedure

As first, the materials that were described above were prepared in containers of 45 ml (3 replicates for each material). For gravel and biochalix it was weighted around 1 gram per container, while for zeolite it was used 0.5 grams. For bioker it was used just one grain of the material in each container. For biochalix it is important to mention that this material was analysed for two groups, the first one were particles that did not have iron content on the material (1 gram), and second one the particles that had a reddish colour (iron). The aim of this was validate if there is any difference for the removal efficiency of phosphorous between these two groups. For the biochalix that contains iron it was used just one grain of the material, as bioker. Once the materials were weighted and put it inside the correspondent containers, the solution of  $\text{KH}_2\text{PO}_4$  (with the correspondent concentration that were mentioned above) was poured into the containers. Finally, they were arranged into a shaker, with the purpose of keep the containers shaking for 24 hours before analysing the content

of total phosphorous after the 24 hours. For the analysis of TP, it was determined through the ascorbic acid method described on section 2.4.3, but with the slight modification that this was done taking 2.5 ml of the solution and adding 2.5 ml of deionized water, instead of 5 mL of each. However, for the higher concentrations it was necessary to have dilutions, so the proportion of these volumes were different.

### Statistical analysis

For the statistical analysis of the data, the software PAST (Paleontological Statistics Software Package for Education and Data Analysis) was utilized. A combination of parametric and non-parametric tests was applied to determine the differences and correlations among the datasets based on their distribution and variance characteristics.

To compare the medians across multiple groups, a one-way ANOVA (Analysis of Variance) was applied when the data met the assumptions of normality and homogeneity of variances. When the data did not meet these assumptions, the Kruskal-Wallis test, a non-parametric alternative to one-way ANOVA, was used to assess if there were statistically significant differences between the medians of the groups. Following the Kruskal-Wallis test, if significant differences were found, Dunn's post hoc test was performed to identify specific group pairs with significant differences in their medians. For datasets that conformed to normal distribution and had equal variances, Tukey's test was conducted post-ANOVA to identify which group pairs differed significantly. All statistical tests were conducted with a significance level set at  $p < 0.05$ .

To assess temporal impacts between two groups, a t-test was utilized under the assumption of normal distribution and equal variances. When these assumptions were not satisfied, the Mann-Whitney U test, a non-parametric equivalent to the t-test, was applied to evaluate the differences between the two groups. Finally, for the analysis of correlations with hydrometeorological factors, Pearson's correlation coefficient was calculated for normally distributed datasets to assess the strength and direction of the relationship between variables. In cases where the data did not meet a normal distribution, Spearman's rank correlation coefficient was used as a non-parametric measure relationship between variables.

## 3 Results

### 3.1 Rain water quality

#### 3.1.1 Spatial impact

The figures that are presented below correspond to the box-plots of the main parameters that were analysed (TSS, pH, TOC, TN and TP) for the samples that correspond to rain (wet and dry deposition) and rainwater from the two sites that were studied. For Site 1 rainwater is named RWS1 and rain RS1. For Site 2 rainwater is named RWS2 and rain RS2. The letters in green over the box plots indicates which pair of groups are significantly different. In the case of the TSS there is no box plot for RS1 due to the small volume of the samples that did not allow their determination. The elevated TSS levels in RWS2 were also characterised by unidentified particles similar to gravel, as shown in Figure 3.2.

The box-plot of TSS indicates that RWS2 has the highest interquartile range among the three samples, with a median concentration of 194.55 mg/L. In contrast, the box-plot for RS1 is nearly imperceptible because of the lower range values and the limited quantity of data. In addition, the graph highlights two outliers for RS1, with concentrations of 17.63 and 59.46 mg/L. Finally, for RWS1, the TSS concentration range is much shorter than RWS2 but larger than RS1, with a median value of 39.92 mg/L.

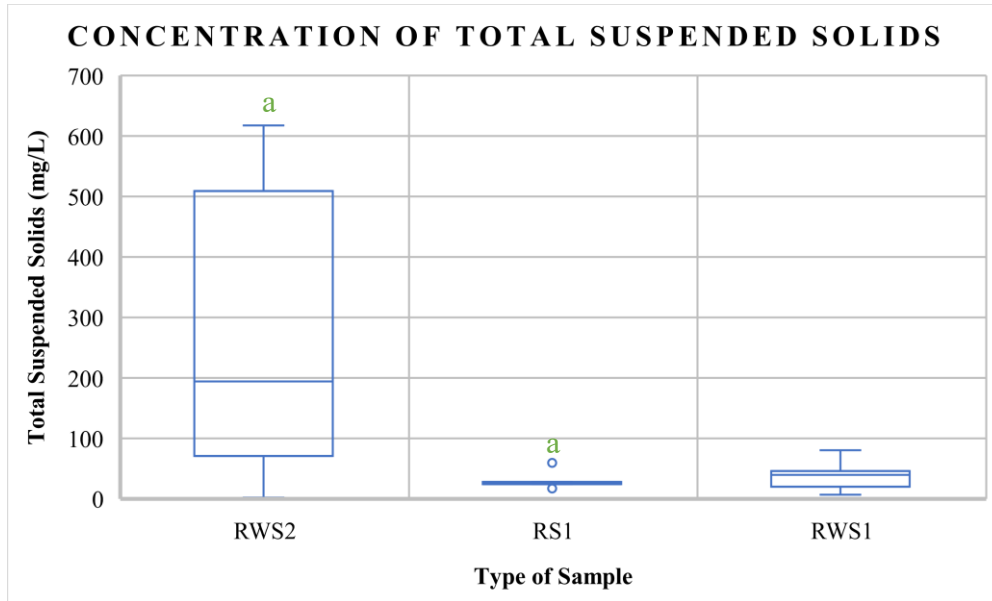


Figure 3.1. Comparative of Total Suspended Solids between RS1, RWS1 and RWS2



Figure 3.2. Small particles identified in RWS2

Regarding the pH samples corresponding to Site 1 (both rainwater and rain) have a median pH value very close to 7. In contrast, samples corresponding to the Rain and Rainwater of Site 2 exhibited a median pH of 6.61 and 6.76 respectively, as illustrated in Figure 3.3. The whiskers for RS2 and RWS2 extended below 6, which is not observed in RS1 and RWS1 samples, where the lower whisker is 6.26 for rain and 6.84 for rainwater. However, RS1 shows one outlier with a pH value of 6.23. The maximum pH value reported was 8.07 corresponded to RS1.

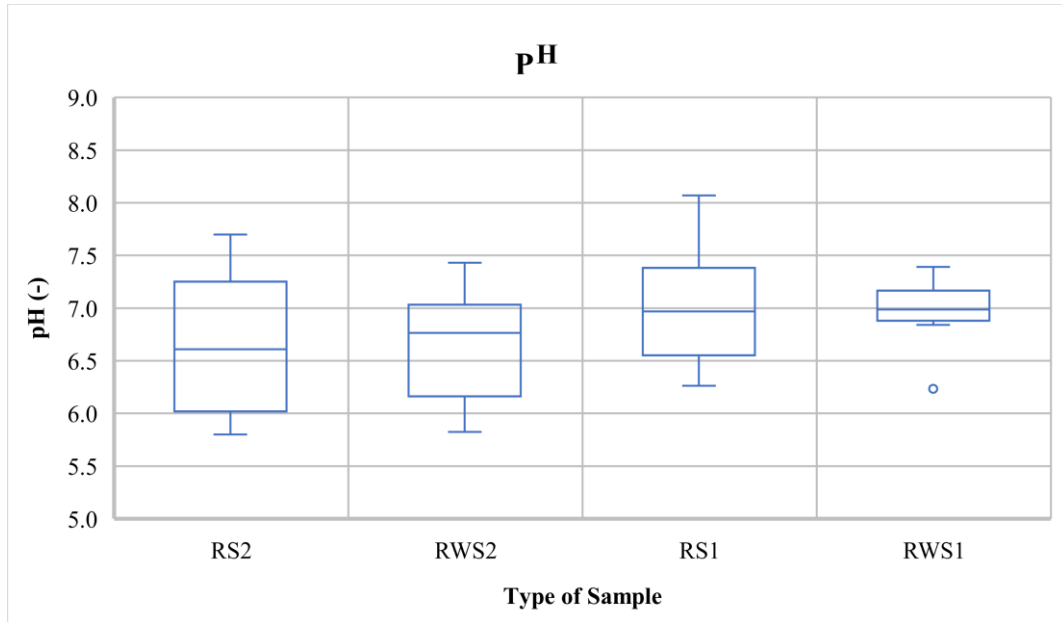


Figure 3.3. Comparative of pH between RS1, RS2, RWS1 and RWS2

The highest median total organic carbon (TOC) value at 55.87 mg/L corresponded to RWS2, with a maximum of 72.17 mg/L. This group also presented one outlier with a TOC value of nearly 140 mg/L. Following this, RS1 had a median TOC value of 8.22 mg/L. The median values for RS2 and RWS1 were 6.61 mg/L and 6.42 mg/L respectively, as it is shown in Figure 3.4.

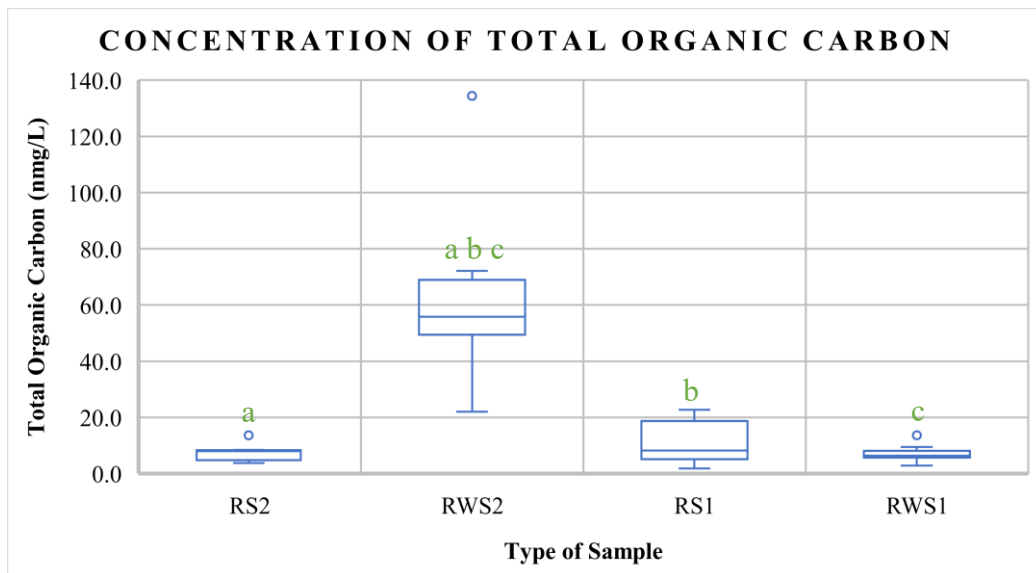


Figure 3.4. Comparative of Total Organic Carbon between RS1, RWS1, RS2 and RWS2

The box plot for total nitrogen indicates that the rainwater groups had higher median values compare to the rain groups. The median value for rainwater is close to 5.5 mg/L, while for rain it

is 3.3 mg/L for Site 2 and 3.98 mg/L for Site 1. Moreover, the upper whisker for Site 2 samples are higher than for Site 1, whereas the lower whisker for Site 1 are lower than Site 2.

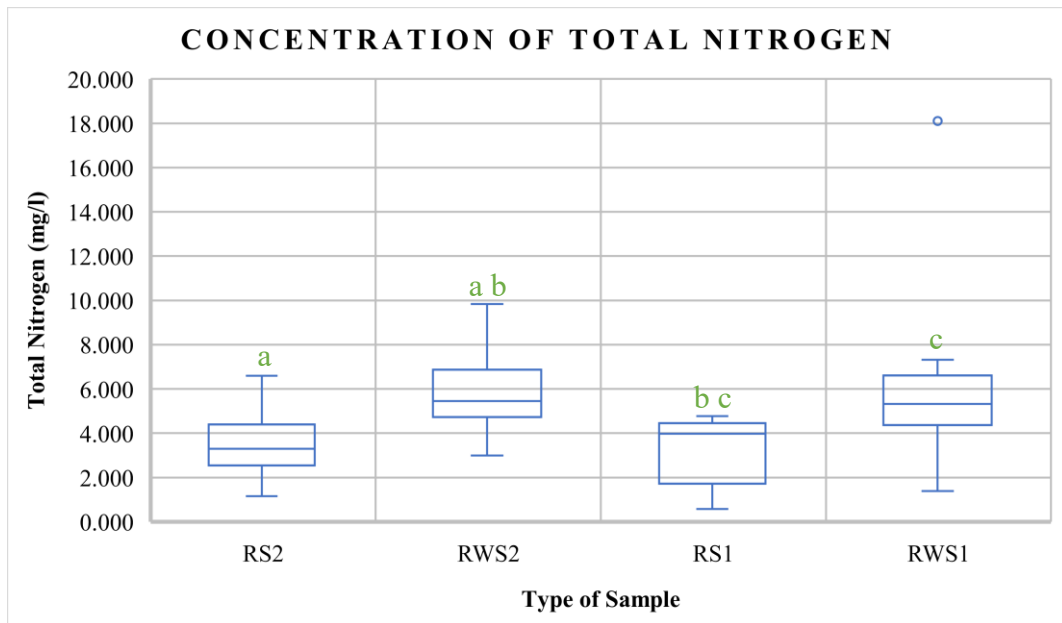


Figure 3.5. Comparative of Total Nitrogen between RS1, RS2, RWS1 and RWS2

For total phosphorous there is a clear difference between the two sampling locations. At Site 1, values range from 0.08 up to 1.25 mg/L, excluding two higher outliers (one from rain and other from rainwater). In contrast, phosphorous values at Site 2 range from 0.09 to 0.25 mg/L. The mean value of Site 1 samples is around five times higher than the mean value of Site 2 samples, however, the median difference between those samples is less pronounced because the box plot shows that the median for RS1 and RWS1 is closer to the first quartile, so the data in this case is asymmetric, which indicates a skewed distribution, as illustrated in Figure 3.6.

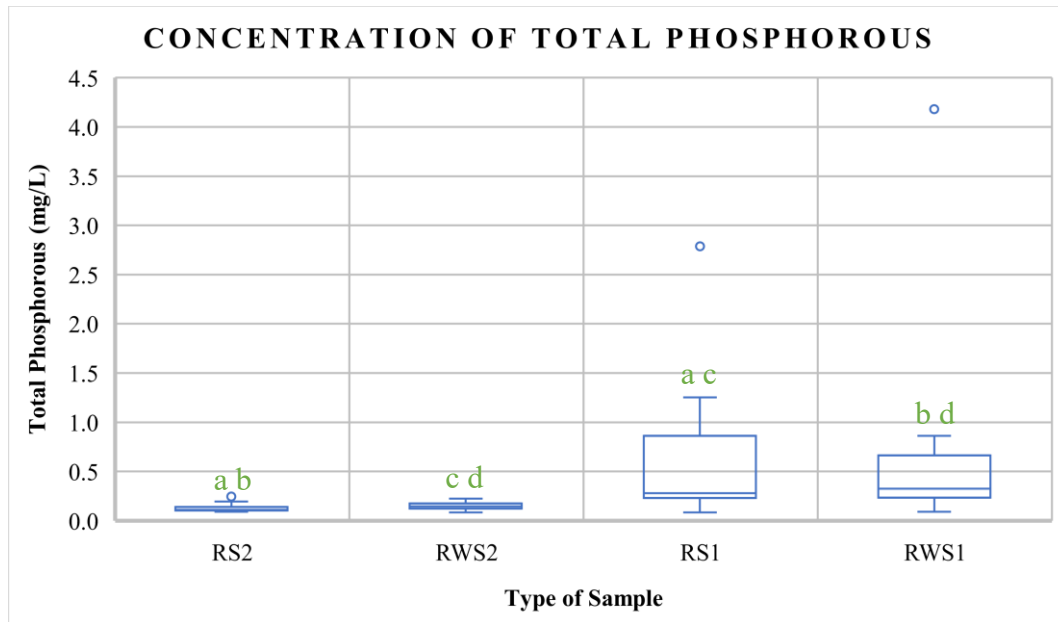


Figure 3.6. Comparative of Total Phosphorous between RS1, RS2, RWS1 and RWS2

As shown in the Figures above, there are no extremely large differences between the four groups evaluated, except for the concentration of TSS found in RWS2 as well as TOC from this group. To validate this, an Analysis of Variance (ANOVA) was used to check for significant differences in the parameters between the four groups. For TSS, TN and TP the distributions were not completely normally distributed so the Kruskal-Wallis test was used to verify if the medians between the four groups had significant differences. Dunn's Post Hoc test was then used to identify which groups differ significantly. For pH and TOC, the groups showed normal distributions; however, TOC did not meet the equal variances assumption (Levene's test), so the Kruskal-Wallis test followed by Dunn's Post Hoc test was applied for TOC as well. For pH equal variances assumption was confirmed so a one-way ANOVA followed by the Tukey test was used to compare the groups. A p-value of 0.05 was used for all the tests.

