Universitat Autònoma de Barcelona

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# The role of forest in the redistribution and isotopic modification of water fluxes

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## THE ROLE OF FOREST IN THE REDISTRIBUTION AND ISOTOPIC MODIFICATION OF WATER FLUXES

**Carles Cayuela Linares**
Doctoral Thesis 2019

Institut de Diagnosi Ambiental i Estudis de l'Aigua (**IDAEA-CSIC**)
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Doctoral Thesis

**Carles Cayuela Linares**

To be eligible for the Doctor degree

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*Programa de Doctorat en Ecologia Terrestre*

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# AGRAÏMENTS

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# ABSTRACT

The present dissertation aims to analyse the role of forest cover on the redistribution of water fluxes and improve the current knowledge on hydrological functioning of Mediterranean headwater catchments. This study has been carried out in the Vallcebre research catchments, an area representative of these Mediterranean mountain environments. Continuous measurements of rainfall, throughfall, stemflow, runoff, meteorological data and stable isotopes of water have been used to investigate hydrological processes at different spatio-temporal scales.

At the plot scale, the findings obtained from a Scots pine (*Pinus sylvestris* L.) and downy oak (*Quercus pubescens* Willd.) forest plots have shown that stemflow, despite being only a small portion of the incident precipitation, is a substantial source of water and particulate matter at the base of trees. Stemflow is the result of a complex combination of biotic and abiotic factors, it increases with the event size but the duration of rainfall, intensity or the evaporative demand highly influence its temporal dynamics. In addition, we have found the size of trees to be the main factor producing differences among individuals of each species. However, between species, main stemflow differences have been attributed to different bark storage capacities and different evaporation rates. Besides, through the analysis of the particles contained in throughfall and stemflow, we have observed that the interaction between particulate matter and vegetative surfaces affects the size and the retention of particles. In general, the presence of leaves in oaks increases the size of particles, and needles of pines enhance its retention. We have also found that Saharan dust events are a substantial source of particulate matter in the study area.

Isotopic differences among rainfall, throughfall and stemflow have been observed. Fractionation processes are more evident for events of low rainfall amount, when canopies are not completely saturated. They can be caused by a mixture of factors, for example, evaporation is more likely to have a higher impact at the beginning of rainfall, however, under low evaporation conditions, isotopic exchange (between water and vapour) may acquire more relevance. In addition, for rainfall events with temporal variations of the isotopic composition, the retention of part of the final portion of rainfall on leaves and stems can also produce isotopic differences in both directions, enrichment or depletion.

At the catchment scale we have found that, in addition to the isotopic changes produced by canopy interception processes, the isotopic composition of rainfall also varies along an

elevation gradient. Throughout the Can Vila catchment and for several runoff events, the effect of the spatio-temporal variability of the input isotopic signal on hydrograph separation results has been tested. Results have shown that although the Isotopic Hydrograph Separations are dominated by pre-event water, for some floods, the pre-event water contribution can differ significantly depending on the single location of the input isotopic signal used. Comparing hydrograph separation results obtained using different single input signals, with results obtained using a catchment scale input isotopic signal, we could determine the most representative sampling location and define a “smart” sampling strategy for improving Isotopic Hydrograph Separations at the small catchment scale.

Overall, findings gathered in the present dissertation highlight the role of stemflow as a preferential flow path of water and nutrients that can enhance biogeochemical processes at the base of trees during rainfall events. Results also emphasize that the isotopic variability of rainfall, due to canopy interception processes and elevation gradients, has to be taken into account for a better understanding of the hydrological processes in Mediterranean headwater catchments.

# RESUM

Aquesta tesi té com a objectiu analitzar el paper de la coberta forestal en la redistribució dels fluxos d'aigua, amb la finalitat de millorar el coneixement sobre el funcionament hidrològic de les conques Mediterrànies de capçalera. L'estudi s'ha realitzat a les conques d'investigació de Vallcebre, representatives dels ambients mediterranis de muntanya. Els processos hidrològics s'han estudiat a diferents escales espai-temporals a partir de mesures continues de pluja, trascol, escolament cortical, escorrentia, variables meteorològiques i mostreig dels isòtops estables de l'aigua.

Els resultats obtinguts a escala de parcel·la, en un bosc de Pi roig (*Pinus sylvestris* L.) i un de roure martinenc (*Quercus pubescens* Willd.) han demostrat que l'escolament cortical, malgrat representar un percentatge petit de la pluja incident, representa una concentració important d'aigua i partícules directament a la base dels arbres. L'escolament cortical és el resultat d'una combinació complexa de factors biòtics i abiòtics, augmenta a major volum de pluja, però la duració de la pluja, la intensitat o la demanda evaporativa determinen la seva dinàmica temporal. D'altra banda, la mida dels arbres determina la diferent resposta d'individus de la mateixa espècie. En canvi, entre espècies, les diferències estan determinades per la capacitat d'emmagatzemar aigua a l'escorça o les diferents taxes d'evaporació. L'anàlisi de les partícules transportades pel trascol i l'escolament cortical, indica que la interacció entre la matèria particulada i les superfícies vegetals afecta a la mida i a la retenció de partícules. En general, la presència de fulles als roures incrementa la mida de les partícules, i les acícules dels pins augmenten la retenció de partícules. Finalment, cal destacar la pols del Sàhara com una font important de partícules a la zona d'estudi.

Hem observat diferències isotòpiques entre l'aigua de pluja, el trascol i l'escolament cortical. Els processos de fraccionament isotòpic són més evidents per als episodis de baixa magnitud, en els que les capçades no s'arriben a saturar del tot. Aquests processos són deguts a una mescla de factors, per exemple l'evaporació pot ser el factor determinant a l'inici de la pluja, tot i que en condicions d'alta humitat ambiental, l'intercanvi isotòpic (entre aigua i vapor d'aigua) pot adquirir rellevància. En episodis on el senyal isotòpic varia al llarg de la pluja, la retenció de part de la pluja a les fulles i troncs pot produir tan enriquiment com empobriment.

A escala de conca, hem observat que el senyal isotòpic de la pluja, a més de canviar per l'efecte de la coberta, canvia al variar el gradient d'elevació. Amb aquesta informació, hem

analitzat l'efecte de la variabilitat espai-temporal del senyal isotòpic d'entrada a la conca de Can Vila sobre els resultats de la separació d'hidrogrames. Els resultats mostren que tot i que els hidrogrames estan dominats per aigua pre-existent a la conca, per algunes crescudes, la contribució d'aigua pre-existent pot variar significativament en funció de la localització del senyal isotòpic d'entrada utilitzat. La comparació dels resultats obtinguts en la separació d'hidrogrames utilitzant diferents senyals isotòpics d'entrada amb els resultats obtinguts utilitzant un senyal mitjà, ha permès definir una estratègia de mostreig "intel·ligent" que millora les separacions d'hidrogrames basades en isòtops estables a escala de petita conca.

En conjunt, els resultats d'aquesta tesi destaquen el rol de l'escolament cortical com a flux preferencial d'aigua i nutrients, que pot afavorir els processos biogeoquímics a la base dels arbres. A més, els resultats recalquen que la variabilitat del senyal isotòpic de la pluja, degut als processos d'intercepció i gradients d'elevació, s'ha de tenir en compte per millorar la comprensió dels processos hidrològics en conques Mediterrànies de capçalera.

# CONTENTS

# CHAPTER 1

## General introduction and Objectives

Mediterranean mountain areas lie between 30º and 45º latitude and are located around the Mediterranean basin and in coastal areas of California, South America, South Africa and South Western Australia. These areas are subject to very extreme conditions with respect to fluctuations in water availability, causing situations of temporary shortage for humans and ecosystems. Still today there is a lack of understanding of the hydrological functioning of these areas, which are fundamental for the water resources of many coastal areas. This dissertation aims to improve the knowledge on hydrological functioning of these Mediterranean mountain environments focussing on the role of forested areas.

In this first chapter, a brief introduction to the importance of Mediterranean mountain areas in the hydrological cycle and to the small catchment approach for research is provided. Furthermore, this chapter includes the overarching aim of the present dissertation, and the specific objectives of each of the following chapters.

## 1.1. THE HYDROLOGICAL IMPORTANCE OF MEDITERRANEAN MOUNTAIN CATCHMENTS

Water is a precious resource that sustains life, fundamental for humans and ecosystems. Even though there is a lot of water on Earth, only about 2.5% is fresh water, and because most of this water is stored as glaciers or deep ground water, only a small amount is easily accessible. Mediterranean regions are characterized by a strong inter- and intra- annual precipitation variability and by a strong climatic seasonality. Water resources in the Mediterranean area are unevenly distributed and they depend mainly on runoff generated in mountain areas (Viviroli *et al.*, 2007). The strong precipitation variability of these areas, with drought periods, convert Mediterranean environments in vulnerable regions in terms of water resources (Woodward, 2009).

The hydrology of Mediterranean mountain areas is, in addition, highly sensitive to changes in their environment. Nevertheless, due to the increase of the population after the industrial revolution, many mountains were partially deforested and replaced by cultivated fields, resulting in landscapes of complex mosaics of forests, cultivated lands, shrubs or pastures (García-Ruiz *et al.*, 1996; Poyatos *et al.*, 2003; Coop and Givnish, 2007). Nowadays, most of the population and most economic activities are located in the lowlands and coastal areas. Consequently, mountain areas have been abandoned producing an imbalance between the location of water resources and human activities. Changes in the land cover have been observed to alter the hydrological responses of these areas, for example, deforestation increases annual runoff, sediment transport and flood frequency (e.g. Lavabre *et al.*, 1993; Wohlgemuth *et al.*, 2001; Cerdà and Lasanta, 2005). Contrarily, the development and densification of forest cover, often observed after land abandonment, generally lead to a reduction in annual flows (e.g. Beguería *et al.*, 2003; Gallart and Llorens, 2004; López-Moreno *et al.*, 2006).