The statistical results showed a significant difference between RWS2 and RS1 for TSS ( $p = 0.04$ ). Although the other pairs were not significantly different, the p-value between RWS1 and RWS2 (0.07) was slightly higher than the critical p-value (0.05). The ANOVA for pH did not show any significant difference among the groups, while for TN the groups that showed a significant difference were: RWS2 and RS2 ( $p = 0.03$ ), RWS2 and RS1 ( $p = 0.01$ ) and RWS1 and RS1 ( $p = 0.03$ ). For TP, statistically significant differences were found between the following pairs: RWS2 and RS1 ( $p = 0.02$ ), RWS2 and RWS1 ( $p = 0.02$ ), RS2 and RS1 ( $p = 0.006$ ), and RS2 and RWS1

( $p= 0.009$ ). Finally, for TOC, significant differences were observed between RWS2 and RS1 ( $p= 0.006$ ), RWS2 and RS2 ( $p= 0.002$ ), and RWS2 and RWS1 ( $p =0.0008$ ).

### 3.1.2 Temporal impact

Although the short sampling period did not allow a deep analysis of the concentration of pollutants across different seasons, a comparison of TN, TP and their related ions ( $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{NH}_4$ , and  $\text{PO}_4$ ) was conducted for two groups: rain during three events in March and rain during three events in June. The aim was to identify any significant differences between the end of the winter (March) and the start of summer (June). In Figure 3.7 and Figure 3.8 it is shown the boxplots of TN, TP and their related ions ( $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{NH}_4$ , and  $\text{PO}_4$ ) for the two comparative months: March and June. Regarding nitrogen, it is observed that in June the total form of nitrogen had a higher value, while  $\text{NO}_3$  is the ion that demonstrated more difference between the two months with higher values in March. For phosphates the graph showed a median value higher for March (0.31 mg/L) and the highest value of Phosphate was also in March (1.68 mg/L). In terms of Total Phosphorous the difference is less evident, however it is observed that in March TP had higher concentrations.

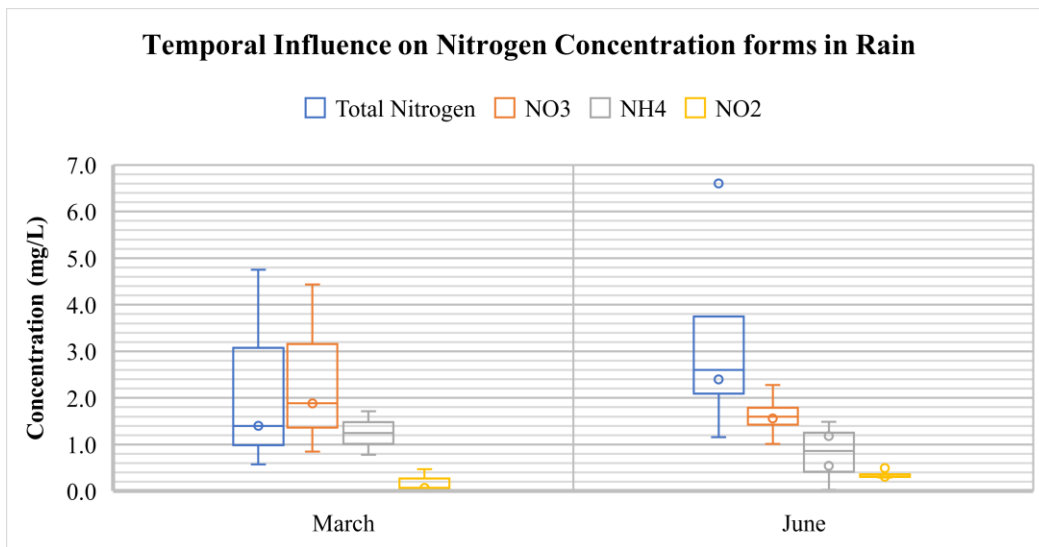


Figure 3.7. Comparative of Nitrogen Concentration forms for Rain in March and June

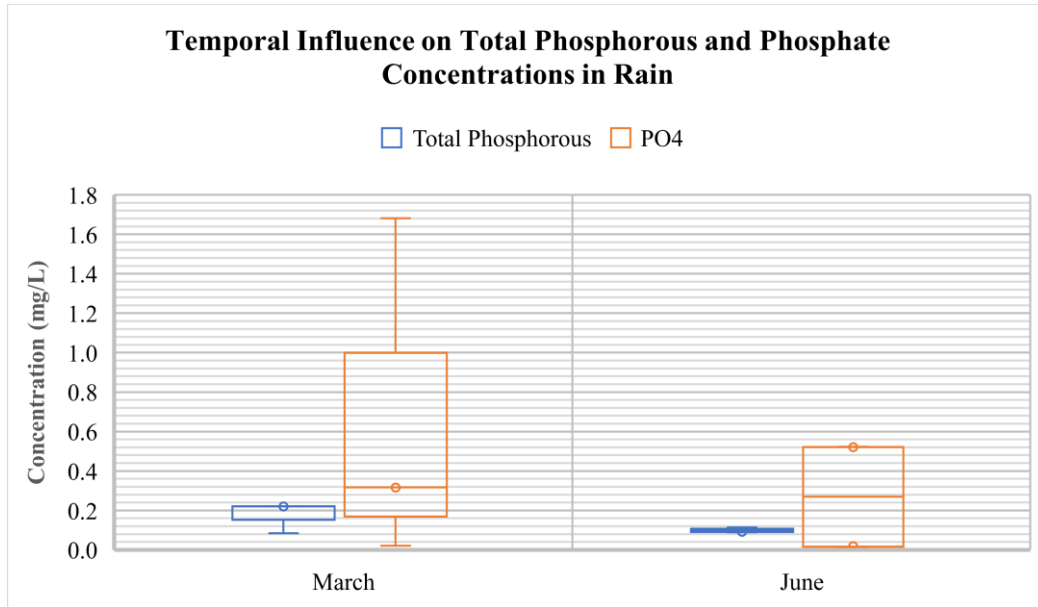


Figure 3.8. Comparative of Phosphorous and Phosphate concentrations for Rain in March and June

A t-test was used for TN and their respective ions, which had a normal distribution, while the Mann-Whitney test was used for TP and phosphate which did not show a normal distribution. The results for all parameters between these two groups did not show any statistically significant differences which in part could be due to the small number of samples used, and also because the difference between the end of March and start of June is still not substantial. The p-values for each parameter were: 0.59 for TN; 0.59 for TP; 0.26 for NO<sub>2</sub>, 0.45 for NO<sub>3</sub>; 0.50 for NH<sub>4</sub>; and 0.59 for PO<sub>4</sub>.

### 3.1.3 Hydrometeorological impact

As the hydrometeorological impact is an essential part of this research, it is important to show the data regarding rainfall for the period of the study (March to June). Figure 3.9 shows the pattern of daily rainfall during the period of the study. It is observed that during March, April and first half of May the rainfall events were not heavy and the antecedent dry period (ADP) increased from March to April and first half of May. From third week of May heavy rainfall events increased, having more peaks and ADP decreased compare to the pattern showed before first half of May.

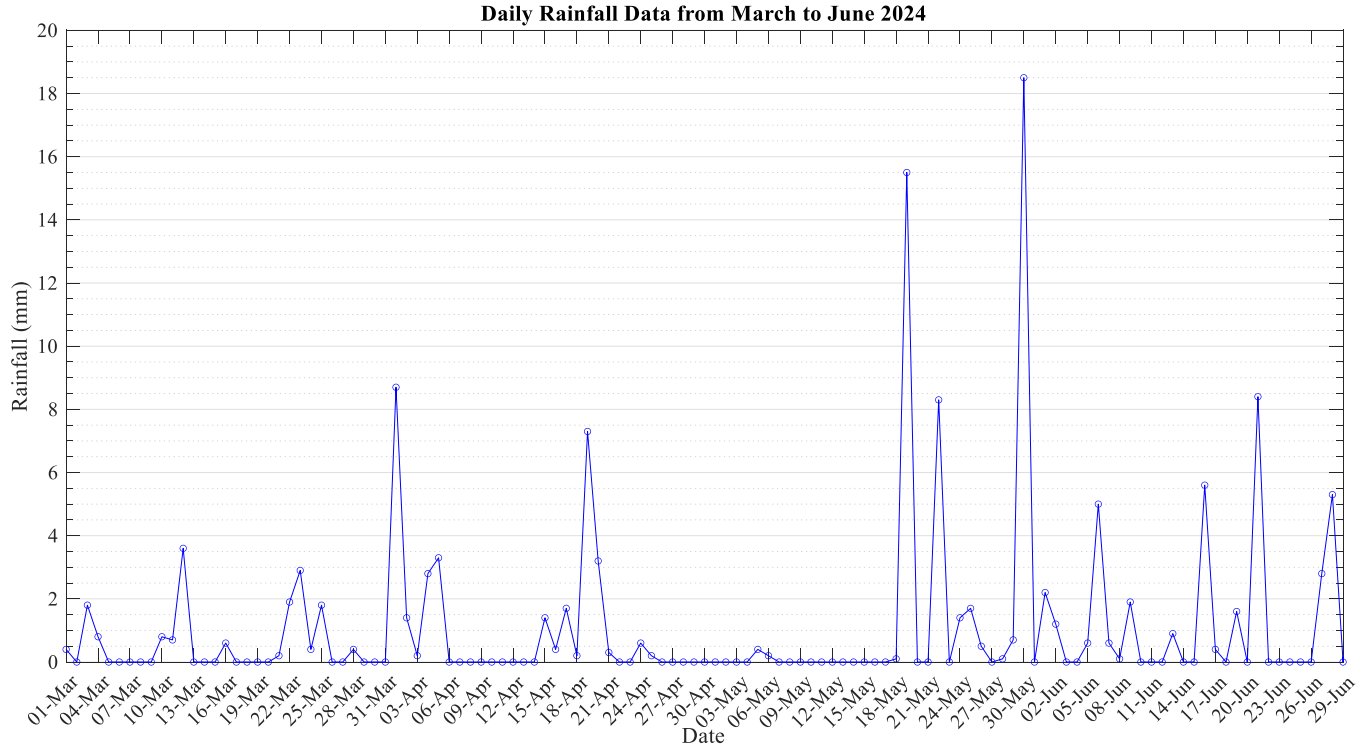


Figure 3.9. Rainfall Pattern During the Study

A. Antecedent dry period

Figure 3.10, Figure 3.11, and Figure 3.12 show the correlation between antecedent dry period (ADP) and pollutant concentrations for Rainwater (RWS1 and RWS2 together), RWS2, and RWS1, respectively. The correlation that are statistically significant are identified by a grey rectangle that surrounds the circle of the correlation. The three figures indicated positive correlations between ADP and pollutant concentrations. For rainwater (combining RWS1 and RWS2) TN, TP, and NH<sub>4</sub> were the parameters that result with statistically significant correlations. In the case of RWS2 none of the pollutants showed a significant correlation, while for RWS1 TP and PO<sub>4</sub> were the parameters with a significant correlation, and TN and TOC had a p-value of 0.10 and 0.07, which is very close to the critical p-value of 0.05.

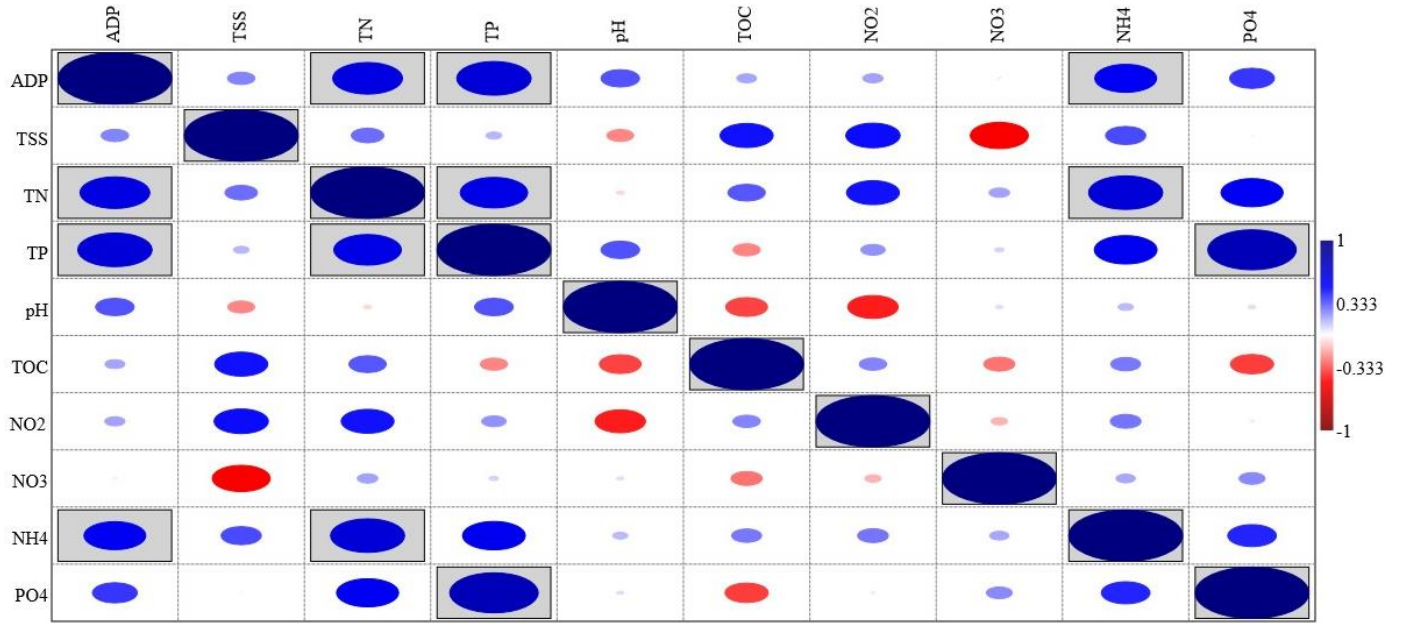


Figure 3.10. Correlation between ADP and pollutants concentration in Rainwater

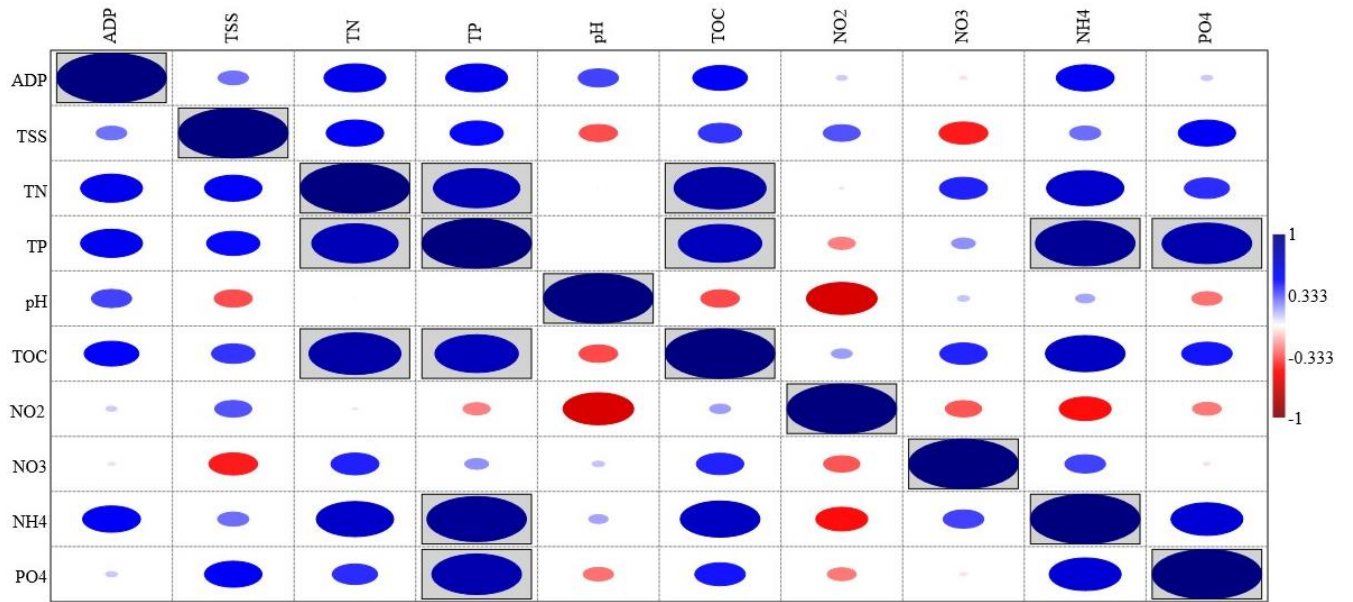


Figure 3.11. Correlation between ADP and pollutants concentration in RWS2

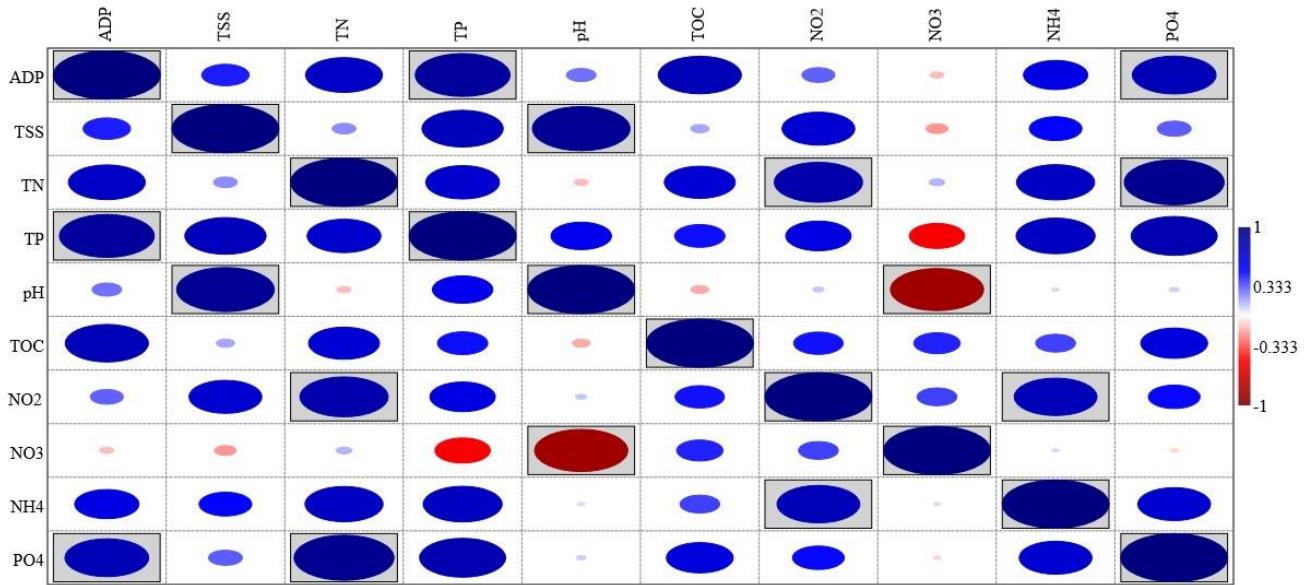


Figure 3.12. Correlation between ADP and pollutants concentration in RWS1

As the first flush has an important influence on the concentration of some pollutants, the correlation of ADP, but only for the first sample of the first flush events were analysed. In this case, TN and TP were the two parameters that showed a significant positive correlation as can be observed in Figure 3.13.

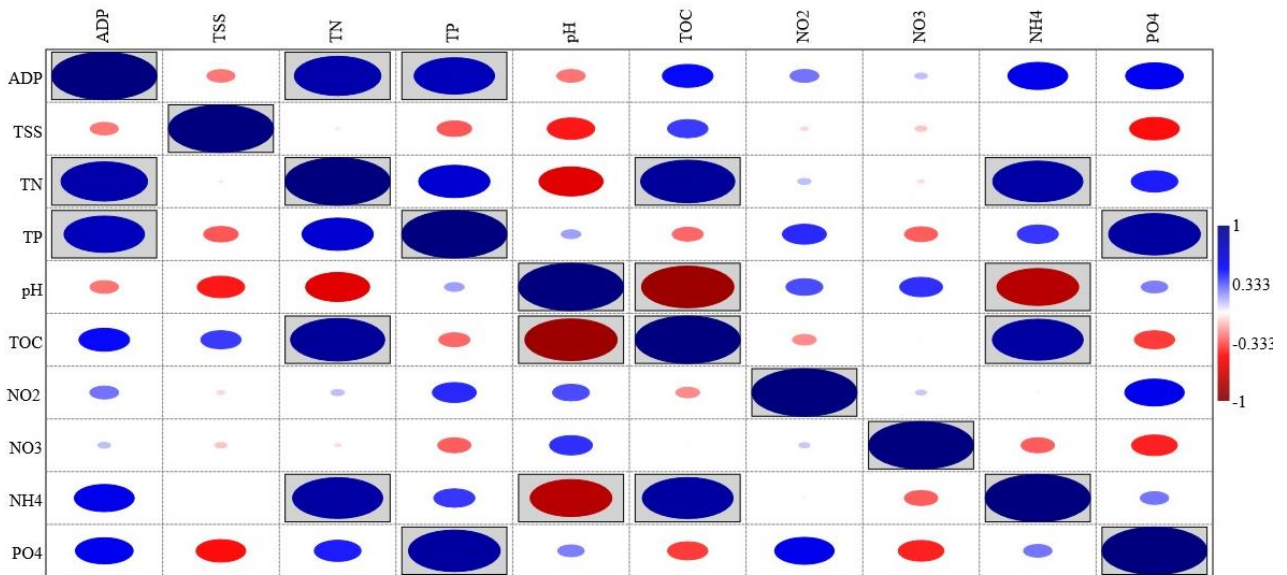


Figure 3.13. Correlation between ADP and concentration of pollutants in First Flush

## B. Rainfall intensity (RI)

The correlation between RI (in mm/d) and pollutant concentrations are illustrated in Figure 3.14, Figure 3.15, and Figure 3.16. The analysis for rainwater combining data of RWS1 and RWS2 showed a significant negative correlation between RI and concentration of  $\text{NO}_3$ . For RWS2 the correlation was negative for some parameters such as  $\text{NO}_3$  and TN, however they are not statistically significant, and for the other parameters there is not a clear correlation. In the case of RWS1 the behaviour was much clear. The correlation was strongly positive for all the parameters, except for  $\text{NO}_3$ . For TN and TP the correlation demonstrated significant difference.

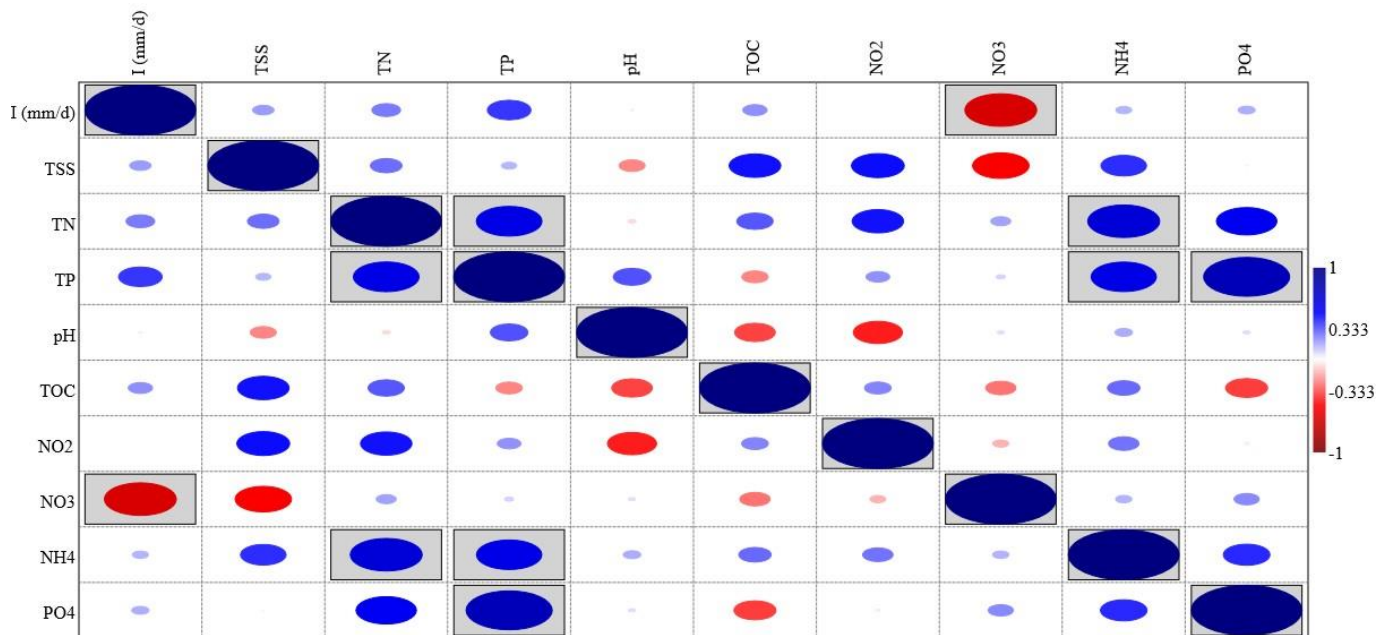


Figure 3.14. Correlation between RI and pollutants concentration in Rainwater

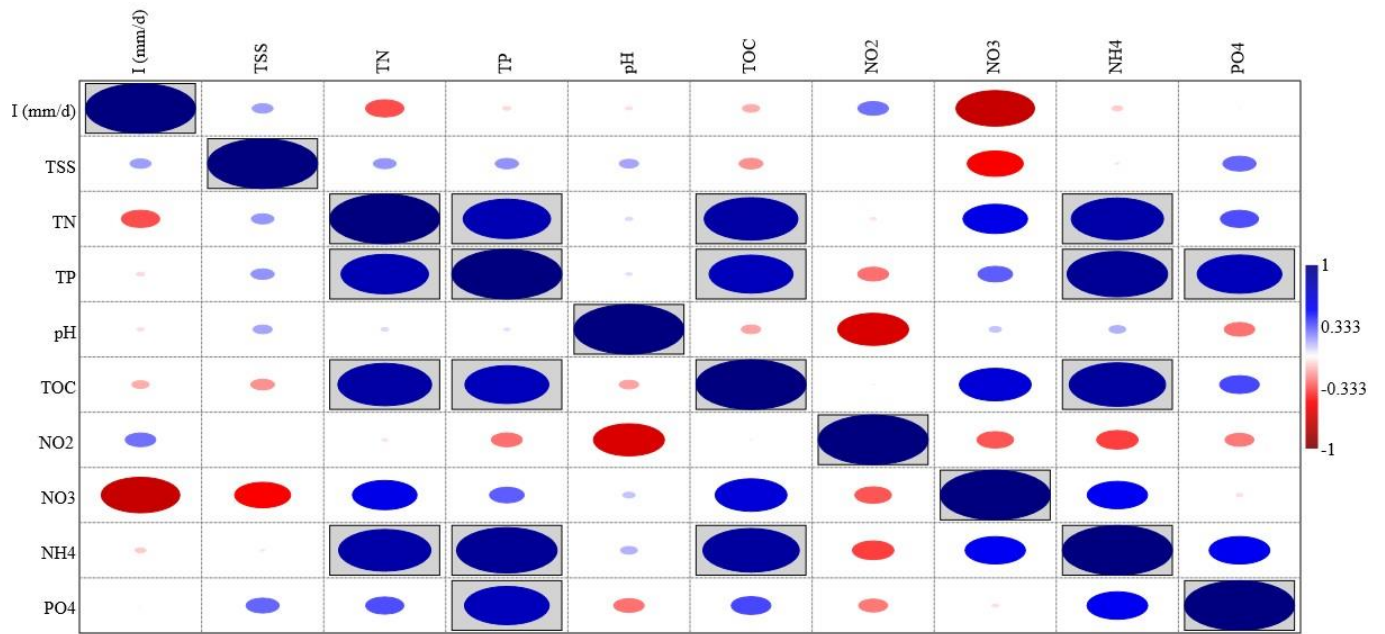


Figure 3.15. Correlation between RI and pollutants concentration in RWS2

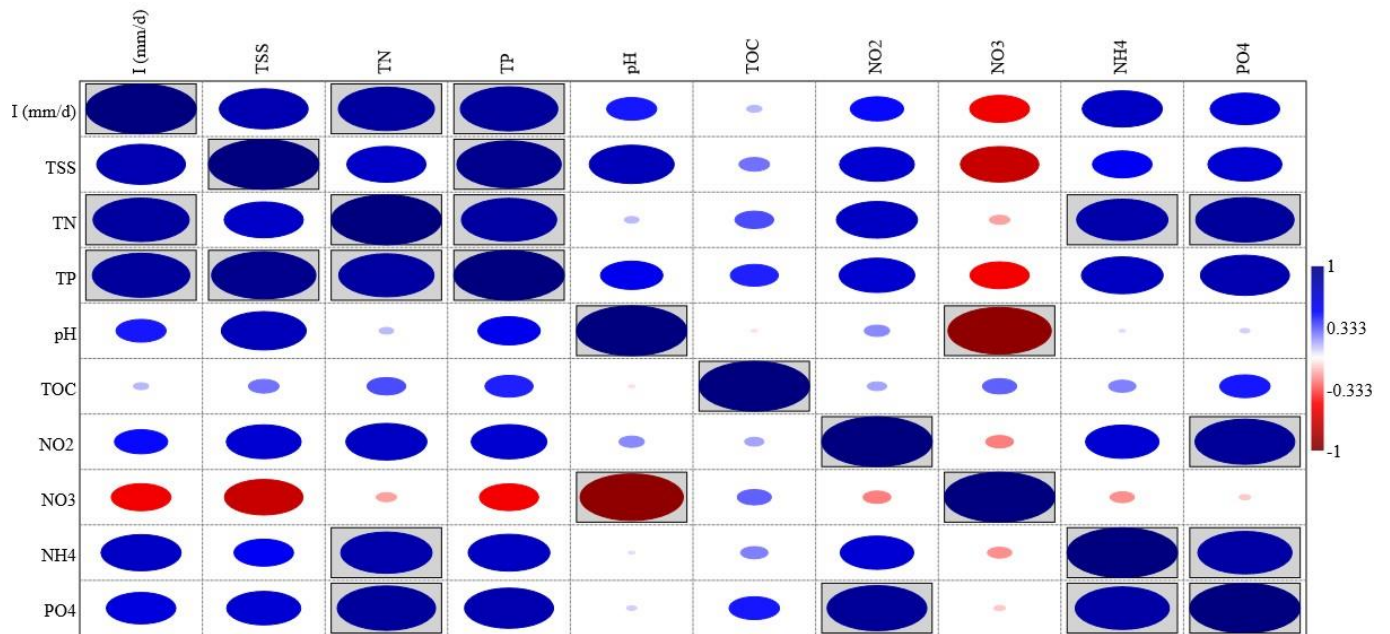


Figure 3.16. Correlation between RI and pollutants concentration in RWS1

It is important to identify also the correlation of the RI coupled with the first flush effect. Analysing RWS1 and RWS2 together it resulted a significant negative correlation with  $\text{NO}_3$ , while for the other parameters the correlation were not significant and weak. For RWS2 the pH showed a significant negative correlation, and for RWS1 TSS had a significant positive correlation. For the

rest of the parameters the result were not statistically significant as Figure 3.17, Figure 3.18, and Figure 3.19 indicate.