However, due to the limited number of hydrological studies in Mediterranean environments, hydrological processes have often been extrapolated from more humid climatic regions without a proper verification of the results (Latron *et al.*, 2009). In the current context of increasing water demand, rapid changes in land uses and uncertainties in climate change projections, a deeper knowledge of the hydrological functioning of these areas is needed to anticipate the hydrological consequences of both climate and land cover change, as well as to design land-use strategies that might counteract these changes (Cudennec *et al.*, 2007; Latron *et al.*, 2009). In addition, as pointed out by recent reports (Burt and McDonnell, 2015; Beven, 2016; Tetzlaff *et al.*, 2017; Latron and Lana-Renault, 2018) field studies in experimental catchments have an invaluable role as a tool to produce long-term quality data needed for understanding the complexities of hydrological processes.

## 1.2. THE SMALL CATCHMENT APPROACH

Hydrological processes can be analysed from multiple spatial and temporal scales. The small catchment approach uses experimental catchments as instruments to understand hydrological processes through planned experiments. The results are analysed from continuous observations of streamflow, precipitation and other variables (Hewlett *et al.*, 1969). The advantage of using small catchments is that they are hydrologic systems where inputs and outputs of water are cycled within topographically restricted landscape units (McGuire and McDonnell, 2007). In addition, when long data sets have been collected in these catchments it is possible to quantify processes, observe trend changes after landscape manipulation or calibrate and validate hydrological models. However, these small scale studies have been sometimes involved in criticism due to their lack of representativeness, expense, and difficulty in interpreting results (McGuire and Likens, 2011). In addition, as computing power becomes cheaper and field work more expensive, there is a trend away from field work and towards more complete dependence on simulation. As a consequence, field studies are in decline, and complex questions in hydrology are being tackled by models despite that their predictions are extending beyond the fundamental understanding of hydrological processes (Burt and McDonnell, 2015). The need for new field-derived insight into the pathways of water in the headwaters, where most runoff is generated, is more needed than ever (Tetzlaff *et al.*, 2017).

### 1.2.1. Canopy-interception studies

The concern in understanding plant interactions with the environment lead to the firsts attempts of measuring how incident rainfall was intercepted and routed to the sub-canopy by throughfall and stemflow. Throughfall is defined as the precipitation that passes directly through a canopy or is initially intercepted by aboveground vegetative surfaces and subsequently drips from the canopy, whereas stemflow is the precipitation that drains from outlying leaves and branches and is channelled to the stem of plants. Those water fluxes usually represent between 70 or 90% of the incoming precipitation (Levia *et al.*, 2011) and they greatly influence the water yield and the biogeochemistry in forested areas (Herwitz, 1986). The remainder is lost by evaporation during and after a precipitation event from the water stored in the canopy. In most cases, this knowledge was used to evaluate the effects of forest management practices on the timing and magnitude of streamflow and sediment load; many of these studies were used to develop best management practices that are still in use today (McGuire and Likens, 2011). At present, although these fluxes are difficult to measure and estimate due to their high variability among climates and tree species (Levia and Frost, 2003; Llorens and Domingo, 2007), the influence of throughfall has been broadly studied across the globe. On the contrary, stemflow is still underrepresented in the literature despite its recognized hydro-ecological and biogeochemical importance in forested and agricultural ecosystems as a direct input of water and nutrients at the plant stem (Carlyle-Moses *et al.*, 2018).

### 1.2.2. Water tracer studies

With the progress of knowledge, scientists realized that physical and hydrometric data alone were not enough to discern among hydrological processes, either to explain the movement of water through a catchment or even to understand canopy interception processes. Then, the application of stable isotopes of water (Hydrogen ($^{2}H$ or D for Deuterium) and Oxygen ($^{18}O$)) in hydrology opened a myriad of new possibilities (Craig, 1961). These environmental tracers are added naturally at the watershed scale by precipitation, further, the isotopic composition of water only changes through mixing of waters and fractionation processes during water phase changes (evaporation and condensation). The stable isotopes of water are conservative in their mixing relationships, thus, the isotopic composition of a mixture of waters will depend only on the proportions of the water sources. This conservative character has been used to identify the origin and movement of water in different water reservoirs within a catchment (McGuire and McDonnell, 2007; Klaus and McDonnell, 2013).

## 1.3. OBJECTIVES AND STRUCTURE OF THE THESIS

This thesis aims to further improve the knowledge on the hydrological functioning of Mediterranean mountain environments focussing on the role of forested areas. The general research questions of the thesis are the following:

a) Which factors determine the contribution of stemflow under forest canopies?
b) How different canopies influence the content of particulate matter that reaches the forest soil?
c) How tree canopies modify the isotopic composition of rainfall?
d) How important is the observed spatio-temporal isotopic variability of the input water at the small-catchment scale for our understanding of hydrological processes?

The thesis consists of eight chapters, including the General introduction and Objectives (Chapter 1), Study area and Field design (Chapter 2), General discussion (Chapter 7) and Conclusions (Chapter 8). Each of chapters 3 to 6 addresses one of the general research questions of the thesis.

Chapter 3. This chapter analyses the effect of the interaction between biotic and abiotic factors on stemflow production. The study uses stemflow data collected at high temporal resolution (5-min steps) for Scots pine and downy oak with the aim (a) to examine stemflow responses and funneling capabilities for Scots pine and downy oak, both within events and between events; (b) to analyse the effect of abiotic factors on stemflow for Scots pine and downy oak; (c) to evaluate which biotic characteristics enhance stemflow during events and among events; and (d) to investigate how does the interaction of biotic and abiotic factors affect stemflow dynamics.

Chapter 4. Rainfall partitioning imply not only a redistribution of water below the canopy but also a redistribution of particulate matter suspended in the atmosphere that is caught by trees. In this chapter, annual fluxes of particulate matter in throughfall and stemflow are examined with the aim (a) to analyse how Scots pine and downy oak influence the content of particulate matter reaching the forest soil and (b) to evaluate the differences in the particulate matter content and size distribution between throughfall and stemflow.

Chapter 5. This chapter focuses on the isotopic shift produced in the stable isotopes of water (in precipitation) during rainfall partitioning processes. Up to date, only few studies have worked with the isotopic composition of throughfall and stemflow, with no concluding remarks. Here, an experiment at the plot scale was designed (a) to examine the spatio-temporal differences between the isotopic composition of rainfall, throughfall, and stemflow for pines and oaks, and (b) to relate these differences to different meteorological conditions and structural forest characteristics, to gain some knowledge on the fractionation factors that occur in the canopy.

Chapter 6. This chapter analyses the implication of the spatio-temporal variability of the isotopic input signal observed in the partly forested Can Vila catchment for hydrograph separation in order to improve our understanding of dominant hydrological processes. Here, several isotopic signals measured within the catchment at different spatial and temporal resolutions were used (a) to analyse the spatio-temporal variability in the isotopic composition of rainfall and its relation to elevation and forest cover, (b) to determine the uncertainty associated with isotope-based hydrograph separation due to the spatio-temporal variability of rainfall and (c) to identify the best sampling strategy to obtain a representative input signal for the entire catchment.

# CHAPTER 2

## Study site and Field design

The field experiments included in this dissertation were carried out between May 2015 and May 2016 in the Vallcebre research catchments. This research area is representative of Mediterranean mountain environments, with a marked inter- and intra- annual precipitation variability and a mixed landscape of forests and cultivated areas resulting from years of resources exploitation.

In this chapter, the study area and the design of the experimental forest plots that have been used to accomplish the aims of the dissertation are described.

## 2.1. STUDY AREA

The study area of this thesis is the Vallcebre research catchments. They are located in North Eastern Spain, at the South-eastern part of the Pyrenees (42º12'N and 1º49'E). The climate is sub-Mediterranean, with a mean annual temperature of 9.1 ºC, a mean evapotranspiration of 823 ± 26 mm, and a mean annual precipitation of 880 ± 200 mm (1989-2013). The research area consists of two clusters of catchments that have been monitored since 1988 by the Surface Hydrology and Erosion group of the Institute of Environmental Assessment and Water Research (IDAEA-CSIC). The main cluster, the Cal Rodó catchment (4.17 $km^2$), has two sub-catchments: Can Vila (0.56 $km^2$) and Ca l'Isard (1.32 $km^2$). The second cluster is formed by the Cal Parisa sub-catchments (0.13 and 0.17 $km^2$). Research for this dissertation has been carried out in the Can Vila catchment and in two experimental forest plots, one within the catchment, and the other in a nearby area (Figure 2.1).

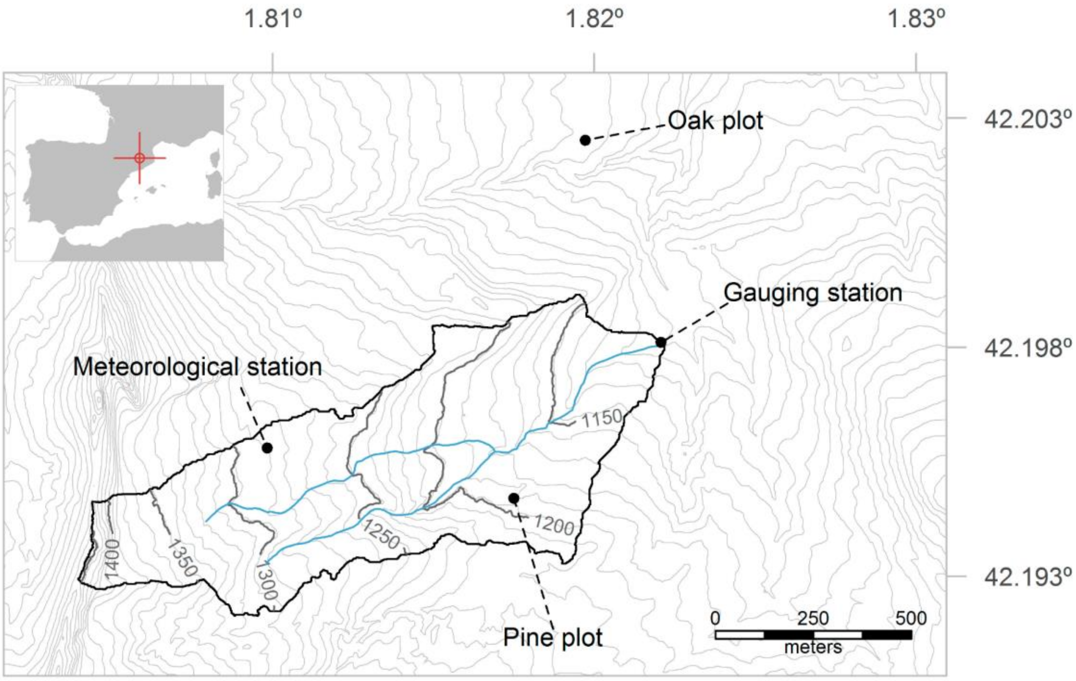


**Figure 2.1.** Location map of the Can Vila catchment, showing the location of the monitored forest plots and of the meteorological and gauging stations.

Research in this area started 30 years ago with the aim to analyse the hydrological consequences of land abandonment, as well as the hydrological and sediment yield behaviour of badland areas. Nowadays, research is focused to improve the understanding of hydrological processes that control the seasonality of the response in Mediterranean catchments and provide new insights into the effects of global change on water resources. With this aim, the Vallcebre research catchments have served as a framework for many studies related to the spatio-temporal dynamics of precipitation, rainfall partitioning, forest transpiration, soil water and groundwater dynamics, hydrological response, runoff generation processes, erosion and sediment transport and modelling at several spatial and temporal scales (Llorens *et al.*, 2018). More than three decades of study and monitoring of the area have provided a large dataset of numerous variables (e.g. precipitation, transpiration, rainfall interception, runoff, piezometric levels, etc.) and a good understanding of hydrological processes. However, many questions still remain unsolved and new others rose from the acquired knowledge.

## 2.2. THE CAN VILA CATCHMENT

The Can Vila catchment is a relatively small mountain catchment (0.56 km$^2$) located within the Vallcebre research area at an altitude that ranges between 1,108 and 1,462 m a.s.l. (Figure 2.2a).

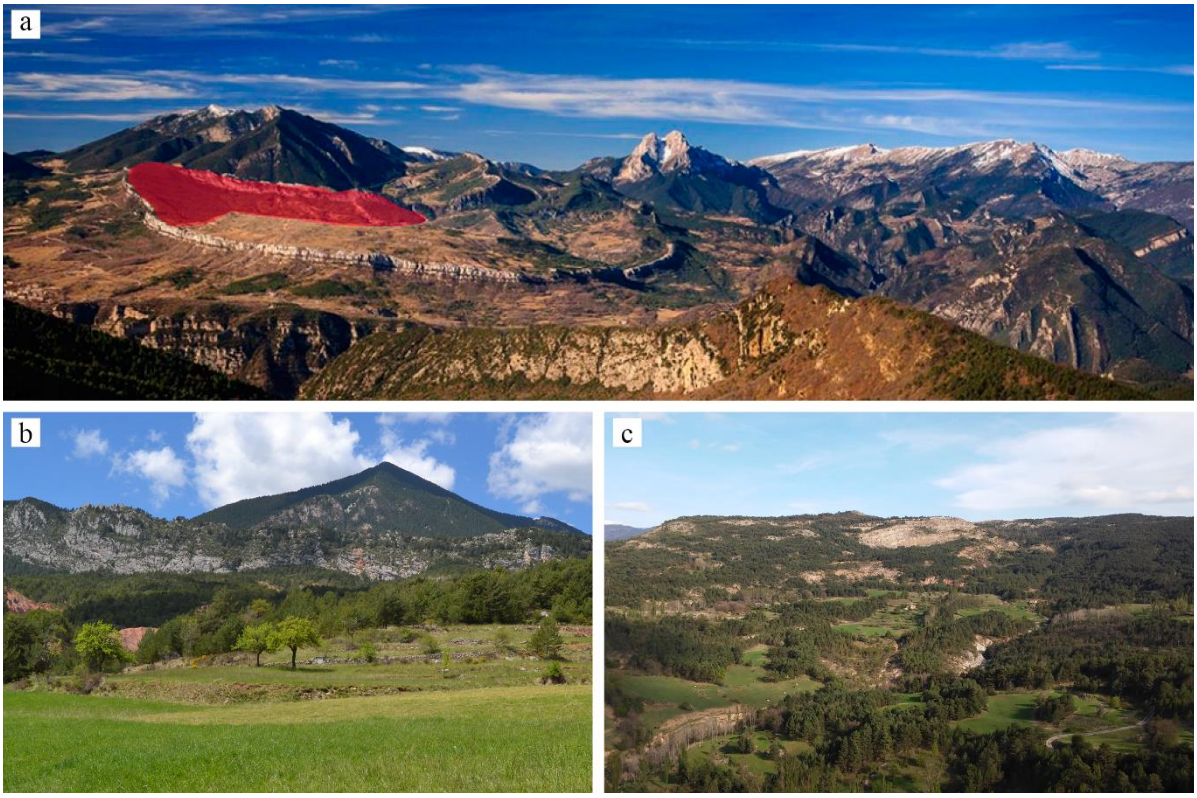


**Figure 2.2.** (a) General view of the study area, the Can Vila catchment is highlighted in red; (b) Terraced areas within the catchment; (c) Forest and agricultural mixed landscape in the catchment.

The catchment drains into the River Llobregat, which supplies most of the surface water for the city of Barcelona. As many other Mediterranean mountain areas, the catchment was deforested and terraced for agricultural purposes in the past (Poyatos *et al.*, 2003) (Figure 2.2b). At present, the landscape of the catchment is a mixed mosaic mostly covered by Scots Pine forests *(Pinus sylvestris* L.*)* (58.3%), grasslands (31.9%) and shrubs (4.1%) (Figure 2.2c). Despite the human impact on the landscape, the primary stream network in the catchment is mostly natural with stream runoff responses that have a clear seasonal pattern, with an alternation between wet periods, when the catchment is hydrologically responsive and dry periods, when the catchment is much less reactive to precipitation (Latron *et al.*, 2008).

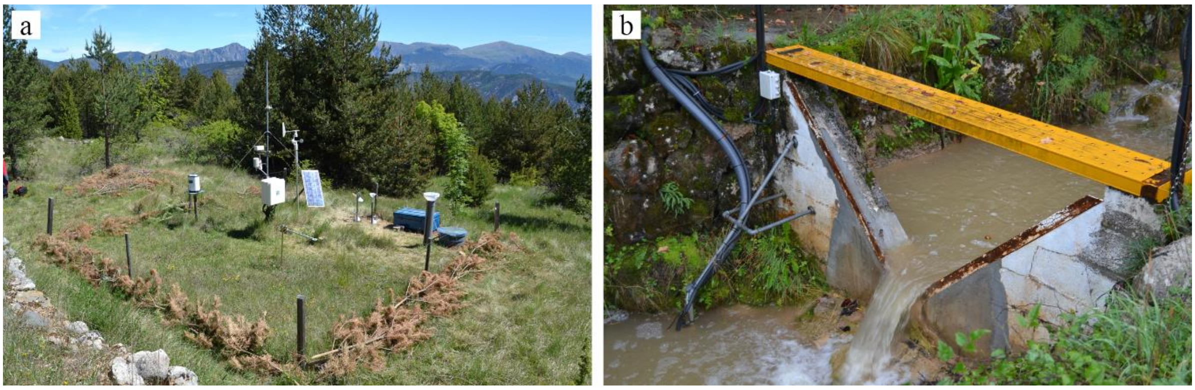


**Figure 2.3.** (a) Meteorological station in the Can Vila catchment; (b) Gauging station in the Can Vila catchment.

The catchment is equipped with a standard meteorological station (Figure 2.3a) located in the upper part (1,287 m a.s.l) and a gauging station (Figure 2.3b) equipped with a 90º V-notch weir and a water pressure sensor that measures the outflow of the catchment (1,114 m a.s.l). All hydrometric data measured in the catchment are stored every 5 minutes by dataloggers (DT 50/80 Datataker, Datataker Inc., USA) (Table 2.1). In this dissertation, the catchment scale approach has been used to analyse the propagation effect of the ecohydrological processes studied at the plot scale.

## 2.3. THE FOREST PLOTS

Canopy interception processes have been studied at the plot scale, comparing two different forests with different canopy covers, a *Pinus sylvestris* L. (Scots pine) plot and a *Quercus pubescens* Willd. (downy oak) plot. The plots are located within 1 km from each other, and have been used to monitor stemflow, throughfall and the particulate matter fluxes. The oak plot (Figure 2.4a) was selected to be representative of the original vegetation in the area, it has an area of 2,200 $m^2$, a tree density of 518 trees $ha^{-1}$, a basal area of 20.1 $m^2$ $ha^{-1}$ and is located at an elevation of 1,100 m. The pine plot (Figure 2.4b) is representative of the vegetation overgrown in terraced areas after the abandonment of the agricultural activities during the second half of the 20th century, it has an area of 900 $m^2$, a tree density of 1,189 trees $ha^{-1}$, a basal area of 45.1 $m^2$ $ha^{-1}$ and is located at an elevation of 1,200 m.