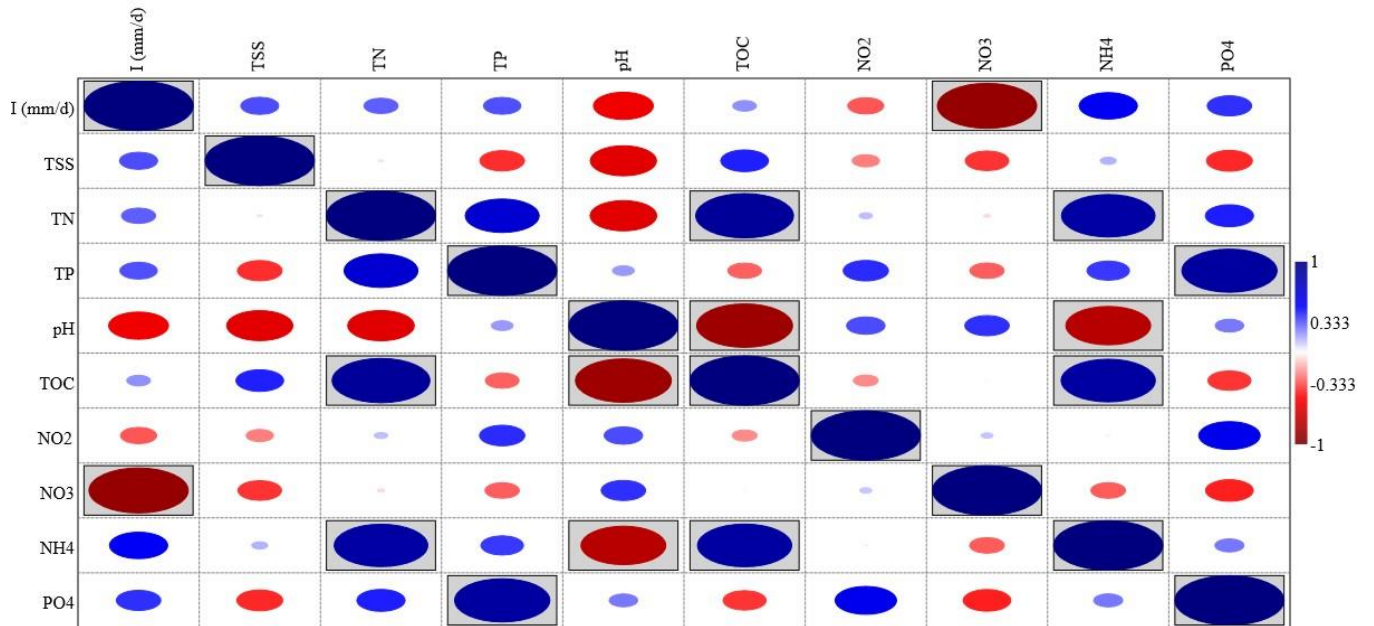


Figure 3.17. Correlation between RI and pollutants concentration in First Flush

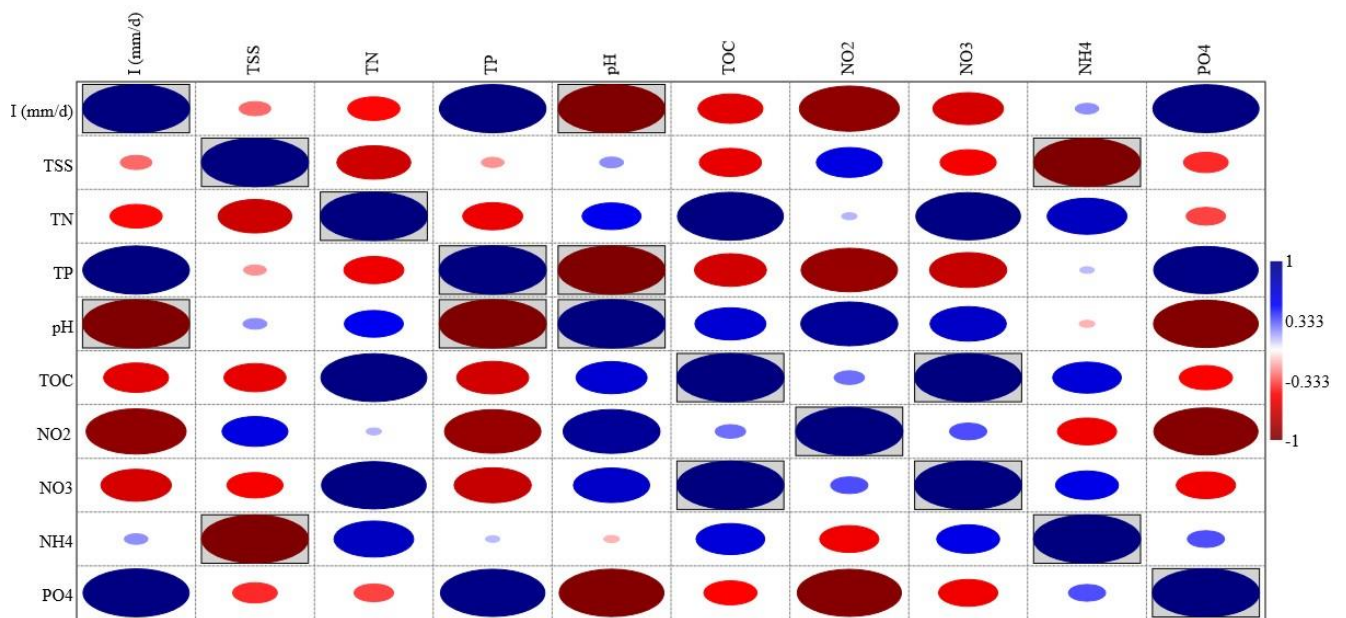


Figure 3.18. Correlation between RI and pollutants concentration in First Flush RWS2

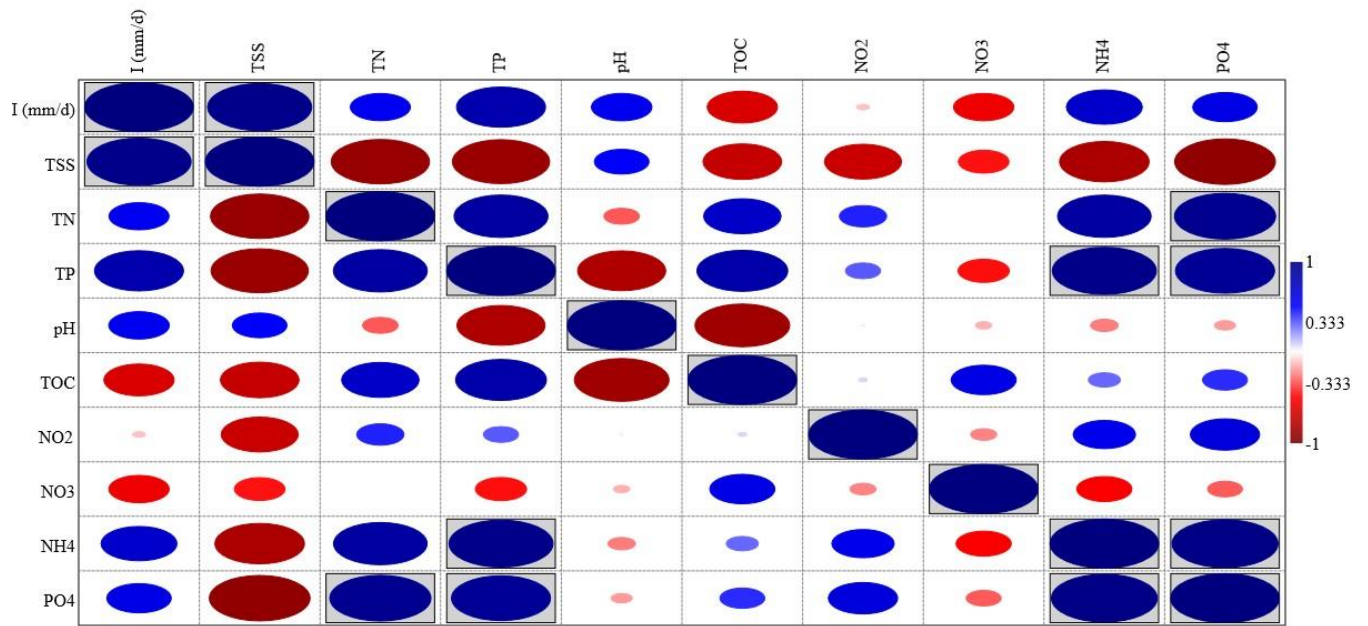


Figure 3.19. Correlation between RI and pollutants concentration in First Flush RWS1

### C. First flush effect

With the purpose of analyse the first flush effect in detail, rainwater samples were taken continuously over the event at different times (t1, t2, t3 and t4 in some cases), in order to identify the behaviour of pollutant concentrations during the whole rainfall event.

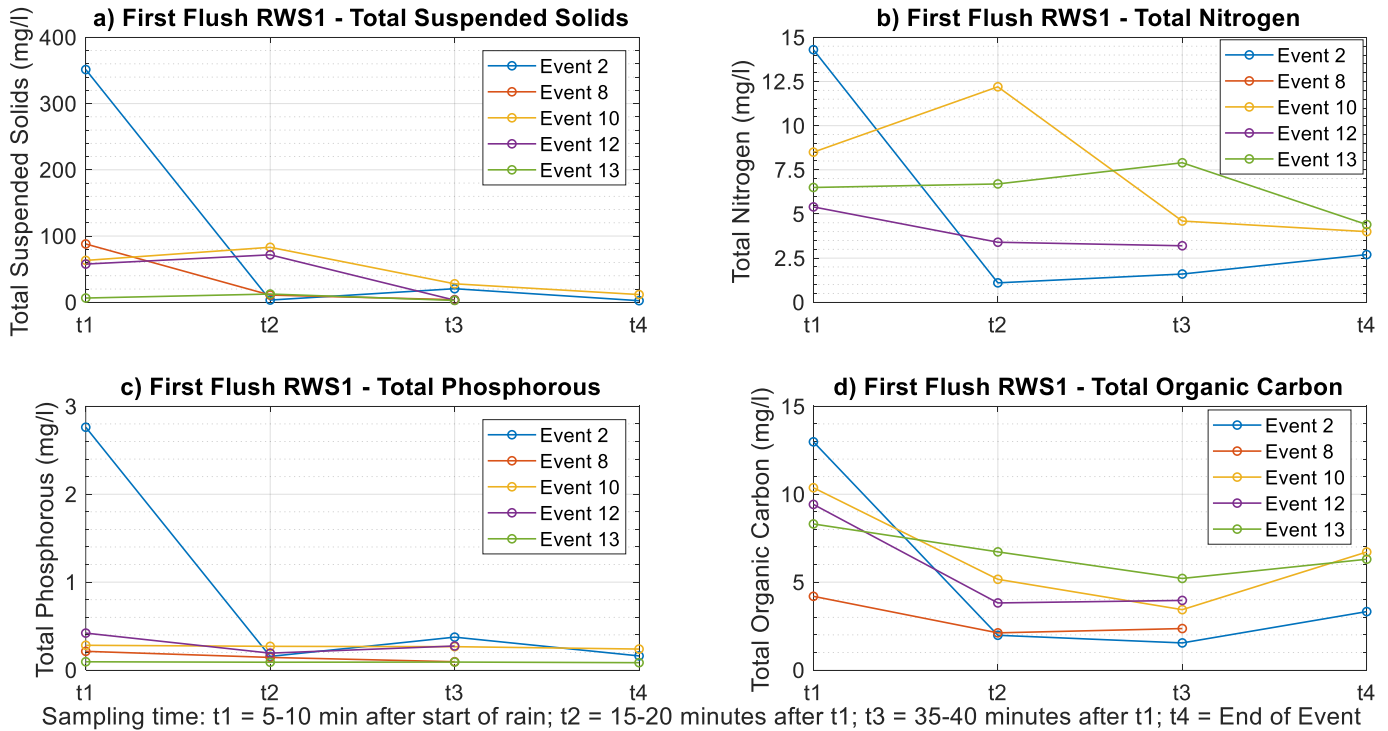


Figure 3.20. First Flush Effect Site 1. a) Total Suspended Solids, b) Total Nitrogen, c) Total Phosphorous, d) Total Organic Carbon

The behaviour of the first flush effect for TSS exhibited for the Event 2 the highest concentration of TSS in the first sample (t1) as can be observed in Figure 3.20 a). Then the concentration decreased substantially. Event 8 exhibited a similar pattern, although only three samples were taken during this event. On the other hand, events 10 and 12 showed an increase in TSS concentration from t1 to t2 samples, followed by a significant decrease in the subsequent samples.

The first flush effect in the case of TN, Figure 3.20 b), presented two type of behaviours. In events 2 and 12 the concentration had a peak in the first sample and then a decrease tendency. For event 2 after the decrease in t2, the concentration increased again in t3 and t4, whereas for event 12, it continued to decrease until t3. In events 10 and 13, the peak concentrations occurred at t2 and t3, respectively, followed by a decrease in TN concentration.

The dynamics of the first flush effect for TP shown in Figure 3.20 c) was particularly pronounced in event 2, with the highest concentration at t1 (2.76 mg/L), followed by a decrease until t4 (0.16 mg/L), although there was a slight increase at t3. For the other events shown in the Figure, the

concentration at t1 was always below 0.5 mg/L and the final TP concentration at t3 or t4 was always below 0.3 mg/L. The behaviour on those events presented slight jumps on the TP concentration.

For TOC, a particular trend was observed. In all the events the concentration at t1 was the highest followed by a decrease at t2 and t3 for the events that were sampled until t4, and t2 for events sampled until t3. The sample taken at t4 for Events 8, 10 and 13 exhibited an increase compared to the sample at t3.

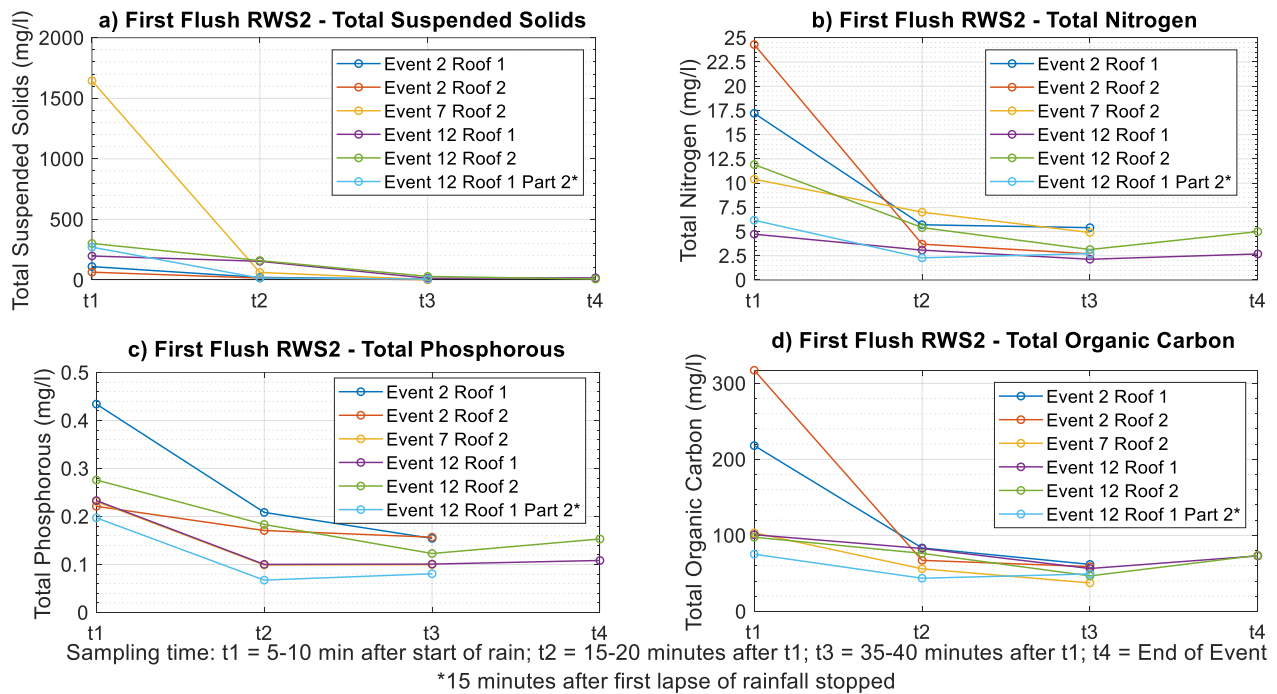


Figure 3.21. First Flush Effect Site 2 a) Total Suspended Solid, b) Total Nitrogen c) Total Phosphorous, d) Total Organic Carbon

The dynamic of the first flush effect for TSS at Site 2 differed from those at Site 1. The initial concentrations at Site 2 were significantly higher, with one event reaching approximately 1700 mg/L. For the other events the initial concentrations at t1 ranged between 50 and 350 mg/L. Throughout these events, the concentration of TSS decreased to values below 20 mg/L.

Regarding TN, the initial concentrations during the first flush effect at Site 2 were between 5 and 25 mg/L as shown in Figure 3.21 b). The sample events typically exhibited a substantial decrease during the first time lapse (t1-t2) followed by either a slight increase or stabilisation of the curve. The final concentrations at the end of the events were always between 2.5 and 5 mg/L, similar to the end values of TN for the first flush analysed at Site 1.

For TP, the first flush effect at Site 2 was very similar to the observed at Site 1. A key difference was that the concentrations at Site 2 were lower than those at Site 1, both at the initial stage (t1) and at the end of the events. In this case the concentrations reached values below 0.16 mg/L.

Finally, for TOC, there is a clear and big difference regarding the concentration values. In the case of Site 2 the initial values are always above 70 mg/L of TOC, and up to almost 320 mg/L. These values showed a first big decrease in t2 that reached levels of TOC below 80 mg/L and then in one event (Event 12 part 2) the concentration of TOC had a slight increase. For the rest of the events the concentration followed a decrease trend until t3. For event 12 roof 1 part 1 and event 12 roof 2 the concentration had again a jump over 70 mg/L at t4.

## 3.2 Experimental roofs

### 3.2.1 Retention capacity of green roofs

The retention capacity of water is one of the most important properties on green roofs. According to the runoff volume that was produced across some of the events that were sampled for the traditional experimental roofs (ExR1 and ExR2) and the green experimental roofs (ExR3 and ExR4), results demonstrated that the green roofs reduced considerably the runoff volume compared to the traditional experimental roofs. For the events 3 and 6 the green roof #2 (ExR4) had a slightly higher water retention than green roof #1 (ExR3), while for the events 8, 10 and 12, the retention of water runoff was equal for both green roofs, illustrated in Figure 3.22. The graph also showed that for the events 3 and 6 the runoff volume was the highest, followed by the Event 8, and the runoff volume from events 10 and 12 was the lowest.