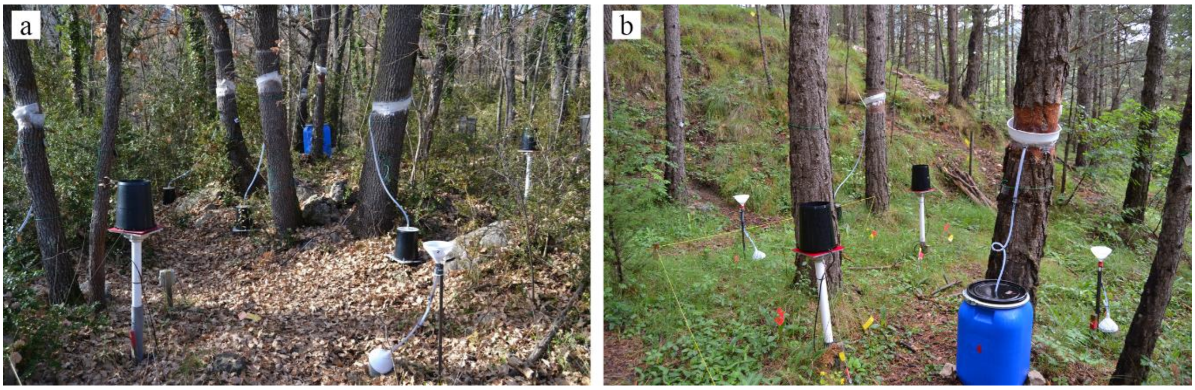


**Figure 2.4.** (a) Downy oak plot; (b) Scots pine plot.

The field design was the same for each plot and consisted of two networks (Table 2.1), one to measure hydrometric data and the other to collect water samples. Meteorological data were obtained from meteorological towers. Each tower monitored air temperature, relative humidity, net radiation, wind speed, and wind direction 1 m above the canopy. In each plot, gross rainfall was measured with a tipping bucket rain gauge (Davis Rain Collector II) located in a clearing less than 100 m from each stand. Throughfall was measured with 20 tipping bucket rain gauges spatially distributed according to canopy cover distribution, which was determined from hemispherical photographs (Llorens and Gallart, 2000). On the other hand, stemflow was measured in seven trees, representing the range of diameter at breast high (DBH) distributions, with stemflow rings, constructed from a longitudinally cut funnel sealed to the trees with silicone, connected to tipping bucket rain gauges (Figure

2.5a). All data were recorded at 5-min intervals by a datalogger (DT80 Datataker, Datataker Inc, OH, USA).

In the study plots, throughfall was sampled with 10 collectors consisting of plastic funnels positioned 50 cm above ground and connected to a 1-L plastic bin (Figure 2.5b). In addition, throughfall was sampled automatically, at 5 mm rainfall intervals, using a plastic funnel connected to an automatic water sampler (ISCO 3700C) (Figure 2.5c). The location of the collectors was chosen to represent all ranges of canopy cover. Stemflow was sampled on four trees representative of the DBH distribution in each stand, using a stemflow ring connected to a 60-L polyethylene bin (Figure 2.5d). The same collectors were used to sample particulate matter contained in each water flux. Finally, rainfall was sampled in a clearing near each stand by means of a bulk collector and an automatic sampler in the same way as for throughfall.


**Figure 2.5.** (a) Stemflow ring; (b) Throughfall collector; (c) Automatic water sampler; (d) Stemflow collector.

**Table 2.1.** Relation of measurement and collection instruments at Can Vila, the location and sampling temporal resolution. Location names refer to the names in Figure 2.1.

| Variables and fluxes | Temporal resolution | Instruments | Number of instruments | Location |
|---|---|---|---|---|
| Rainfall | 5 min | Tipping bucket rain gauge | 1 | Pine plot |
| | 5 min | Tipping bucket rain gauge | 1 | Oak plot |
| | 5 min | Tipping bucket rain gauge | 1 | Meteorological station |
| | 5 min | Tipping bucket rain gauge | 1 | Gauging station |
| Throughfall | 5 min | Tipping bucket rain gauge | 20 | Pine plot |
| | 5 min | Tipping bucket rain gauge | 20 | Oak plot |
| Stemflow | 5 min | Tipping bucket rain gauge | 7 | Pine plot |
| | 5 min | Tipping bucket rain gauge | 7 | Oak plot |
| Meteorological data | 5 min | Meteorological tower | 1 | Meteorological station |
| | 5 min | Meteorological tower | 1 | Oak plot |
| | 5 min | Meteorological tower | 1 | Pine plot |
| Streamflow | 5 min | Water pressure sensor | 1 | Gauging station |
| Rainfall water/PM samples | Event | Bulk collector | 1 | Meteorological station |
| | Event | Sequential collector | 1 | Meteorological station |
| | Event | Bulk collector | 1 | Gauging station |
| | Event | Sequential collector | 1 | Gauging station |
| Throughfall water/PM samples | Event | Bulk collector | 10 | Pine plot |
| | Event | Sequential collector | 1 | Pine plot |
| | Event | Bulk collector | 10 | Oak plot |
| | Event | Sequential collector | 1 | Oak plot |
| Stemflow water/PM samples | Event | Bulk collectors | 4 | Pine plot |
| | Event | Bulk collectors | 4 | Oak plot |
| Streamflow samples | Weekly | Bulk collectors | 1 | Gauging station |
| | Event | Sequential collector | 1 | Gauging station |

# CHAPTER 3

## Effect of biotic and abiotic factors on inter- and intra-event variability in stemflow rates in oak and pine stands in a Mediterranean mountain area

Stemflow, despite being a small proportion of gross rainfall, is an important and understudied flux of water in forested areas. Recent studies have highlighted its complexity and relative importance for understanding soil and groundwater recharge. Stemflow dynamics offer an insight into how rain water is stored and released from the stems of trees to the soil. Past attempts have been made to understand the variability of stemflow under different types of vegetation, but rather few studies have focused on the combined influence of biotic and abiotic factors on inter- and intra-storm stemflow variability, and none in Mediterranean climates. This study presents stemflow data collected at high temporal resolution for two species with contrasting canopies and bark characteristics: *Quercus pubescens* Willd. (downy oak) and *Pinus sylvestris* L. (Scots pine) in the Vallcebre research catchments (NE of Spain, 42º 12'N, 1º 49'E). The main objective was to understand how the interaction of biotic and abiotic factors affected stemflow dynamics. Mean stemflow production was low for both species (~1% of incident rainfall) and increased with rainfall amount. However, the magnitude of the response depended on the combination of multiple biotic and abiotic factors. Both species produced similar stemflow volumes and the largest differences were found among trees of the same species. The combined analysis of biotic and abiotic factors showed that funneling ratios and stemflow dynamics were highly influenced by the interaction of rainfall intensity and tree size.

**Original work:** Cayuela, C., Llorens, P., Sánchez-Costa, E., Levia, D.F., Latron, J. 2018. Effect of biotic and abiotic factors on inter- and intra-event variability in stemflow rates in oak and pine stands in a Mediterranean mountain area. *Journal of Hydrology*. 560, 396–406. doi:10.1016/j.jhydrol.2018.03.050

## 3.1. INTRODUCTION

Stemflow, expressed as volume of water per unit area, usually represents a small proportion of gross incident precipitation and has often been neglected in hydrological studies. Nonetheless, stemflow is a concentrated point source of water that reaches the base of trees, and can affect the spatial variability in soil moisture and groundwater recharge (e.g. Durocher, 1990; Liang *et al.*, 2007; Klos *et al.*, 2014; Spencer and van Meerveld, 2016). Moreover, stemflow fluxes, due to their ability to transport nutrients, may enhance soil biogeochemical “hot spots” and “hot moments” (McClain *et al.*, 2003; Levia *et al.*, 2012; Michalzik *et al.*, 2016). Stemflow is highly variable across climate regions; its variability is partly attributed to the different climatic conditions and species composition, thereby making the prediction of stemflow volumes difficult (Levia and Germer, 2015). Stemflow can vary between less than 0.5 up to 20% of gross precipitation (Levia and Frost, 2003; Johnson and Lehmann, 2006); in the Mediterranean climate, stemflow represents 3.2 ±0.7% for trees and 19.2 ±5.4% for shrubs (Llorens and Domingo, 2007).

Stemflow is the result of a complex and dynamic interaction of biotic and abiotic factors. The main biotic factors affecting stemflow production are tree structure and morphology (including tree size, branch structure, branch angle, leaf shape, and bark texture) and tree water holding capacity (including canopy and stem storage capacity or epiphyte cover) (Levia and Frost, 2003). Large projected canopy areas and bigger exposed canopies with upwardly inclined branches promote stemflow (Herwitz, 1986; Aboal *et al.*, 1999; McKee and Carlyle-Moses, 2017); likewise, species with smooth bark tend to hold less water and enhance stemflow (Kuraji *et al.*, 2001; Carlyle-Moses and Price, 2006; Reid and Lewis, 2009). Recently, it has been found that smaller trees would have relatively higher funneling ratios (Germer *et al.*, 2010; Levia *et al.*, 2010; Spencer and van Meerveld, 2016) and may contribute more to overall stand total stemflow, but this relationship seems to be species-specific (Carlyle-Moses and Price, 2006).

The main abiotic factors are rainfall (amount, intensity, duration) and wind (speed and duration) characteristics (Levia and Germer, 2015). Research showed that stemflow increases with rainfall amount, in addition, higher rainfall intensities can result in larger quantities of stemflow (e.g. Aboal et al., 1999; Spencer and van Meerveld, 2016). At the event scale, rainfall rates also affect stemflow dynamics; for example, laboratory experiments by Dunkerley (2014) showed that intense rainfall could saturate the canopy and the stem storage capacity resulting in earlier stemflow. In addition, rainfall with multiple high intensity peaks produced more stemflow than rainfall events of uniform intensity (Dunkerley, 2014). Carlyle-Moses and Price (2006) and Staelens *et al.* (2008) found that high intensity rainfall tended to reduce stemflow rates in favour of throughfall; the same effect was suggested by Levia *et al.* (2010) who found that funneling ratios decreased as the 5-min precipitation intensity increased as a consequence of the stemflow dripping from the branches, when the maximum transport capacity of stemflow was exceeded. Some authors (Neal *et al.*, 1993; Llorens *et al.*, 1997; Staelens *et al.*, 2008; Van Stan *et al.*, 2014) also suggested that high vapour pressure deficits enhance evaporation and diminish the water contributing to stemflow, therefore, decreasing stemflow rates. On the other hand, precipitation events with high wind velocities or a major prevailing wind direction would promote the wetting of the tree crown, thereby generating preferential stemflow paths and inducing enhanced stemflow production even before reaching the interception storage capacity (Xiao *et al.*, 2000; Kuraji *et al.*, 2001; Van Stan *et al.*, 2011).

The importance of stemflow is not only related to the mean volumes produced in a specific space or time, but also related to the stemflow rates at the intra-storm time scale; different stemflow intensities can produce different infiltration rates into the soil (e.g. Germer, 2013; Liang *et al.*, 2007, 2011; Spencer and van Meerveld, 2016). As pointed out by Levia and Germer (2015), until now there are only a few studies that have measured intra-storm stemflow production. For instance, Reid and Lewis (2009) observed a positive correlation between rainfall intensity and water stored in the bark. Germer *et al.* (2010) showed the relevance of small trees and palms, as their maximum 5-min stemflow intensities were 15 times greater than rainfall. Levia *et al.* (2010) showed the synchronicity between rainfall and stemflow once the bark storage capacity was filled. And recently, Spencer and van Meerveld (2016), confirmed that stemflow intensity was highest when high-rainfall intensity occurred later in the event.

In this study we use 5-min data to examine stemflow dynamics of two species with a different architecture that are common in Mediterranean mountain areas (Roskov Y. et al, 2017): downy oak (*Quercus pubescens* Willd.) and Scots pine (*Pinus sylvestris* L.). Even though there are studies that focused on stemflow produced by pines or oaks, a comparison of stemflow dynamics between both species, in the same climatic conditions, has to our knowledge never been done. The understanding of their stemflow dynamics will shed light on the hydrological processes that take place under both canopies and could help to improve ecohydrological models. Accordingly, the novelty and main objective of this study is to quantify and analyse the inter- and intra-storm stemflow dynamics of these two species taking into account the interaction between biotic and abiotic factors. We specifically aim to answer the following questions: (i) are stemflow responses and funneling capabilities for Scots pine and downy oak different, both within events and between events?; (ii) how is stemflow from Scots pine and downy oak affected by different abiotic factors?; (iii) what biotic characteristics enhance stemflow during events and among events?; and (iv) how does the interaction of biotic and abiotic factors affect stemflow dynamics? Answers to these questions are necessary to better understand the cycling of water within the canopy during storm events, especially in Mediterranean areas due to their strong inter- and intra-event variability in precipitation.

## 3.2. STUDY AREA

### 3.2.1. The Vallcebre research catchments

The study area is located in the Vallcebre research catchments (NE Spain, 42º 12'N, 1º 49'E) in the eastern Pyrenees at 1100 m asl (meters above sea level). The research catchment has been monitored for different hydrologic purposes since 1988 (Llorens *et al.*, 2018). Today, the study area consists of a cluster of nested catchments: Cal Rodó (4.17 $km^2$), Ca l'Isard (1.32 $km^2$) and Can Vila (0.56 $km^2$). There are two long-term monitored forest plots in the catchments: one covered by Scots pine and the other by downy oaks. The climate is Sub-Mediterranean, with a mean annual temperature of 9.1 ±0.67 ºC, a mean annual reference evapotranspiration of 823 ±26 mm, as calculated by the Hargreaves-Samani (1982) method, and a mean annual precipitation of 880 ±200 mm (1989-2013). Precipitation is seasonal, with autumn and spring usually being the wetter seasons, while summer and winter are often drier. Summer rainfall is characterized by intense convective events, while winter precipitation is caused by frontal systems, with snowfall accounting for less than 5% of the precipitation (Latron *et al.*, 2010b, 2010a; Llorens *et al.*, 2018).

Slopes of the study area were originally vegetated by downy oaks; however, the site was deforested and terraced in the past for agricultural production. At present, the abandonment of agricultural activities has led to a spontaneous afforestation by pine (Poyatos *et al.*, 2003). As a result, the forest is predominantly Scots pine, although isolated populations of the original deciduous downy oak forests remain.

### 3.2.2. The forest plots

Our study used the long-term monitored stands of downy oak and the Scots pine, located within 1 km from each other, to monitor stemflow. The Scots pine stand has an area of 900 $m^2$, a tree density of 1189 trees $ha^{-1}$, a basal area of 45.1 $m^2$ $ha^{-1}$, and is oriented towards the northeast at an elevation of 1200 m. The downy oak stand has an area of 2200 $m^2$, a tree density of 518 trees $ha^{-1}$, a basal area of 20.1 $m^2$ $ha^{-1}$, and is oriented towards the southeast, at an elevation of 1100 m. Both species have different biometric characteristics. Scots pine develops a long and straight trunk with a thick bark topped with a roughly rounded crown and downy oak is a rough-barked deciduous tree that usually develops several trunks and a broad and irregular crown. Generally speaking, pine trees usually have a more regular tree architecture, whereas oak trees are more irregular.

## 3.3. DATA AND METHODS

### 3.3.1. Rainfall and meteorological data

Meteorological data were obtained from 15 and 18 m towers at the oak and pine stands, respectively. Each station monitored air temperature, relative humidity, net radiation, wind speed, and wind direction 1 m above the canopy. Temperature and relative humidity were used to calculate the vapour pressure deficit (VPD). Gross rainfall was measured for both stands in a nearby clearing (located less than 100 m from each stand) by a tipping-bucket rain gauge (Davis Rain Collector II). All data were measured every 30-seconds and recorded at 5-min intervals by a datalogger (DT80 Datataker, Datataker Inc, OH, USA).

### 3.3.2. Monitored trees

In each monitored stand, seven trees were selected to measure stemflow, representing the range of diameter at breast height (DBH) distributions. For each tree, the following parameters were measured: DBH, basal area, height, crown area, crown volume, branch angle, branch diameter, bark depth and trunk lean (Table 3.1). Moreover, stem bark surface and bark specific storage capacity were estimated. Stem bark surface was calculated using a logarithmic regression of surface area from DBH (Whittaker and Woodwell, 1967), and bark specific storage capacity was estimated from wetting and drying curves obtained by soaking different-sized branches, following Llorens and Gallart (2000).

**Table 3.1.** Biometric characteristics of the monitored trees.

| Species | Tree number | DBH (cm) | Basal area (cm²) | Height (m) | Crown area (m²) | Crown volume (m³) | Mean branch angle (°) | Mean branch diameter (cm) | Bark depth (cm) | Stem bark surface (m²) | Bark storage capacity (mm) | Tree lean (°) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Scots pine | P1 | 18.0 | 254.5 | 17.5 | 7.5 | 59.7 | 29.5 | 3.1 | 1.5 | 6.3 | 0.40 | 4.6 |
| | P2 | 14.8 | 172.0 | 16.9 | 10.8 | 98.4 | 38.3 | 3.3 | 1.5 | 4.9 | 0.41 | 2.9 |
| | P3 | 20.2 | 320.5 | 21.2 | 11.9 | 118.9 | 29.3 | 2.8 | 2.1 | 7.3 | 0.37 | 0.0 |
| | P4 | 35.2 | 973.1 | 22.3 | 17.3 | 228.0 | 19.2 | 4.4 | 3.3 | 15.0 | 0.50 | 7.9 |
| | P5 | 27.7 | 602.6 | 18.3 | 23.8 | 289.1 | 17.7 | 5.6 | 2.9 | 11.0 | 0.58 | 5.7 |
| | P6 | 14.2 | 158.4 | 15.5 | 4.7 | 28.1 | 7.6 | 2.1 | 1.0 | 4.7 | 0.32 | 4.0 |
| | P7 | 25.2 | 498.8 | 18.1 | 20.1 | 195.2 | -7.0 | 4.3 | 2.6 | 9.8 | 0.49 | 0.0 |
| **Mean (+/-1 SD)** | | **22.2 +/-8** | **425.7 +/-292** | **18.5 +/-2** | **13.7 +/-7** | **145.3 +/-95** | **19.2 +/-15** | **3.7 +/-1** | **2.1 +/-1** | **8.4 +/-4** | **0.44 +/-0.1** | **3.6 +/-3** |
| Downy oak | Q1 | 28.9 | 656.0 | 11.7 | 28.0 | 325.0 | 56.4 | 6.2 | 1.8 | 11.6 | 0.67 | 4.0 |
| | Q2 | 32.6 | 834.7 | 13.2 | 39.9 | 398.5 | 63.8 | 4.4 | 1.0 | 13.6 | 0.51 | 7.7 |
| | Q3 | 24.8 | 483.1 | 15.6 | 13.1 | 176.2 | 59.1 | 5.2 | 0.9 | 9.6 | 0.58 | 0.0 |
| | Q4 | 20.5 | 330.1 | 10.6 | 7.5 | 77.6 | 18.5 | 3.3 | 1.0 | 7.5 | 0.41 | 7.4 |
| | Q5 | 23.4 | 430.1 | 11.2 | 9.1 | 47.5 | 20.2 | 5.1 | 1.1 | 8.9 | 0.57 | 7.9 |
| | Q6 | 19.3 | 292.6 | 13.3 | 22.3 | 294.0 | 18.6 | 4.1 | 1.1 | 6.9 | 0.48 | 2.8 |
| | Q7 | 15.7 | 193.6 | 10.8 | 13.5 | 140.5 | 24.1 | 3.1 | 0.8 | 5.3 | 0.39 | 8.2 |
| **Mean (+/-1 SD)** | | **23.6 +/-6** | **460.0 +/-222** | **12.3 +/-2** | **19.0 +/-12** | **208.5 +/-133** | **37.2 +/-21** | **4.5 +/-1** | **1.1 +/-0.3** | **9.1 +/-3** | **0.52 +/-0.1** | **5.5 +/-3** |