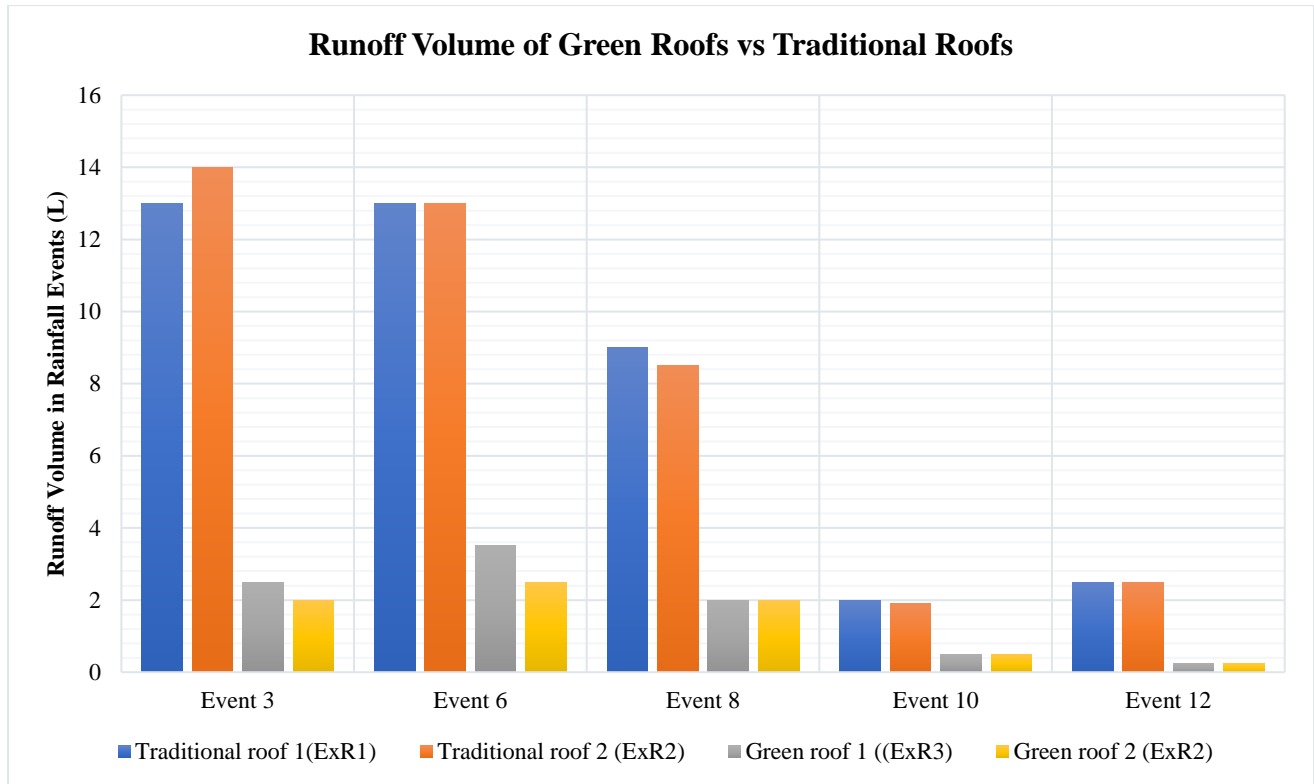
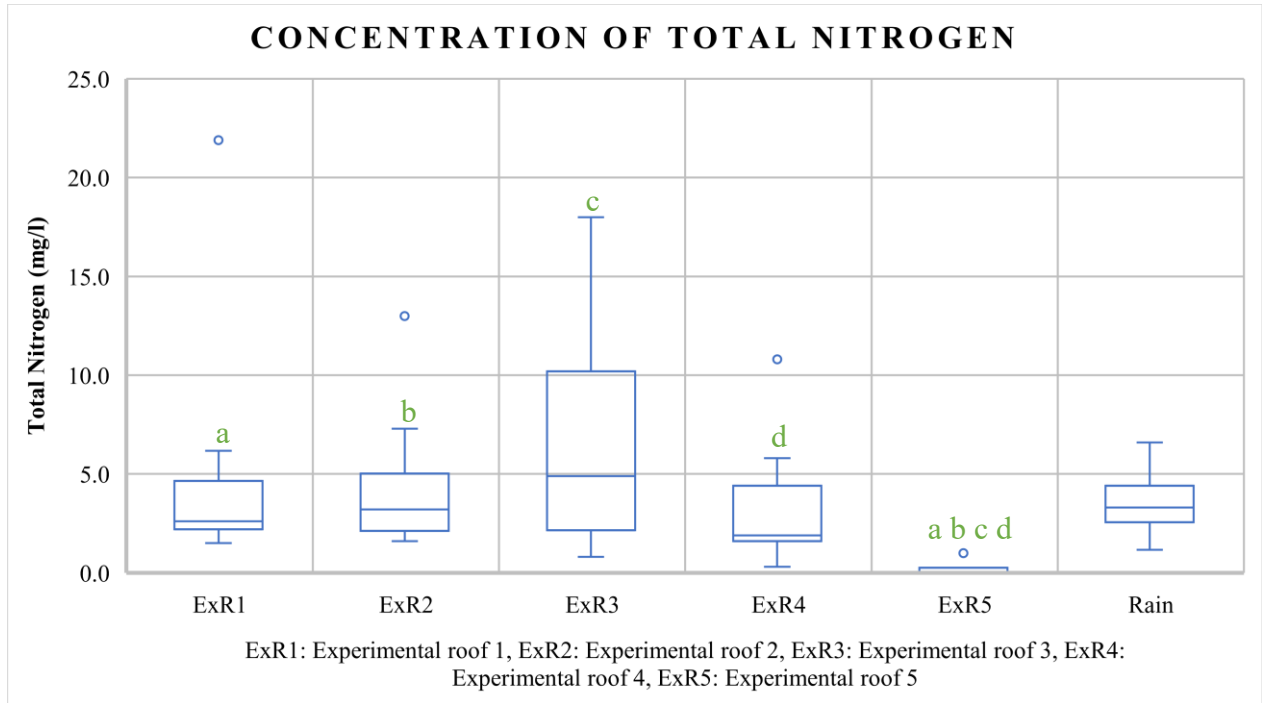


Figure 3.22. Comparison of runoff volume for traditional roofs and green roofs

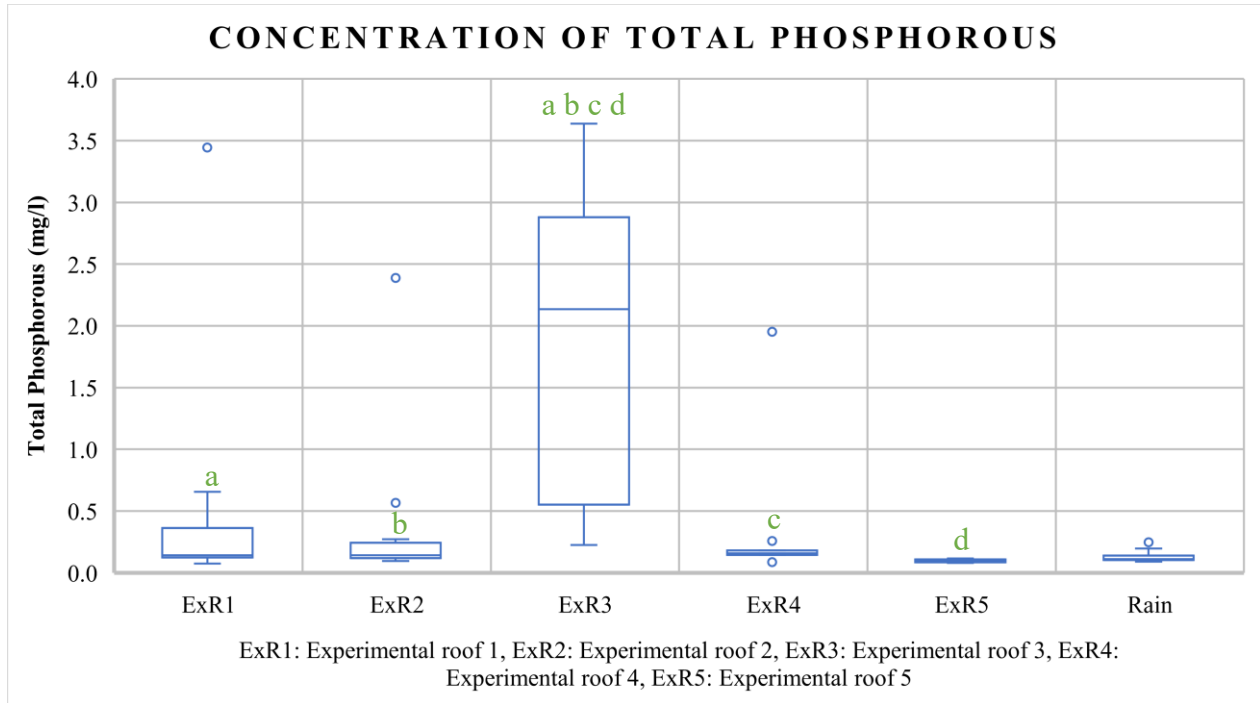
### 3.2.2 Water quality

The follow graphs describe the water quality of the runoff from experimental roofs regarding the parameters of TN, TP, TOC and ions. The letters in green over the box plots indicates which pair of groups are significantly different. For TN it can be observed that ExR3 is the one with a highest concentration of TN having a median value of 4.9 mg/L. Then, the two traditional roofs and the rain itself showed a median value around 3 mg/L. ExR4 had a median value of 1.9 mg/L, although the box plot indicated values up to 5.8 mg/L. ExR5 was the one with the lowest value of TN being his highest concentration 0.250 mg/L, as can be seen in Figure 3.23.



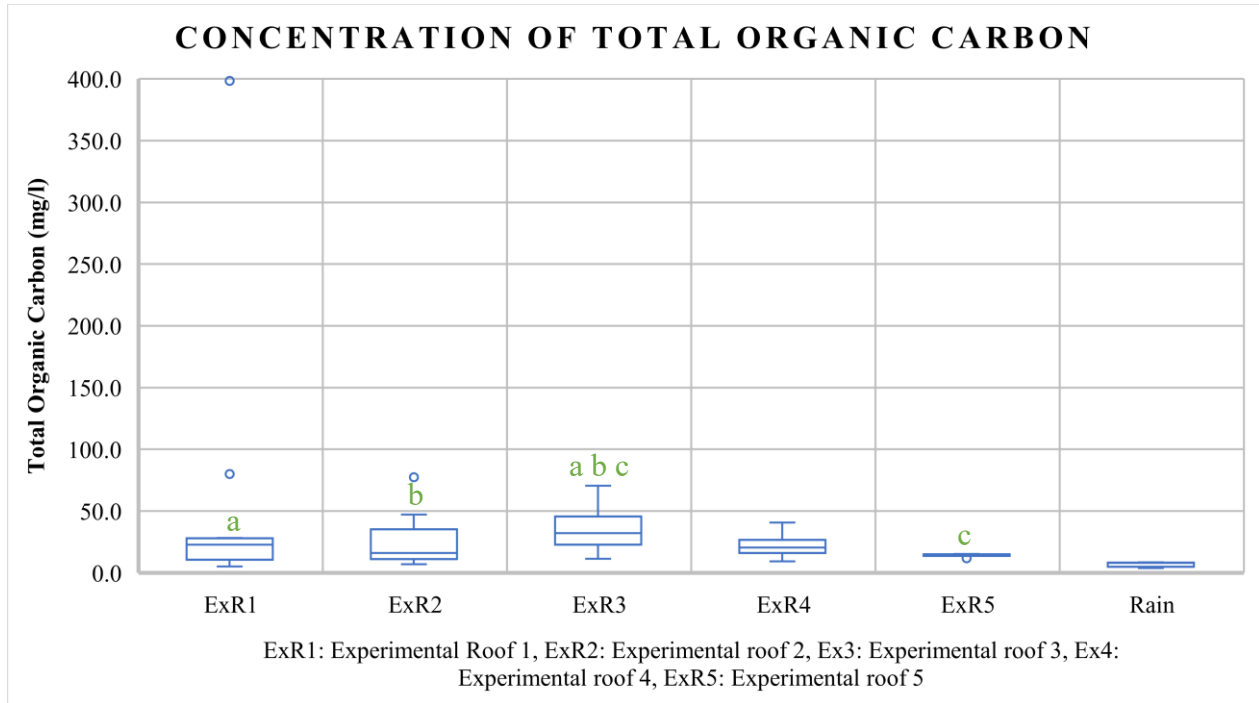
*Figure 3.23.* Concentration of total nitrogen for experimental roofs runoff and rain

For TP the results indicated that runoff from ExR3 has the highest values of TP up to 3.64 mg/L. The median value was 2.14 mg/L. ExR1 runoff showed values up to 0.65 mg/L without taking into account the outlier of 3.44 mg/L. For the other samples (ExR3, ExR4, ExR5 and rain) the result values were under 0.3 mg/L. ExR2 runoff had two outliers of 0.57 and 2.39 mg/L and ExR4 runoff had one outlier: 1.95 mg/L.



*Figure 3.24.* Concentration of total phosphorous for experimental roofs runoff and rain

Regarding the TOC, as it happened with TN and TP, the concentration in ExR3 runoff was the highest. The median value corresponded to 32.01 mg/L and the values went up to 70.45 mg/L. ExR1 and ExR4 runoff have both median values around 20 mg/L, however ExR4 showed values up to 40 mg/L while for ExR1 was around 30 mg/L. ExR2 runoff had a median value of 15.99 mg/L but the range of values was larger than ExR1 and ExR4. ExR5 had 14.5 mg/L as its maximum value and for rain the values were between 3 and 9 mg/L of TOC. It is important to highlight the presence of three outliers: two correspond to ExR1 (79.88 and 398.40 mg/L) and one to ExR2: 77.44 mg/L.



*Figure 3.25.* Concentration of total organic carbon for experimental roofs and rain

Figure 3.26 shows the result for some ions:  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{NH}_4$ ,  $\text{PO}_4$  and  $\text{SO}_4$ . It is important to mention from these results that regarding nitrogen forms the highest one was  $\text{NO}_3$ . For this parameter traditional roofs obtained a higher concentration than the green roofs and the wetland roof, while for  $\text{NO}_2$  the median values of the experimental roofs except the wetland roof were about 0.3 mg/L. The concentration of  $\text{NH}_4$  was lower for green roofs than traditional roofs, specially ExR4 that had values around 0, similarly to the results of the wetland roof. For  $\text{PO}_4$  the result is closely related to TP result (Figure 3.24), showing a significantly higher value of  $\text{PO}_4$  for ExR3 followed by the traditional roofs and ExR4.