### 3.3.3. Stemflow monitoring

A stemflow collector ring constructed from a longitudinally cut funnel was placed around the trunk at breast height of each selected tree and gaps were sealed with silicone. Each stemflow ring drained to a tipping-bucket rain gauge (Davis Rain Collector II). Data were collected at 5-min intervals by a datalogger (DT80 Datataker). Recorded data were downloaded and the stemflow rings were cleaned and checked for leakage weekly. Data were evaluated for potential errors and converted to stemflow volume through a dynamic calibration of the tipping-buckets (Calder and Kidd, 1978; Iida *et al.*, 2012). The dynamic calibration was crucial due to the high frequency of the tips. For stemflow intensities that exceeded 50 tips in 5 minutes, the capacity of the tipping-bucket mechanism was overwhelmed, resulting in an underestimation of the stemflow amount if using the regular calibration. In addition, we compared the volumes obtained with the tipping-buckets with the volumes of 8 additional trees equipped with stemflow rings and collection bins (60 litres); the regression analysis showed a good correlation between mean volumes (slope 1.1, intercept 0.1 and $r^2 = 0.84$).

### 3.3.4. Stemflow and funneling ratios calculation

Stemflow data for this study was collected from May to October 2015. To reduce differences between stands due to significant phenological changes in the oak canopy over the year, as well as different rainfall patterns in the leafed and leafless periods (Muzylo *et al.*, 2012a), only the leafed period was considered. Individual rainfall events were defined according to the time without rainfall between two successive events with at least 1 mm of rainfall. To ensure that the canopy was dry at the beginning of each rainfall event, an interval of six hours was considered for events occurring during the day and an interval of twelve hours for night events (Llorens *et al.*, 2014). The end of the event was established when stemflow finished.

Stemflow depth (mm) was calculated by dividing the measured stemflow volume (litres) by tree basal area ($m^2$). Following Levia and Germer (2015), relative stemflow ($S_{(\%R)}$) was calculated as the stemflow percentage of gross rainfall weighted by the number of trees per group of DBH in each stand.

$$S_{(\%R)} = \frac{\left(\frac{\sum_{i=1}^{k}(S_{y,i} \cdot N_{Trees,i})}{A}\right) \cdot 100}{P} \tag{3.1}$$

Where $S_y$ is mean stemflow of all sampled trees (litres), $N_{Trees}$ is the number of trees per area, A is the area ($m^2$), P is incident rainfall (mm) and k is the number of groups of trunk diameter ranges. In each stand, five groups of DBH were selected: <15cm, 15-20 cm, 20-25 cm, 25-30 cm and >30 cm. Finally, funneling ratios were calculated following Herwitz (1986).

$$FR = \frac{V}{B \cdot P} \tag{3.2}$$

Where V is the volume of stemflow (litres), B is the trunk basal area ($m^2$), P is incident rainfall (mm), and FR is the funneling ratio. Funneling ratios above 1 indicate that trees start to concentrate rainfall as stemflow.

### 3.3.5. Data analysis

A linear mixed model (LMM) with repeated measurements structure was performed to check possible differences between stemflow and funneling ratios between stands. Biotic and abiotic factors were included into the model as covariate fixed effects, and the factors “tree” and “event” were used as random effects. A *p*-value $\leq 0.05$ was used as a threshold for statistical significance. To ensure data symmetry, only rainfall events which produced stemflow were used and all stemflow values were log-transformed to guarantee normality of the error distribution and homoscedasticity of the errors. In addition, two unrotated principal component analyses (PCA) with normalized data were performed to analyse the differential effects of biotic and abiotic factors; a *k*-means clustering analysis was performed to classify events with similar characteristics.

To analyse the combined effect of biotic and abiotic factors on the stemflow dynamics, 12 events with similar magnitudes but with marked differences in their maximum 30-minute rainfall intensity and duration were selected. Among the biotic variables measured, DBH was selected to represent the biotic factors, because it was found to be correlated with most of the other measured biotic factors, although this correlation was stronger in pines. Therefore, in order to generalise and compare results, and keeping in mind the complexity of oak morphology compared with pines', trees were separated in two DBH classes (<25cm and >25cm).

## 3.4. RESULTS

### 3.4.1. Gross rainfall

Total rainfall measured during the study period was 519 mm and 528 mm in the pine and oak stands, respectively. The study period was the second rainiest year over the last 20 years in the study area. From the 33 rainfall events measured, 66% were smaller than 15 mm, 28% between 15 and 40 mm, and 6% were larger than 40 mm. These percentages matched the distribution of rainfall events measured in the 1989-2010 period at the study site (Latron *et al.*, 2010b). At the event scale, differences in gross rainfall between the two forested stands were in general less than 1 mm and differences in maximum intensity were less than 0.5 mm $h^{-1}$, but differences tended to be larger for rainfall events with a higher intensity. This was the case of the July 23rd thunderstorm, for which rainfall differed by 14 mm between the two stands. This was a short duration event (less than 2 hours) with a maximum intensity of 41 mm in 30 minutes at the pine stand, and 29 mm in 30 minutes at the oak stand; and rainfall amounts of 72 mm and 58 mm for the pine and oak stands, respectively.

### 3.4.2. Stemflow and funneling ratios

Relative stemflow ($S_{(\%R)}$) was low in both stands, with mean $S_{(\%R)}$ values of 1.2 ±1.4% for pine and 1.1 ±1.4% for oak. Nonetheless, it was highly variable among events, for example, in some events $S_{(\%R)}$ reached up to 6% of the gross rainfall (Figure 3.1a).

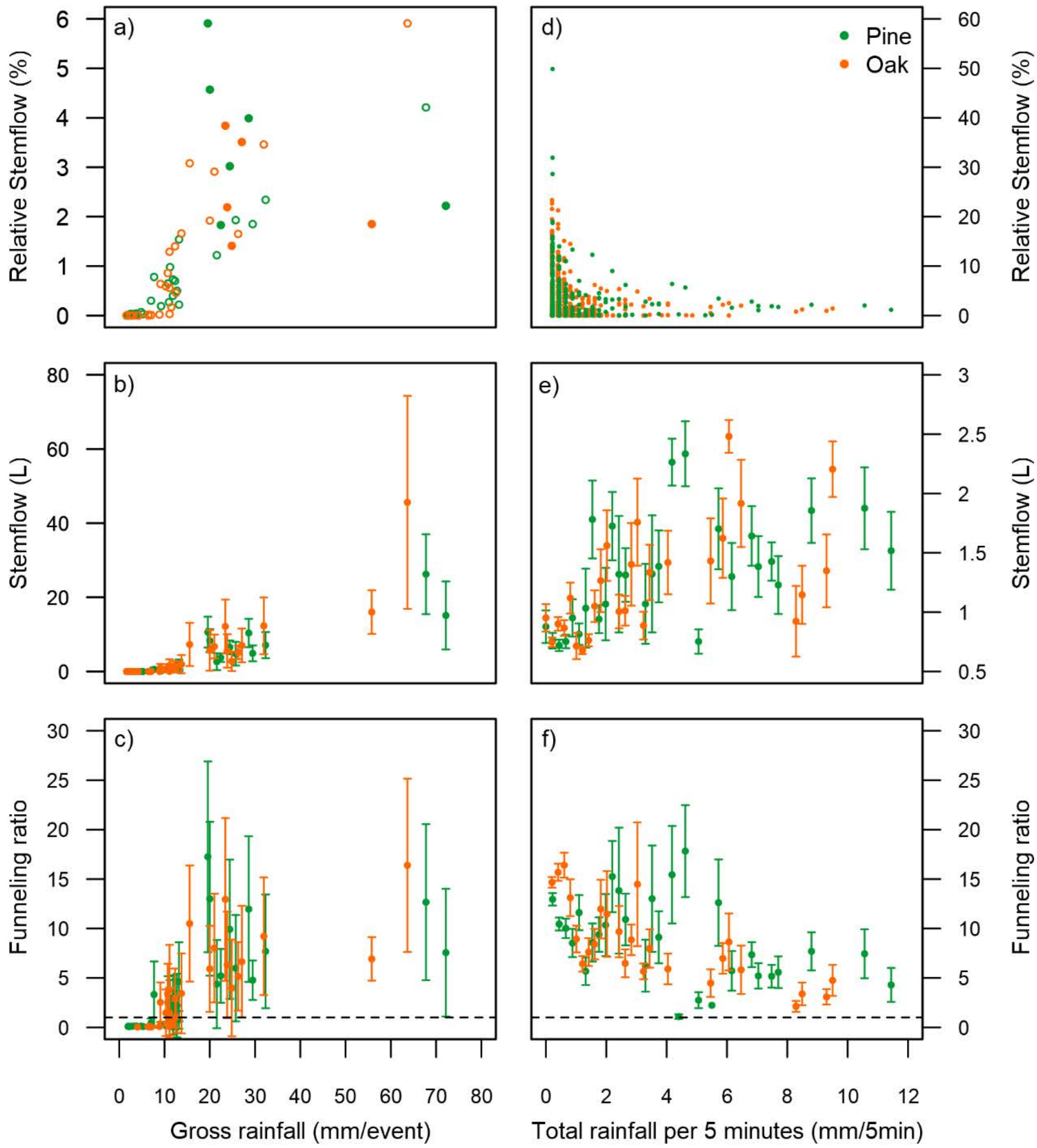


**Figure 3.1.** (Left) Relationship between gross rainfall and (a) relative stemflow ($S_{(\%R)}$), open circles indicate events with maximum 30-minute rainfall intensities below 10 mm $h^{-1}$, and filled dots above 10 mm $h^{-1}$ (b) stemflow volume (litres) and (c) funneling ratio. (Right) Relationship between total rainfall at 5 minutes for any time interval and (d) relative stemflow ($S_{(\%R)}$) (e) stemflow volume (litres) and (f) funneling ratio.