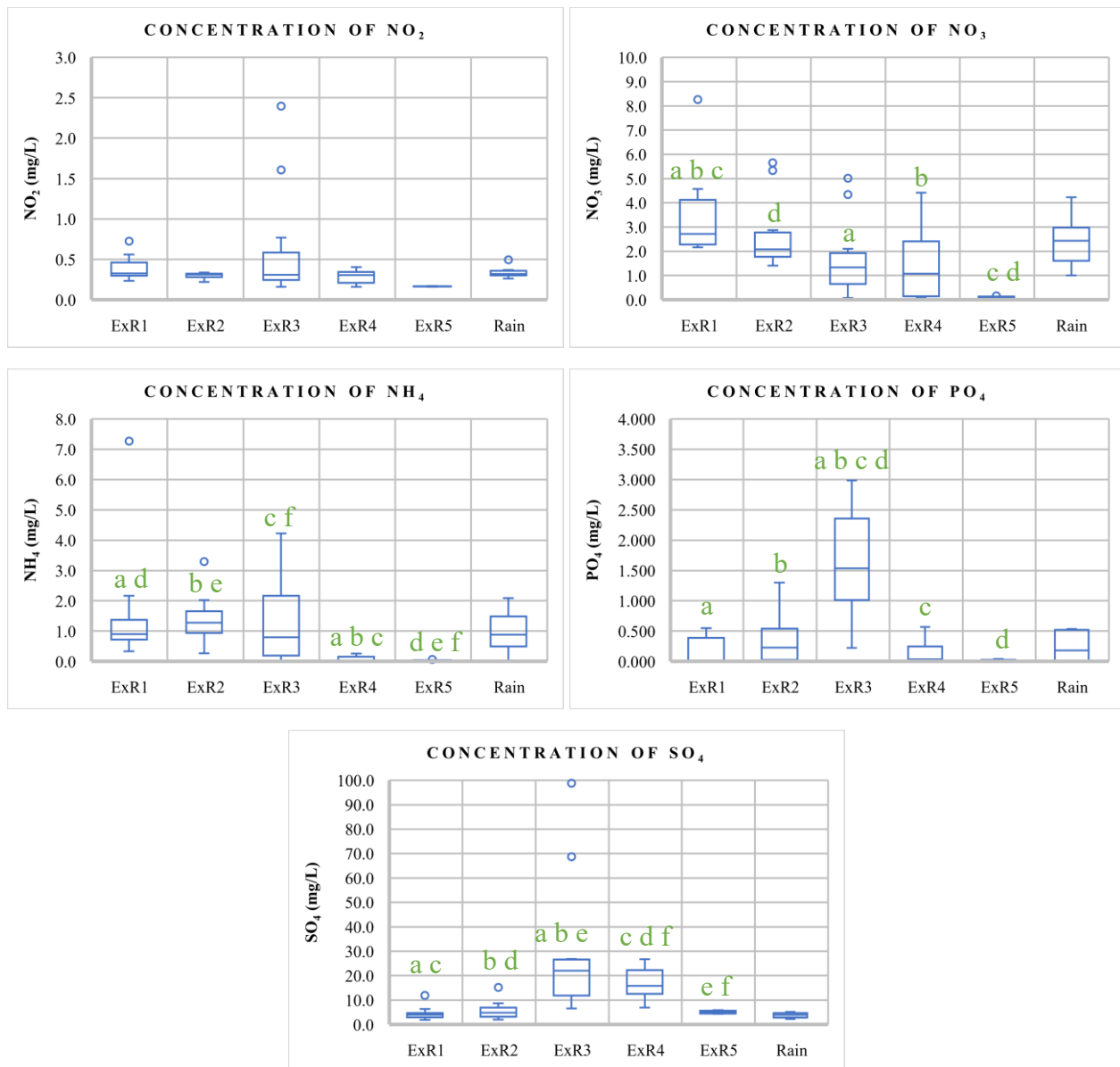


Figure 3.26. Concentration of ions for runoff from experimental roofs and rain

The ANOVA was used to validate if there is any significant difference between sample medians. For TN the p-value was 0.02 and there was a significant difference between runoff from ExR5 and runoff from the others experimental roofs. In the case of TP the p-value was  $8.52 \times 10^{-5}$  and the pairwise comparison showed that the median of runoff from ExR3 had a significant difference with the runoff from the other experimental roofs. Finally for TOC, the test exhibited a p-value of 0.06, which indicates that there is no significant difference between sample medians, however the pairwise comparisons showed that median of ExR3 had significant differences with experimental ExR1, ExR2 and ExR5.

### 3.3 Sorption test

According to the results of the sorption test, the behaviour for each material across varying concentrations of P-PO<sub>4</sub> which were initially prepared based on PO<sub>4</sub> concentrations of 1, 5, 10, 20 and 50 mg PO<sub>4</sub>/L, as well as the concentration found in the rainwater sample (0.05 mg P-PO<sub>4</sub>) are illustrated in Figure 3.27. The Table 3-1 shows the relationship between the initial prepared concentrations of PO<sub>4</sub> and the corresponding initial value of P-PO<sub>4</sub> found as controls in the sorption test.

*Table 3-1.* Relation between concentration prepared of PO<sub>4</sub> and concentration of P-PO<sub>4</sub> found as the control sample

Prepared concentration of PO <sub>4</sub>	Concentration of P-PO <sub>4</sub> found as the control sample in the test
1	0.35
5	2.12
10	4.22
20	13.93
50	21.39

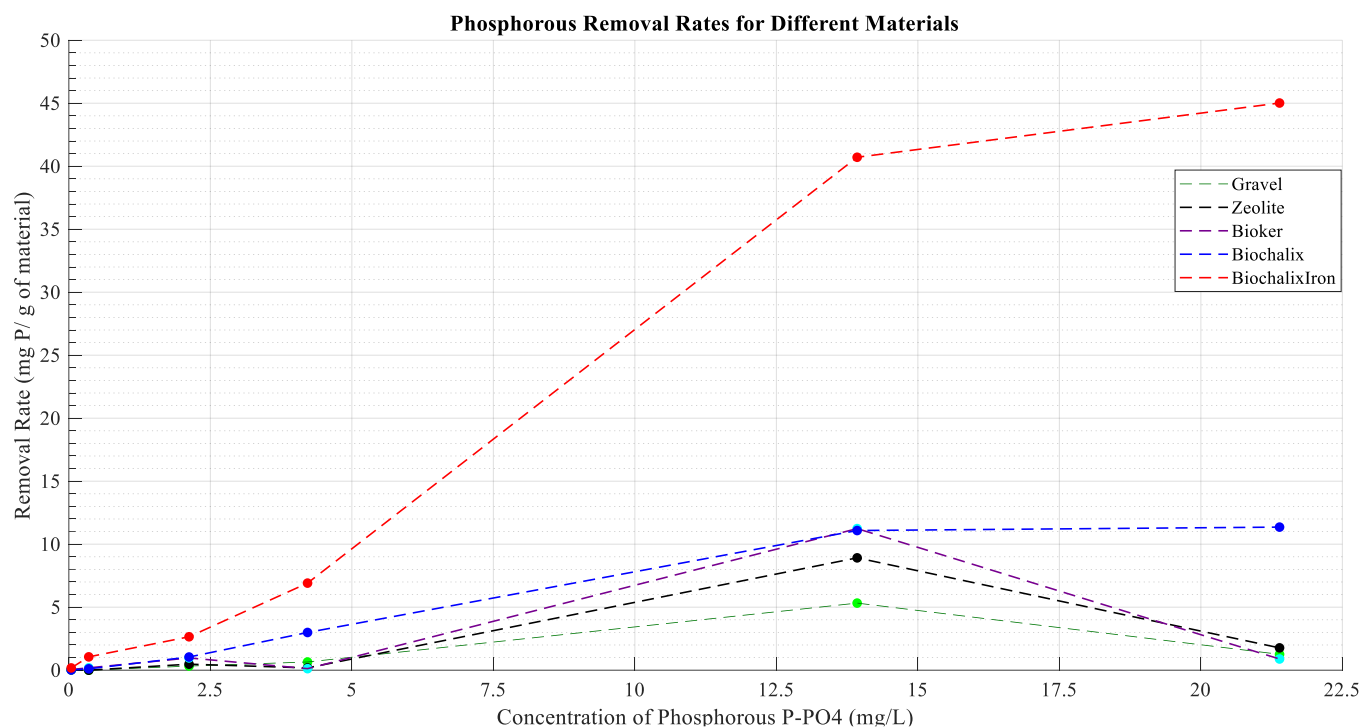


Figure 3.27. Phosphorous sorption rate for different materials

Results clearly demonstrated that the removal rate of Phosphorous for the materials analysed can be divided in two distinct groups: First, Biochalix and Biochalix Iron exhibited a significant increase in removal rate as the concentration was increasing, especially in the case of biochalix iron, where the removal rate jumped from 7 mg P/ g of biochalix iron to about 40 mg P/g of biochalix iron from the concentration of 4.22 to 13.93 mg P-PO<sub>4</sub>/L. At the highest concentration (21.39 mg/L) the removal rate stabilises reaching 45 mg P/g for biochalix iron and 11.35 mg P/g for biochalix. The second group consists of gravel, zeolite and bioker. These materials showed a linear increase in removal rate, reaching the removal rate peak at a concentration of 13.92 mg/L. However, at the highest concentration of P-PO<sub>4</sub>, the removal rate decreased significantly, dropping to values below 3 mg P/ g of material.

The removal efficiency of each material across the five different concentrations tested showed that Biochalix and biochalix iron consistently are the ones that outstand the others achieving efficiencies up to 80% for all tested concentrations (Figure 3.28). Among the remaining materials, bioker shows higher efficiencies, up to 20%. Gravel and zeolite did not exhibit a unique pattern, their efficiencies vary, reaching up to 30-40% at some concentrations, but dropping to 0% at others.

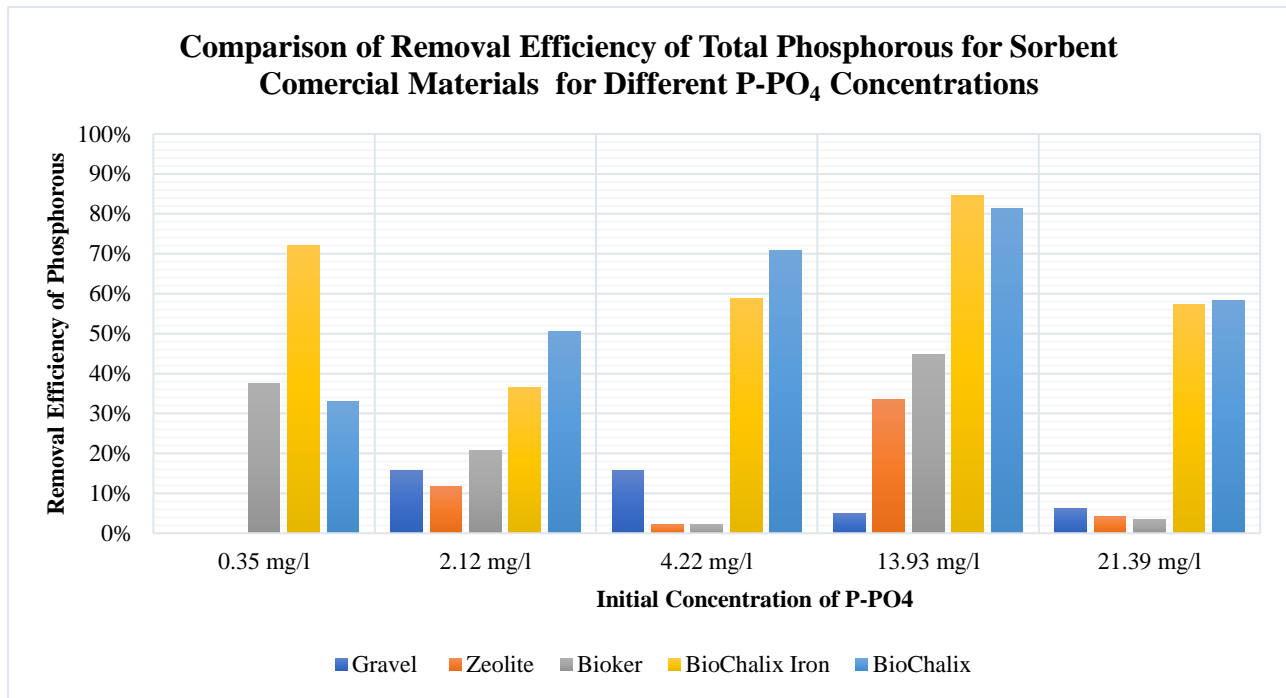


Figure 3.28. Comparison of percentage removal efficiencies for the sorbent materials tested.

Table 3-2 indicates the removal efficiency for the different materials tested in rainwater sample. Biochalix iron had the highest possible efficiency (100%), followed by bioker and gravel with an efficiency over 70%. At the end, Zeolite and Biochalix showed an efficiency of 48.3%.

Table 3-2. Comparison of Removal Efficiency of P-PO<sub>4</sub> for Rainwater

Removal Efficiency for Rainwater	
Material	Efficiency (%)
Gravel	74.8
Zeolite	48.31
Bioker	72.79
Biochalix Iron	100
Biochalix	48.31

To determine if there are significant differences between the materials, a one way ANOVA was conducted on the efficiency results. The data was not completely normally distributed so the Kruskal-Wallis test was used followed by the Dunn Post Hoc test to compare the groups and identify significant differences. The results showed that there is a significant difference between the biochalix iron and gravel ( $p= 0.03$ ), biochalix iron and zeolite ( $p= 0.004$ ), biochalix and gravel ( $0.006$ ) and biochalix and zeolite ( $0.007$ ).

## 4 Discussion

### 4.1 Rainwater quality

The next table shows the concentration of some of the parameters analysed in this study that were found in literature for rain, rainwater and stormwater.

Table 4-1. Review of pollutants concentrations Part 1. <sup>a</sup> The concentrations were found as a range e.g. 13-120, or the mean value plus some times the standard deviation e.g 5.98 (0.95). CR= Concrete roof; TR = Tile Roof; RF1= Roof 1of the study; RF2:Roof 2 of the study; AR: Asphalt roof

Reference	Place of the study	Type of sample	Parameter/Pollutant Concentration (mg/L) <sup>a</sup>				
			TSS	pH	TOC	TN	TP
Present Study	Łódź, Poland	Rainwater	RWS1: 282.10 (258.49) RWS2: 40.03(26.99)	RWS1: 6.63 (0.63) RWS2: 6.96 (0.34)	RWS1: 7.22(3.45) RWS2: 64.15 (34.98)	RWS1: 6.54 (4.99) RWS2: 5.92 (2.23)	RWS1: 0.85 (1.37) RWS2: 0.15 (0.047)
Farreny et al. 2011	Barcelona, Spain	Rainwater	5.98 (0.95)	7.59 (0.07)	11.6 (1.7)		
Melidis et al. 2007	Xanthi, Greece	Rainwater		7.44			
Göbel et al. 2007	Different places (review)	Rainwater	13-120	4.7-6.8			0.06-0.50
Wang et al. 2013	Chongqing, China	Rainwater	CR: 65 (37); TR: 37(37)			CR: 5.6 (1.9); TR: 4(2)	CR: 0.2(0.15); TR: 0.12(0.12)
Zhao et al. 2007	Wuhan, China	Rainwater	RF1: 62(55); RF2: 74(41)			RF1: 6.4(4.7); RF2: 10.4 (2.6)	RF1: 0.67(0.77); RF2: 0.93(0.17)
Zhang et al. 2014	Chongqing, China	Rainwater	CR: 120; AR: 70	CR: 7.6; AR: 7	CR:10; AR: 20	CR:6; AR:8	CR: 0.18; AR: 0.15
Torres et al. 2013	Bogotá, Colombia	Rainwater	3-304	7.55 (0.52)			
Tsakovski et al. 2010	Gdansk, Poland	Rainwater				5.4	0.2
Teemusk & Mander, 2007	Tartu, Estonia	Rainwater		6.73-8.43		1.4-2.6	0.102-0.104
Hou et al. 2012	Beijing, China	Rainwater				7.69 (4.99)	0.044 (0.034)
Göbel et al. 2007	Different places (review)	Rain	0.2-52	3.9-7.5			0.01-0.19
He et al. 2011	Singapore, Singapore	Rain				0.55-0.73	0.025-0.027
Zhang et al. 2011	Shanghai, China	Rain				2.43	0.027
Hou et al. 2012	Beijing, China	Rain				13.86 (10.56)	0.122 (0.085)

Reference	Place of the study	Type of sample	Parameter/Pollutant Concentration (mg/L) <sup>a</sup>				
			TSS	pH	TOC	TN	TP
Göbel et al. 2007	Different places (review)	Runoff trafficked areas	66-937	6.4-7.9			0.23-0.34

Table 4-2. Review of pollutant concentrations Part 2. <sup>a</sup> The concentrations were found as a range e.g. 13-120, or the mean value plus some times the standard deviation e.g 5.98 (0.95). CR= Concrete roof; TR = Tile Roof; RF1= Roof 1of the study; RF2:Roof 2 of the study; AR: Asphalt roof

Reference	Place of the study	Type of sample	Parameter/Pollutant Concentration (mg/L) <sup>a</sup>				
			NO <sub>2</sub>	NO <sub>3</sub>	NH <sub>4</sub>	PO <sub>4</sub>	SO <sub>4</sub>
Present Study	Łódź, Poland	Rainwater	RWS1: 0.39 (0.20) RWS2: 0.55(0.37)	RWS1: 4.57 (3.61) RWS2: 3.96(6.15)	RWS1: 2.24 (1.29) RWS2: 2.40(1.24)	RWS1: 1.23(2.12) RWS2: 0.12(0.18)	RWS1: 5.11 (2.74) RWS2: 8.98 (9.17)
Farreny et al. 2011	Barcelona, Spain	Rainwater	0.13 (0.05)	1.75 (0.26)	0.50 (0.07)	0.32 (0.14)	3.54 (0.39)
Melidis et al. 2007	Xanthi, Greece	Rainwater		1.48(0.71)	0.47 (0.34)		0.057(0.61)
Göbel et al. 2007	Different places (review)	Rainwater		0.1-4.7	0.1-6.2		0.56-14.40
Wang et al. 2013	Chongqing, China	Rainwater		CR: 1.9(0.8); TR: 2.1(2)			
Zhang et al. 2014	Chongqing, China	Rainwater					CR: 35; AR: 30
Tsakovski et al. 2010	Gdansk, Poland	Rainwater	0.024	1.565	0.85	1.9	1.33
Teemusk & Mander, 2007	Tartu, Estonia	Rainwater		0.19-0.4	0.09-0.43	0.032-0.054	
Melidis et al. 2007	Xanthi, Greece	Rain		1.86(0.96)	0.41 (0.32)		0.024(0.018)
Göbel et al. 2007	Different places (review)	Rain		0.0-7.4	0.1-2		0.56-14.40
He et al. 2011	Singapore, Singapore	Rain		0.22-0.30	0.014-0.032	0.001	
Zhang et al. 2011	Shanghai, China	Rain		0.63	1.31	0.016	
Göbel et al. 2007	Different places (review)	Runoff from trafficked areas		0.0-16	0.5-2.3		5.1-139

The analysis of rain and rainwater quality parameters revealed interesting findings. Although the difference of TSS concentration between RWS2 and RWS1 was not statistically significantly ( $p= 0.07$ ), Figure 3.1 suggest that TSS concentration range for RWS2 is larger than RWS1. Furthermore, the average concentration for RWS2 (282.10 mg/L) is 7 times higher than the TSS average concentration for RWS1 (40.03 mg/L). The larger roof area of RWS2 compared to RWS1 may have a significant impact on the difference. Additionally, the slope of RWS1 roof is steep, whereas RWS2 roof is nearly flat. These factors could contribute RWS2 to accumulate and retain TSS during dry periods, which are then washed off during rainfall. For RS1 the box is nearly imperceptible, and for this case the mean concentration of TSS in RWS2 was significantly higher compared to RS1 ( $p= 0.04$ ). Comparing these results with other studies, Farreny et al. (2011) found a lower average TSS concentration of 5.98 mg/L across four roofs that were evaluated, with a maximum TSS concentration of 20 mg/L identified on a flat roof. Similarly, in a review by Göbel et al. (2007), the event mean concentration of TSS in roof runoff ranged from 13 to 120 mg/L, more closely to the results of the present study. In contrast, trafficked areas with high density present TSS concentrations from 66 to 937 mg/L.