There were no statistically significant differences in stemflow volumes between the forest stands ($F_{1, 12} = 0.23$; $p = 0.64$). For both species, stemflow volumes increased with rainfall ($F_{1, 250} = 193.43$; $p < 0.01$) (Figure 3.1b). The relationship between stemflow and rainfall amount suggested three types of responses: (1) events with less than 15 mm of rainfall produced small stemflow volumes, on average 0.4 ±0.7 litres, with the largest coefficient of variation between trees for these events being 112% for pines and 132% for oaks; (2) events between 15 and 40 mm of rainfall produced a mean stemflow volume of 7.0 ±4.1 litres, with coefficients of variation of 46% for pines and 69% for oaks; and (3) events greater than 50 mm of rainfall produced on average 25 ±16 litres of stemflow and had lower coefficients of variation, 50% for pines and 49% for oaks (Figure 3.1b). At the intra-event time scale, the 5-min data showed that relative stemflow was more variable for lower intensities and that it decreased with increasing rainfall intensities (Figure 3.1d). Besides, it was observed that for intensities lower than 5 mm in 5 minutes (48 mm $h^{-1}$), stemflow volumes increased with rainfall intensity ($F_{1, 2195} = 721.32$; $p < 0.01$) (Figure 3.1e), but beyond this threshold, stemflow volume remained stable ($F_{1, 87} = 0.27$; $p = 0.60$).

**Table 3.2.** Rainfall characteristics and stemflow production at 5-min interval of 4 rainfall events. Mean Pg = mean gross rainfall, Mean I = mean rainfall intensity, Imax = maximum peak of rainfall intensity, Duration = rainfall duration, VPD = vapour pressure deficit, $S_{(\%R)}$ = relative stemflow, DBH = diameter at breast height, Mean S = mean stemflow volume, $S_{Imax}$ = maximum peak of stemflow intensity, Mean FR = mean funneling ratio. P refers to Scots pine and Q refers to Downy oak.

| **Event** | **Mean Pg (mm)** | **Mean I (mm h⁻¹)** | **$I_{max}$ (mm 5min$^{-1}$)** | **Duration (h)** | **VPD (kPa)** | **$S_{(\%R)}$** | | **DBH (cm)** | **Mean S (L)** | | **$S_{Imax}$ (mm 5min$^{-1}$)** | | **Mean FR** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *P* | *Q* | | *P* | *Q* | *P* | *Q* | *P* | *Q* |
| a | 22 | 1.2 | 1.3 | 18 | 0.12 | 1.2 | 2.9 | <25 | 3.3 | 4.9 | 5.0 | 6.3 | 6.7 | 10.0 |
| | | | | | | | | >25 | 1.7 | 7.3 | 1.1 | 4.4 | 1.2 | 6.5 |
| b | 33 | 1.3 | 2.5 | 25 | 0.07 | 2.3 | 3.4 | <25 | 7.7 | 8.0 | 14.5 | 15.9 | 11.5 | 10.8 |
| | | | | | | | | >25 | 5.1 | 15.2 | 3.6 | 10.5 | 2.5 | 7.9 |
| c | 26 | 5.2 | 7.7 | 5 | 0.07 | 3.9 | 3.8 | <25 | 10.8 | 8.8 | 108.6 | 73.9 | 17.1 | 15.8 |
| | | | | | | | | >25 | 9.7 | 14.3 | 29.0 | 17.9 | 5.1 | 10.8 |
| d | 24 | 4.0 | 8.1 | 6 | 0.30 | 5.9 | 3.5 | <25 | 10.7 | 5.7 | 113.9 | 54.0 | 24.4 | 9.2 |
| | | | | | | | | >25 | 10.3 | 7.8 | 29.0 | 19.0 | 7.7 | 4.7 |

Funneling ratios of both species increased with rainfall amount ($F_{1,\ 250} = 76.54$; $p < 0.01$). However, beyond 20 mm of rainfall, more rainfall did not necessarily imply a major concentration of stemflow at the base of the trees (Figure 3.1c). No statistical differences between funneling ratios of the two stands were observed ($F_{1,\ 12} = 0.55$; $p = 0.47$). On the other hand, examining the 5-min rainfall intensity, we observed that funneling ratios decreased as the intensity increased ($F_{1,\ 5923} = 267.47$; $p < 0.01$) (Figure 3.1f). When rainfall intensity was higher than 5 mm in 5 minutes, mean funneling ratios were smaller than 10. Below this threshold, mean funneling ratios were generally higher, with values up to 20. There were no statistically significant differences between the species in the lag time ($F_{1,\ 12} = 1.65$; $p = 0.22$), the rainfall needed to produce stemflow ($F_{1,\ 12} = 1.08$; $p = 0.32$), or the stemflow produced after the end of the rainfall event ($F_{1,\ 12} = 0.02$; $p = 0.89$).

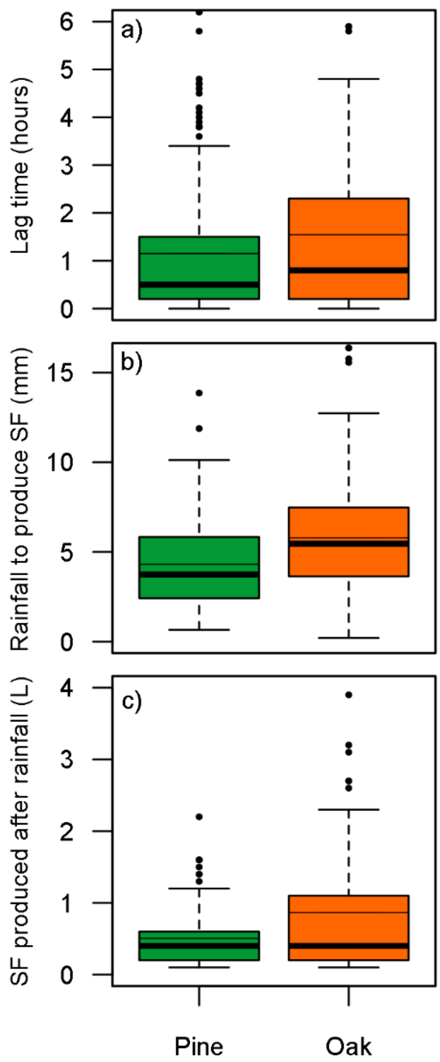


**Figure 3.2.** Box-plots (a) of the lag time between the beginning of rainfall and the beginning of stemflow, (b) of the volume of rainfall needed to produce stemflow and (c) of the stemflow produced once rainfall ended. The horizontal thick black line indicates the median, boxes correspond to the 25th and 75th percentiles, whiskers represent values that fall within 1.5 times the interquartile range and circles represent outliers. Mean values are represented with the thin black line.

However, some trends were observed. For example, the mean lag time between the start of rainfall and the start of stemflow was 1 h for pine and 1 h 30 min for oak, but median values were 30 min and 48 min respectively (Figure 3.2a). The mean amount of gross rainfall needed to produce stemflow was 4 mm for pine and 6 mm for oak (Figure 3.2b). Nonetheless, during some rainfall events, stemflow did not begin until the gross rainfall was approximately 15 mm. Once rainfall ceased, the volume of stemflow produced was greater for oak than for pine (Figure 3.2c), indicating that oak could remain wet longer and divert more stemflow after the event (0.9 ±1.2 litres) compared to pine (0.5 ±0.4 litres).

The intra-event stemflow dynamics (5-min step) of four rainfall events with similar rainfall volumes, but differing in rainfall duration and intensity revealed that for all kinds of events and sizes of trees, maximum stemflow intensities were much higher than maximum rainfall intensities (Table 3.2, Figure 3.3). For long duration-low intensity events (Figure 3.3 a and b), there was a delay between the beginning of the rainfall and the start of stemflow. Furthermore, the stemflow time series for the oaks suggested that stemflow matched the rainfall pattern better than for pines (e.g. Figure 3.3a from 15:35 h). Moreover, for two consecutive periods of similar rainfall intensities, stemflow intensity was higher during the second period (e.g. first and second peak in Figure 3.3a, third and four peaks in Figure 3.3b). On the other hand, shorter and more intense rainfall events (Figure 3.3 c and d) resulted in stemflow intensities almost 10 times higher than long duration-low intensity events (Figure 3.3 a and b). In these events, we also observed that when the peak of rainfall was at the onset of the event, the lag time was reduced considerably (e.g. in Figure 3.3a the lag time was 5h and for the events in Figure 3.3 b, c and d only 30-45 minutes). In general, during low intensity events (<2 mm $h^{-1}$), pines and oaks with DBH < 25 cm had peak stemflow rates up to 12 and 9 times greater than larger trees. For higher rainfall intensities, these figures were up to 80 and 60. However, at the end of the event, oaks with DBH > 25 cm produced more stemflow.