Regarding the particles presented in Figure 3.2 they could result from the roof's aging process, where material detaches and is washed off during moderate or heavy rainfall events. A further analysis of these particles is necessary to assess their physicochemical characteristics and the potential impact on the transport of another pollutants that could bind to it. It is important to remark that the TSS parameter is very significant due to the possible for another pollutants to bind these particles, potentially transporting them to final water recipient bodies.

Similarly to TSS results, TOC concentration in RWS2 was significantly higher than RS1 and RS2, and notably, it was also significantly higher than in RWS1. According to the water quality parameters used by Davis & McCuen (2005), a TOC value above 35 mg/L represents a poor quality, which indeed is the case of RWS2. The relation between TSS and TOC levels suggests that elevated concentrations of TOC could be linked with the high percentage of organic matter present in TSS, indicating the presence of organic carbon. In the case of the RWS2, the roofing material, which includes layers of bitumen and organic compounds such as cellulose or asphalt, may lead to the leaching of organic compounds, especially if the roof is already aged and degraded. This hypothesis is supported by the study of Nachshon et al. (2021), who found that for bitumen sheets in roofs the

exposure to UV radiation may accelerate the physical and chemical degradation through the break of bitumen polymer chains, that in consequence promotes the release of organic and inorganic solutes the water. Regarding the TOC levels on RS1, the results could be attributed to the presence of vegetation or small animals, which can add organic carbon to the water. However, it is surprising that TOC levels in RS1 were higher than in RWS1, despite the latter's potential sources of organic material.

When comparing nutrients levels, TN showed significant differences between the groups of rainwater and rain samples. For rainwater (RWS1 and RWS2) the mean values were around 6 mg/L whereas for rain (RS1 and RS2) they were around 3.3 mg/L. In RWS2, TN concentrations reached up to 10 mg/L, compared to a maximum of 7.3 mg/L in RWS1. Conversely, the minimum TN value for RWS2 was around 3 mg/L, while RWS1 recorded a lower minimum of 1.3 mg/L. This pattern was similarly observed in the rain samples, suggesting that the site location may influence TN concentration levels. As it was mentioned previously the slope of the roof for RWS2 can impact the accumulation of more organic material that can contain nitrogen. In addition to this, Sánchez et al. (2015) stated that “organic nitrogen in the form of pollen, spores, bacteria and other substances can make a significant contribution to the total nitrogen concentration, depending on the season of the year and on some climatic conditions”.

Concerning concentration of TP, it was evident that samples from site 1, including both rain and rainwater, had higher values than those from site 2. The presence of pigeons in site 1, particularly on the roof (See Figure 4.1) likely contributes to the elevated phosphorus levels due to the deposition of inorganic compounds such as phosphorus. Additionally, in the rain samples from site 1, the presence of leaves, needles, and other plant debris, as well as various insects or animals such as snails, could further contribute to the higher total phosphorus concentrations observed in these samples. Compared to previous studies (Göbel et al. 2007; Wang et al. 2013; Zhao et al. 2007) the values are within the ranges found it, and the review of Göbel et al. (2007) concluded that nutrient concentrations show an increase from rain to roof runoff caused at some part by moss and lichens on the roofs and bird excrement.



Figure 4.1. *Columba livia domestica* (pigeons) observed on the roof of Site 1

#### 4.1.1 Temporal and hydrometeorological impact

The comparison of nutrients levels and their related ions on rain between March and June did not reveal any significant differences. However, it is important to notice that many studies have documented variations in pollutant levels across different seasons. This is the case of Xing et al. (2017), in which study was found that significant seasonal/monthly variations were observed for all nutrient species, suggesting that human activities and meteorological factors conducted these differences. Zhang et al. (2007) also observed clear seasonal signatures for nutrient species in both wet and dry deposition events. For instance, dry deposition fluxes for the dry season (spring and winter) for  $\text{NO}_3$ ,  $\text{NO}_2$ ,  $\text{NH}_4$  and  $\text{PO}_4$ , were 1–2 times higher than those during summer and fall.

For the TN pollution, in June a higher median value of 2.6 mg/L was observed in comparison to 1.4 mg/L in March, although the concentrations of nitrogen in the forms of  $\text{NO}_3$  and  $\text{NH}_4$  were higher in March. For TP, higher values were recorded in March compared to June, particularly for phosphates. Despite this, the comparison of median values showed only a slight difference, with March recording a median  $\text{PO}_4$  level of 0.31 mg/L while June recorded a median of 0.26 mg/L. Since the collected data was very limited, further studies are needed to accurately determine whether the concentration of certain pollutants varies over time in the city, along with the potential

differences that can exist also on the rainwater quality from the roofs as it was determined by Zhang et al. (2014), in which study was identified that the mean concentration of most of the water quality parameters in summer and autumn was lower than those in winter and spring. They supported this fact because most rainfall events were in summer and autumn, proposing that rainwater dilution in the atmosphere and on the roof was greater in summer and autumn.

Along with the study of temporal impact on pollutants concentration in rainwater, the hydrometeorological influence represents a major focus of this research. RI and ADP factors will become increasingly important in the coming years since the climate change alters the dynamics of heavy rainfall events and prolongs dry periods (Esfandiar et al., 2024). These changes could significantly impact the accumulation of pollutants on roofs, roads, and other impervious surfaces, which may then be washed away with greater force during heavy rainfall events. Figure 3.9 illustrates the dynamic of daily precipitation and dry days from March to June. The graph clearly indicates that higher-intensity rainfall events occurred primarily in the second half of May, which aligns with the data presented in Figure 2.5 showing that May and June have a higher amount of precipitation compared to March and April. Regarding ADP, it was observed that April and May had longer dry periods, some reaching up to 12 days. For the remainder of the study period, the ADP was in average between 1-3 days.

In first place, a significant positive correlation was found between ADP and concentrations of TN, TP and  $\text{NH}_4$  in rainwater, considering data from both RWS1 and RWS2. Vegetation debris and excrement of small insects or other animals as pigeons on the roofs may potentially contribute nitrogen and phosphorous compounds. Since animal excrement is directly linked with ammonia, a higher presence of animals on roofs increases the probability of elevated levels of nitrogen and phosphorous in the rainwater. This explanation is supported by the results of correlations tests conducted separately for RWS1 and RWS2. In the case of RWS2, although none of the parameters showed a statistically significant correlation with ADP, many parameters, including TN, TP, and  $\text{NH}_4$ , exhibited a strong positive trend. On the other hand, the correlation for RWS1 revealed that TP and  $\text{PO}_4$  had significant correlations with ADP. Phosphorus and ammonium are known to be present in bird excrement (Göbel et al. 2007; Sánchez et al. 2015), and pigeons were frequently observed on the roofs of Site 1 (see Figure 4.1 ). Despite of the other compounds that did not show

a statistically significant correlation, TN, TOC, and NH<sub>4</sub> clearly indicated a strong positive correlation.

The first flush effect was simultaneously evaluated, and the correlation analysis revealed that nutrients, nitrogen and phosphorous, had a significant correlation with ADP. This indicates that during the first flush of rainfall events the wash-off of nutrients from impervious surfaces, particularly roofs, is directly related to the number of dry days in which these nutrients accumulated. Validating this, Zhang et al. (2014) found that ADP noticeably affected the quality of runoff water, except for pH, Na<sup>+</sup> and F<sup>-</sup>. A very significant positive correlation ( $p < 0.01$ ) was identified for parameters such as TP, TN, TSS, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Si<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>-</sup>, TOC and Cu(aq), and a significant positive correlation ( $p < 0.05$ ) for K<sup>+</sup> and Zn. However, other studies, like Wang et al. (2013) have found that correlation is not always significant. In their research, TN had a significant correlation with ADP for concrete roofs, however TSS, COD, TP, NO<sub>3</sub>, and NH<sub>3</sub> did not show statistical significance for concrete roofs, and none of these parameters had significant correlation with ADP for tile roofs. Additionally, Jani et al. (2020) studied nitrogen forms in residential catchment stormwater runoff and found that inorganic nitrogen forms were significantly correlated with total rainfall ( $r = 0.90$ ,  $p < 0.001$ ), and ADP ( $r = 0.94$ ,  $p < 0.001$ ), indicating that longer dry periods followed by high rainfall events lead to greater nutrient wash-off. In the same way, Li et al. (2015) demonstrated that the “first flush effects in an urban catchment in China were driven by ADP and rainfall amounts”. Certainly, ADP is a central hydrometeorological factor that contributes to elevated pollutant levels as it provides an extended window for accumulation of dry deposits and nutrient build-up on urban surface. It is crucial to analyse the dynamics of ADP throughout the year to predict when certain pollutants, such as nutrients, might have an increase on the concentrations due to prolonged dry periods that could potentially impact rainwater quality.

In addition to ADP, rainfall intensity (RI) is another key factor that can influence the mobility of pollutants during wet deposition, potentially affecting their concentration. The correlation analysis for combined data from RWS1 and RWS2 revealed that NO<sub>3</sub> was the only parameter with a significant negative correlation with RI, indicating a dilution effect. For the other parameters the correlations were mostly weak and statistically not significant. When analysing the data separately, RWS2 parameters did not show any significant correlation with RI. However, in the case of RWS1 a remarkable positive correlation was observed across all pollutants except NO<sub>3</sub>. Both nitrogen and

phosphorous revealed significant correlations with RI, while TSS, NH<sub>4</sub> and PO<sub>4</sub> had also a strong positive correlation, though these were not statistically significant ( $P > 0.05$ ).

The study of Li et al. (2015), found similar results regarding the event mean concentrations of nitrogen and phosphorous indicating that higher mean RI led to an increased flush of contaminants from surface. Similarly, the research of Wang et al. (2013) reported interesting findings and consistent with the present study, where pollutants on concrete roof had positive correlations with RI, obtaining statistical significance only for TP. On the other hand, for tile roofs, a negative correlation was observed, meaning that stronger RI resulted in decreased pollutants concentrations. Although these findings are not exactly the same of the present study, the differences in roof area, material and slope could impact pollutant wash off. In the case of RWS1, the smaller roof area, and the steep slope facilitate the wash off of contaminants, causing an increase on the pollutant concentrations due to the increased force of water removing accumulated dry deposition. On the other hand, the larger and flatter roof of RWS2 makes pollutant wash off more challenging. The higher runoff volume from the larger roof area enhances the dilution effect, leading to a negative correlation between the pollutant concentration and RI.

Similar to the analysis of first flush effect in relation to ADP, a correlation analysis considering the first flush effect for RI was conducted. The results suggested that for RWS2 pH had a significant negative correlation with RI. Negative correlations were also observed for TN, NO<sub>2</sub>, NO<sub>3</sub> and TOC. Interestingly, TP and PO<sub>4</sub> revealed a strong but not statistically significant positive correlations, suggesting that the first flush behaviour can differ from the analysis of the entire rainfall event. For RWS1, TSS was the only parameter showing a statistically significant positive correlation. Positive correlations were also present for TN, TP, pH, NH<sub>4</sub> and PO<sub>4</sub>, although they were not statistically significant. Conversely, TOC and NO<sub>3</sub> had a negative correlation during the first flush.

To analyse the first flush effect in detail, concentration vs time curves were used. They were useful to identify how the concentration change during the initial minutes and track the decrease of the concentrations after reaching the peak concentration. Additionally, as it was discussed before, it is important to relate the first flush with other hydrological factors, for instance RI, ADP and runoff depth (Perera et al. 2021) which impact the water quality of that first flush. In the case of ADP, Lee et al. (2004) showed that “concentration of contaminants in the first part of the wet season

ranges from 1.2 to 20 times higher than the end of the season, as during the dry season a long period for pollutant build-up on the catchment's surfaces is created”.

The concentration vs time curves shown in Figure 3.20 and Figure 3.21 clearly illustrate the first flush effect for TSS, TN, TP and TOC. In the case of RWS1, in some events, such as event 2, the highest pollutant concentration was observed in the first sample (t1). However, for other events, such as event 10, the peak concentration occurred in the second sample (t2), specifically for TSS and TN. Additionally, the graphs indicate that for TOC there was a slight increase in concentration at t4, or in some cases at t3 as seen with TP for event 2. The dynamic suggests that the peak concentration typically occurs within the first 10-20 minutes depending on the RI. This fact is confirmed by Sánchez et al. 2015, who claimed that the duration of the first flush varies with the intensity of the rainfall event. In the case of Egodawatta et al. 2009, it was found that only around 75% of the available particles present on roof surfaces were removed by a 20 mm/hr rainfall event while almost 100% of particle were removed during a 115 mm/hr rainfall event. After reaching that peak, a sharp decrease in concentration usually follows, and then stabilization or a slight increase in concentration may be observed. The behaviour in RWS2 supports this pattern, with peak concentrations for all parameters generally occurring at t1, followed by decreases at t2 and t3. In some cases, t4 showed a slight increase for certain events and parameters.

Comparing the results with other studies, Yufen et al. (2008) showed that the initial and ending concentrations of pollutants in runoff varied significantly between rain events. Among the pollutants measured on the study, all of them reached their peak concentration in the first sample, although the followed decrease in concentration did not follow a consistent pattern. Additionally, the study observed that the initial and final concentrations of COD, BOD<sub>5</sub>, total nitrogen, and total phosphorus in roof runoff increased with the number of dry days preceding the rainfall.

The consideration of the first flush is crucial as numerous studies have concluded that this portion of the rainfall events is the most polluted, potentially compromising the use of this source of water. Moreover, addressing the first flush is very important to prevent high pollution loads from entering water bodies. As it was mentioned before, the combination of factors such as ADP and RI, as well as other factors not examined in this research, for instance, duration of the rainfall event and wind, can significantly impact pollutants concentration in rainwater. Understanding these dynamics is a priority when implementing nature based solutions in order to identify critical factors that influence

pollutant levels and help determining which pollutants are the most relevant, depending on the specific objectives of managing rainwater or stormwater.

## 4.2 Nature-Based Solutions: Rainwater quantity and quality of experimental roofs

The use of Nature-Based Solutions (NbS) for rainwater/stormwater retention, peak runoff delay, and quality treatment is becoming more important due to rapid urbanisation and climate change. Traditional grey infrastructure often lacks the capacity to effectively manage both wastewater and stormwater, making NbS an excellent alternative to support stormwater treatment. In this study, the experimental green roofs demonstrated a significant retention capacity, averaging 80% of the water runoff volume that occurred on the traditional experimental roofs. Although all events shown in Figure 3.22 had a positive and great retention capacity over 70%, certain events (6, 8 and 10) had retention capacities below 80%. These events, which occurred between May 18<sup>th</sup> and June 3<sup>rd</sup>, coincided with the period of higher rainfall, identified by Figure 3.9. This observation could indicate that experimental green roof soil may become saturated at certain level of precipitation.

The retention capacity of green roofs has been widely studied in the literature. For instance, Teemusk & Mander (2007), found that green roofs retained 85.7% of runoff during light rain events following dry periods. However, during heavy rainstorms, while the green roof was able to delay runoff up to 15 minutes, it could not completely retain the water. Similarly, Carpenter et al. (2016) investigated the quantity and quality of discharge from a green roof in Syracuse, NY, over an annual cycle. Their results showed consistently a high retention, with a mean percent retention of 96.8%. However, they also found that once the amount of precipitation increased the retention capacity decreased, concluding that the green roof reaches saturation after certain amount of water, beyond which its capacity reduces. This is also confirmed by Fioretti et al. (2010), who states that when rainfall intensity is especially low, there is almost no runoff, so the retention rate is 100%. On the other hand, when the rainfall is extremely high or the length of preceding dry period is short, the initial soil moisture is higher and reduces the soil retention capacity resulting in some cases in a zero value of the retention rate. Another relevant field experiment in Warsaw was conducted by Baryła et al. (2024) comparing three green roof models varying the drainage layers. The average water retention was similar across the three models, with retention rates of 84%, 87% and 81%. In the review conducted by Zheng et al. (2021) across 21 countries results indicated a widely range in retention rates (0–100%), with an average of 62%. According to the review, rainfall intensity,

substrate depth, GR surface coverage, climate type, vegetation type, and season type partially explain the variances in retention performance. The study remarked the complex interactions between these factors, which collectively influence the overall retention performance of the green roofs.

As important as the water retention capacity of green roofs, assessing water quality is to understand the overall effectiveness of NbS such as green roofs and raingardens. In this case, Figure 3.23, Figure 3.24, Figure 3.25, and Figure 3.26 showed that runoff from ExR3 exhibited the highest concentration of TN, TP and TOC among the tested experimental roofs. This result was expected as the organic matter present in the vegetation on this roof is likely to leach nutrients into the rainwater. It is also observed that runoff from ExR4, which contains the sorbent material Caxit, effectively reduced the concentration of both nitrogen and phosphorous, with a particularly notable decrease in the last one. The median phosphorous concentration on roof 4 was about 90% lower compared to roof 3 that did not contain the sorbent material. This significant reduction is further corroborated by the results of  $\text{PO}_4$  concentration, which also showed a marked decrease in ExR4 compared to ExR3.

The findings from Teemusk & Mander (2007) on water quality were quiet similar to the behaviour observed for ExR4. In their study, they implemented a substrate layer composed by lightweight aggregates (LWA), humus and clay, which effectively retained phosphorous, especially during moderate rain events. The use of this LWA could be compared with the use of the Caxit in this study as the LWA is often used as filtrate material to bind phosphorus in constructed wetlands (Jenssen et al. 2005). Furthermore, the study of Toland et al. (2012), which focused on the evaluation of nutrient concentrations in runoff from green roofs, conventional roofs, and urban streams, found that TN, TP and TOC concentrations were higher in green roofs compared to conventional roofs, confirming the results of the present study. The elevated phosphorous concentrations observed suggested that green roofs are a potential nutrient source, especially when fertilized with compost. For instance, phosphate concentration in green roofs range from 1.56 to 1.82  $\text{mgPO}_4/\text{L}$  when compost is used, while for roofs without compost the result lows to an average of 0.14  $\text{mg PO}_4/\text{L}$ . In this case, the green roof ExR3, which did not contain Caxit, had an average of 1.5  $\text{mg PO}_4/\text{L}$ , aligning with the results for compost-fertilized roofs. In contrast, the green roof

with Caxit (ExR4) showed a lower PO<sub>4</sub> concentration, averaging 0.165 mg PO<sub>4</sub>/L, demonstrating the effectiveness of the sorbent material in reducing nutrient concentration on runoff.

Based on the studies mentioned above, and others more including Jennett & Zheng (2018), Pęczkowski et al. (2018) and Rey et al. (2020), it can be concluded that green roofs represent a potential a source of phosphorus, as higher concentrations of TP are found in leachate from green roofs compared to the concentrations present in rainwater or soils without vegetation. Regarding nitrogen, Marín et al. (2023) reviewed existing literature and noted mixing findings about whether green roofs function as a source or sink for nitrogen. Marín et al., (2023) stated that several researchers have found that concentrations of different forms of nitrogen, such as nitrate (NO<sub>3</sub>) are lower in runoff from green roofs (0.156 mg/L) than in rainwater or conventional soil (0.412 mg/L). However, other studies (Carpenter et al., 2016; Castro, 2020) have reported significant nitrogen concentrations in runoff from green roofs.

Given that NbS including green roofs and raingardens, are designed to address environmental challenges such as the increased stormwater runoff, pollutant retention, and urban heat island effect, it is crucial to evaluate the elements of these systems that can increase the concentration of nutrients in the runoff. As the runoff often discharges into sewer systems or directly into receiving water bodies, the potential nutrient export from green roofs or raingardens could be problematic. Nutrients acts as key regulators of water eutrophication, and the implementation of green roofs or raingardens without measures to prevent nutrients release could significantly contribute to the eutrophication of urban water bodies and potentially harmful algae blooms.

To prevent the negative effects of rainwater quality runoff , the inclusion of sorption materials within NbS systems is a promising strategy for enhancing pollutant retention. The sorption tests conducted in this study demonstrated that commercial sorbent materials, such as biochalix and bioker, have a great potential to retain pollutants, particularly phosphorous. Similarly, the sorbent material used in ExR4, Caxit, effectively retained phosphorous, as previously mentioned.

According to the results presented in Figure 3.27, biochalix iron and biochalix were the most effective materials in capturing phosphorous. The sorption rate curves for both materials demonstrated an increase in removal rate as the background phosphorous concentration increased. Although the ANOVA analysis did not indicate a significant difference in removal efficiency between biochalix iron and biochalix, the sorption curve revealed that biochalix iron consistently

showed higher removal rates across the five concentrations tested. The iron content in the sorbent material likely enhances removal due to iron's capacity to bind with dissolved phosphorous through the formation of iron oxides (rust), that allows the process of surface adsorption (Erickson & Gulliver, 2010)

Many studies have documented the effectiveness of iron amended materials in increasing phosphorous removal. For instance, Erikson and Gulliver (2010) implemented on filtration trenches a mix of sand and iron to assess the capture of dissolved phosphorous from synthetic and natural runoff. Their finding showed a phosphorus removal efficiency varying between 29% and 90%, with most tests achieving greater than 50% capture. Similarly, Reddy et al. (2014), compared the efficiency of four filter materials -calcite, zeolite, sand, and iron filings- to remove nutrients, specifically nitrate and total phosphorus, from synthetic urban stormwater run-off concentrations. Their results suggested that Iron filings were the most effective sorbent material achieving removal efficiencies of 73% to 100 % for both nitrate and phosphate. The removal of phosphate ranged from 35 % to 41 % for calcite, 59 % to 100 % for zeolite and 49 % to 100 % for sand.

Although Bioker, zeolite and gravel showed lower efficiency compared to biochalix iron and biochalix, they were still able to retain some phosphorous. A particular behaviour was observed for these three materials: the removal rate significantly decreased at the highest phosphorous concentration. This suggests that at elevated phosphorous levels, these materials may reach their retention capacity and become less effective. In the sorption test with rainwater (See Table 3-2), biochalix iron confirmed its high efficiency in capturing phosphates. Interestingly, biochalix showed a lower removal percentage compared to gravel and bioker, and performed similar to zeolite. Further studies are needed to analyse the performance of these materials under varying rainwater conditions, as different events of May have different phosphorous concentrations.

Beyond the studies highlighting the efficiency of iron amended materials to remove phosphorous, several authors have investigated different natural or synthetic materials to enhance the removal of phosphorous and other pollutants. Esfandiar et al. (2024) evaluated various sorbent amendments including coconut coir fibre, blast furnace slag, and waste tire crumb rubber for their ability to remove metals, nutrients, and polycyclic aromatic hydrocarbons from stormwater. Among these sorbents, the blast furnace slag exhibited a high phosphate removal capacity, achieving over 90 % removal of influent phosphate. Additionally, biochar has been widely reported as an effective

sorbent material. Biswal et al. (2022) reviewed studies showing that total phosphorous removal efficiency in biochar-amended biofilters ranges from 48% to 94%. Notably, biochar impregnated with metal or metal oxides, such as MgO or Fe<sub>3</sub>O<sub>4</sub>, demonstrated increased phosphate removal efficiency (R. Li et al., 2016; Yu et al., 2016).

In this context, the present study highlights the importance of applying the ecohydrology approach for effective water management in urban areas, with the aim to create sustainable and resilient cities in the next years. Harvesting rainwater in urban areas represents both opportunities and challenges. As water scarcity increase in many cities around the world, rainwater is seen as a potential source of water. However, since the quality of rainwater is affected by different processes, it becomes essential to understand the correlation between pollutants and hydrometeorological factors. These factors may be further influenced by the acceleration of climate change, which alters in the end precipitation patterns, leading to longer dry periods and more intense rainfall events.

Beyond rainwater harvesting, urban runoff from impervious surfaces that flows through the drainage systems or is directly discharged into water bodies such as rivers and lakes, posed a significant threat to ecosystem health. Pollutants, including nutrients, can lead to problems like eutrophication, and also a reduction in ecosystem services, including biodiversity loss and diminished recreational areas. Additionally, the changing patterns associated with climate change result in heavier rainfall events that cause floodings, affecting year by year thousands of people. To address these challenges in urban areas, NbS offer a promising approach to mitigating negative impacts and integrating ecohydrological principles into urban planning. Solutions like green roofs and raingardens harness natural processes to manage water sustainably. However, these approaches also have limitations and potential side effects, for instance, the release of nutrients (specially phosphorous) from green roofs. Therefore, exploring innovative materials and methods to enhance processes like sorption is an important step forward in advancing ecohydrological research and application in urban areas. As Zalewski et al. 2021 claimed in his review about ecohydrology and adaptation to climate change, the necessity to increase stormwater retention, but also the importance of cleaning of the stormwater, are fundamental for the application of an ecohydrology approach in urban areas through the conversion into blue-green cities.

## 5 Conclusion and recommendations

In conclusion, this study revealed significant differences in rain and rainwater quality between the two sites studied, particularly for pollutants such as total phosphorous. These differences suggest that the presence of animals, like birds, may contribute to the pollution. The research confirmed that rainwater has significantly higher concentrations of pollutants including TSS, TN, TP, TOC primarily due to surface wash off. Although no significant temporal differences in pollutant concentrations were observed further studies with a longer sampling period are necessary to understand seasonal effects. Regarding hydrometeorological factors, a positive correlation was found between ADP and pollutants concentration. RI showed varying correlations across sites, indicating that other factors such as roof type, slope and roughness also influence pollutant concentrations. For the first flush effect, the study demonstrated significantly higher concentration of pollutants during the initial minutes of rainfall, although this effect is also influenced by hydrological factors like RI.

The analysis of experimental units supported the hypothesis that green roofs improve water retention. Experimental green roofs reduced runoff volume by approximately 80% compared to experimental traditional roofs. However, regarding rainwater quality, the results showed a contrast behaviour. Green roof #1 (ExR3) showed higher levels on runoff of TN, TP, TOC, PO<sub>4</sub> and SO<sub>4</sub> than traditional experimental roofs, while green roof #2 (ExR4) only showed higher SO<sub>4</sub> concentration than traditional experimental roofs. This suggests that the Caxit material enhanced pollutant capture, as supported by sorption tests, indicating high sorption rates for Biochalix Iron and Biochalix achieved very high sorption rates, and lower rates for bioker, zeolite and gravel, suggesting a limit capacity for these materials. Further studies on the sorbent materials should be done to study that limit capacity and the behaviour of other pollutants such as nitrogen and heavy metals.

Rainwater harvesting is a promising alternative water source of water in cities facing water scarcity. However, rainwater often contain pollutants due to dry and wet deposition, and surface leaching. The presence of these pollutants is significantly influenced by hydrometeorological factors like ADP and RI, which are expected to be further affected by climate change. Therefore, implementing

NbS in in urban areas will be crucial for mitigating environmental issues such as floodings and urban heat islands.

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# APPENDIX

Table A- 1. Sampling campaign in Site 1

Event	Sample Collection				ADP (days)	Roof	Volumes of samples (mL)			Observations
	Start date	Start hour	End date	End hour			Container 1	Container 2	Container 3	
1	12/03/2024	9:00	12/03/2024	16:00	1	Yes	100	101	100	From the roof it was taken just one sample (1 litre). This sample was not taken in the first minutes of event (first flush).
2	18/03/2024	9:00	18/03/2024	16:00	0	Yes				Missing the volume of the sample.
3	25/03/2024	10:00	25/03/2024	16:00	3	No	400	415	415	
4	28/03/2024	9:00	29/03/2024	9:00	2	No	12	23	25	Just ion chromatography analysis because of small volume of the samples.
5.1	2/04/2024	8:30			4	Yes				Sample from the roof. The rain already started time before. Not first flush
5.2	2/04/2024	8:30	3/04/2024	10:00	4	No	52	57	42	
6	5/04/2024	15:00	6/04/2024	8:00	1	No	189	184	194	Containers with a lot of small animals and vegetation. No analysis of these samples because of organic material.
7.1	15/04/2024	0:00	15/04/2024	14:00	8	No		71	68	Container 1 was rejected because of too many vegetation inside.
7.2	15/04/2024	10:00	15/04/2024	14:00	8	Yes	32			The container was put on 15/04/24 to sample the direct rain, but the container was not the same as always (another bucket).
8	19/04/2024	14:45	19/04/2024	15:30	0	Yes	380	364	324	Three samples at different time from the roof, one from direct rain, and three from the containers.

Event	Sample Collection				ADP (days)	Roof	Volumes of samples (mL)			Observations
	Start date	Start hour	End date	End hour			Container 1	Container 2	Container 3	
9.1	18/05/2024	0:00	19/05/2024	14:00	12	Yes				First sample from the roof.
9.2	19/05/2024	14:00	20/05/2024	9:30	0	Yes				Second sample from the roof.
9.3	18/05/2024	0:00	20/05/2024	10:00	12	No	720	700	760	Container 2 was moved to another place due to extensive vegetation on the area.
10.1	22/05/2024	15:30	22/05/2024	17:15	2	Yes				Four samples of roof during the rainfall event.
10.2	22/05/2024	15:30	23/05/2024	9:40		No	390	350	375	
11	24/05/2024	10:00	27/05/2024	10:00	1	Yes	233	180	170	
12	29/05/2024	17:15	29/05/2024	17:50	3	Yes	860	640	720	Three samples from the roof.
13	13/06/2024	15:13	13/06/2024	16:00	2	Yes	130	135	100	Four samples from the roof.

Table A- 2. Sampling campaign in Site 2

Event	Sample				ADP (days)	Roof	Experimental roofs					Observations
	Start date	Start hour	End date	End hour			R1	R2	R3	R4	R5	
1	10/04/2024	-	-	-	2	No	Yes	Yes	Yes	Yes	Yes	Samples taken from the containers directly. There are not start and end hours because was the first sampling from the containers, so the water was from previous days
2	15/04/2024	9:30	15/04/2024	11:30	8	Yes	Yes	Yes	Yes	No	Yes	The rain starts at 7:30, but is so light. The sample takes place at 09:30, samples taken from gutters. Not samples from roof 4. Roof 5 the samples is taken however is stagnant water
3	19/04/2024	14:00	19/04/2024	16:00	0	Yes	Yes	Yes	Yes	No	Yes	The samples are taken from the upper part of the container minutes later that the rain stops.
4	19/04/2024	16:00	22/04/2024	9:15	0	No	Yes	Yes	Yes	Yes	Yes	Samples taken directly from containers.
5	5/05/2024	0:00	6/05/2024	9:30	8	No	Yes	Yes	Yes	Yes	No	Samples taken from containers directly. Rain from the day before
6	18/05/2024	0:00	20/05/2024	8:30	12	Yes	Yes	Yes	Yes	Yes	No	Samples taken from containers directly.
7	22/05/2024	15:00	22/05/2024	17:45	2	Yes	Yes	Yes	Yes	Yes	No	Samples taken from the containers.
8	22/05/2024	17:45	27/05/2024	9:30	1	No	Yes	Yes	Yes	Yes	No	Samples taken from containers.
9	29/05/2024	9:30	1/06/2024	10:30	3	No	Yes	Yes	Yes	Yes	No	Samples taken from containers.
10	1/06/2024	10:30	3/06/2024	8:30	0	Yes	Yes	Yes	Yes	Yes	No	Samples taken from containers.

Event	Sample				ADP (days)	Roof	Experimental roofs					Observations
	Start date	Start hour	End date	End hour			R1	R2	R3	R4	R5	
11	16/06/2024	0:00	17/06/2024	8:30	2	Yes	Yes	Yes	Yes	Yes	No	Samples taken from containers.
12	27/06/2024	14:45	27/06/2024	15:20	2	Yes	No	No	No	No	No	Samples only from the roof (first flush). Event starts at 14:45 very intense, then at 15:00 it stops, at 15:12 it re starts and the 15:20 stops again.