### 3.4.3. Abiotic factors affecting stemflow and funneling ratios

In addition to gross rainfall, other abiotic factors were found to have a significant effect on stemflow volumes and funneling ratios. Higher intensity ($F_{1,\ 250}$ = 69.68; $p$ < 0.01) and longer rainfall duration ($F_{1,\ 250}$ = 55.29; $p$ < 0.01) increased stemflow volumes, whereas higher windspeed ($F_{1,\ 250}$ = 4.80; $p$ < 0.05) and VPD ($F_{1,\ 250}$ = 11.77; $p$ < 0.01) decreased them. Funneling ratios also increased with rainfall intensity ($F_{1,\ 250}$ = 34.44; $p$ < 0.01) and longer durations ($F_{1, 250} = 31.61$; $p < 0.01$), and decreased for higher VPD ($F_{1, 250} = 10.00$; $p < 0.01$); however, the effect of windspeed was marginally significant ($F_{1, 250} = 2.83$; $p = 0.09$).

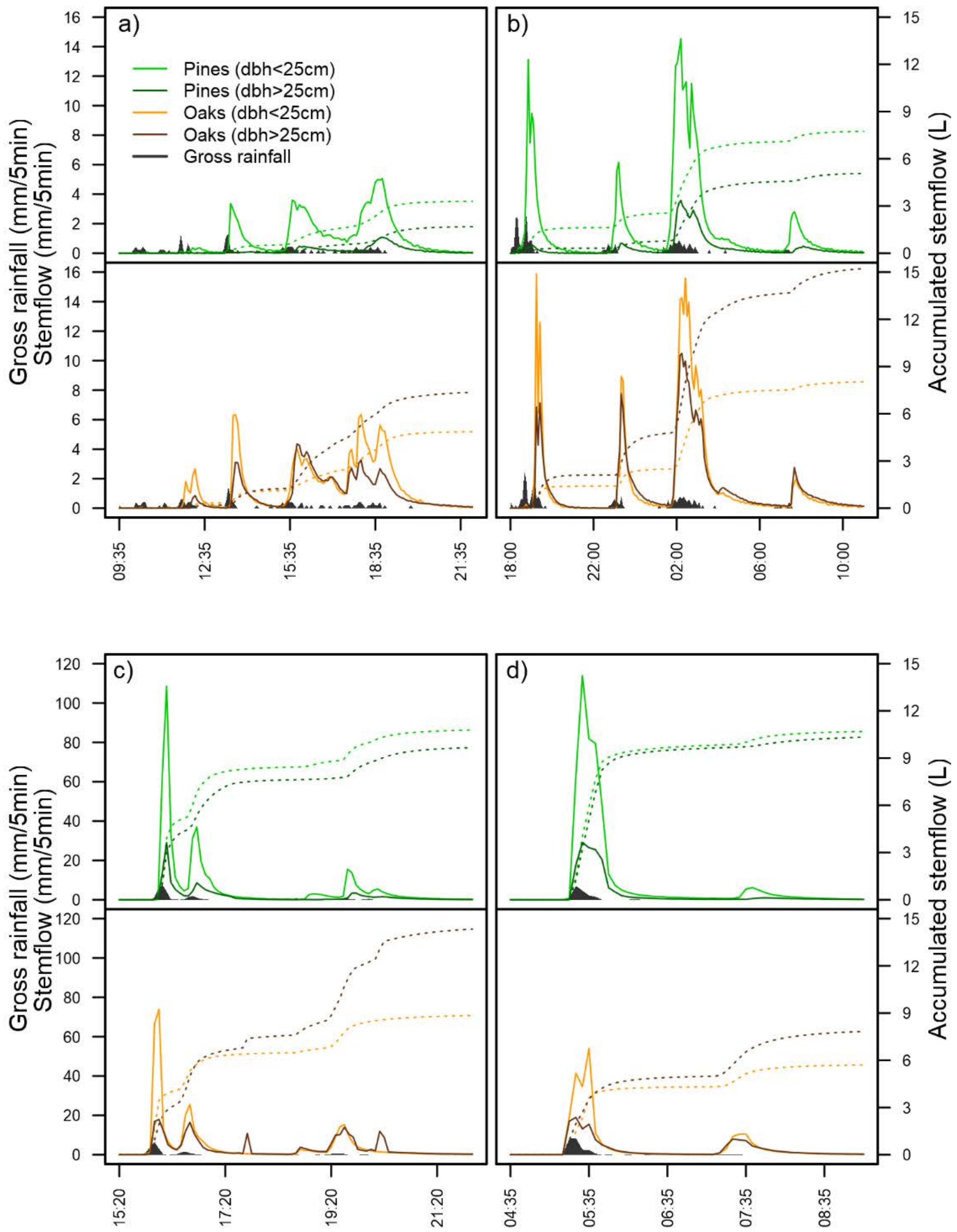


**Figure 3.3.** Time series (5-min interval) of four rainfall events. (a and b) are events of long duration and low mean rainfall intensity and (c and d) are events of short duration and high intensity. Rainfall depth is represented by a grey area, continuous lines represent the stemflow evolution in mm and the dotted lines indicate the accumulated stemflow in litres.

The PCA for the abiotic factors (Figures 3.4a and 3.4b) explained 78.2 and 76.3% of the stemflow variance for pine and oak, respectively. For both species, the first component contrasted short events, with high VPD and high wind speeds, against long events, with wet atmospheric conditions and low wind speeds. The second component was demarcated by rainfall intensity.

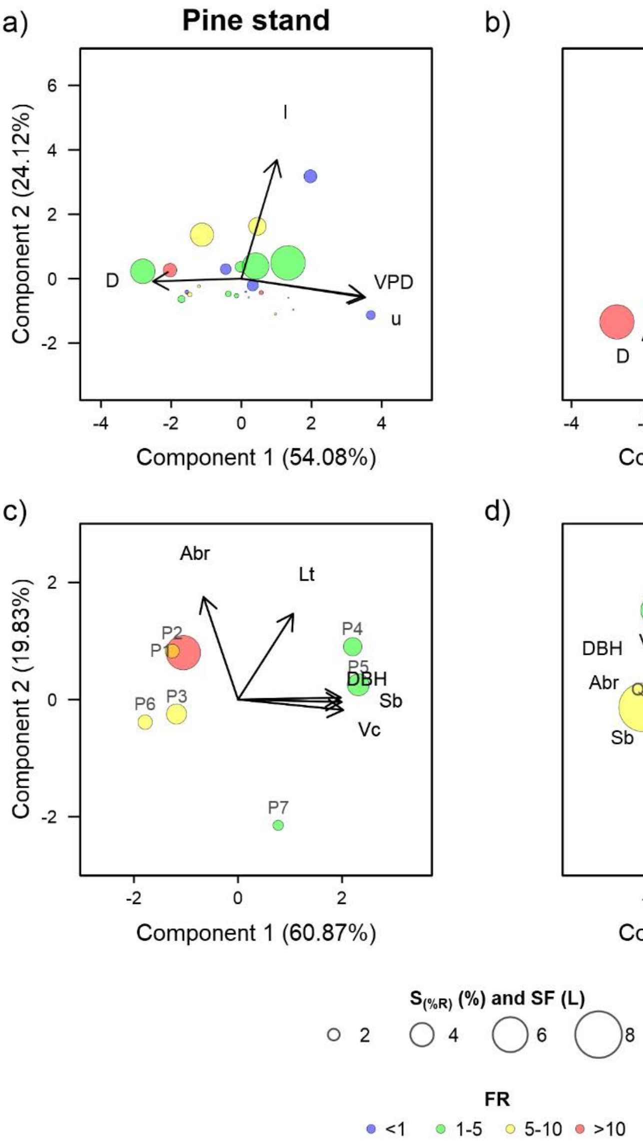


**Figure 3.4.** Bi-plots of the Principal Component Analyses (PCA). Figures a and b plot the PCA performed with the abiotic variables measured in the pine (a) and oak (b) stands. Size of circles is proportional to the relative stemflow ($S_{(\%R)}$). Figures c and d plot the PCA performed with the biotic variables measured in the pine (c) and oak (d) stands. Size of circles is proportional to mean stemflow volume produced by tree (Sf (litres)). D = event duration, I = maximum rainfall intensity measured in 30 minutes, VPD = vapour pressure deficit, and u = wind speed. DBH = diameter at breast height, Vc = crown volume, Abr = mean branch angle, Sb = bark storage capacity, and Lt = tree lean. Colours indicate the mean funneling ratio.

PCA results, in conjunction with the *k*-means clustering, suggested three types of rainfall events generating different stemflow responses: (1) Events with moderate intensities (between 5 and 10 mm in 30 mins) and long durations (>8 hours) increased mean stemflow volumes in oak (9 ±16 litres) more than in pine (3 ±6 litres). These events had mean funneling ratios of 4 ±4 in pine and 7 ±4 in oak. (2) Events of high intensity (>10 mm in 30 mins) and short duration (<5 hours) produced similar stemflow volumes, 4 ±5 litres in pine and 3 ±4 litres in oak, and mean funneling ratios of 6 ±4 in pine and 6 ±6 in oak. (3) Events of low intensity (<4 mm in 30 mins) and short duration (< 5 hours) produced low stemflow in both stands, 0.5 ±0.4 litres pine and 1 ±2 litres in oak, with mean funneling ratios of 2 ±0.3 in the pine stand and 6 ±3 in the oak stand.

### 3.4.4. Biotic factors affecting stemflow and funneling ratios

The analysis of the influence of each biotic factor separately indicated that crown volume had a statistically marginal effect on stemflow volume ($F_{1, 10} = 4.47$; $p = 0.06$), and DBH had a statistically marginal effect on funneling ratio ($F_{1, 10} = 3.68$; $p = 0.08$). Smaller DBH increased funneling ratios for both species; and bigger crown volumes increased stemflow volumes in oak, and decreased them in pine. The PCA (Figures 3.4b and 3.4c) explained a variance of 80.7 and 83.4% for the stemflow of pine and oak respectively. The comparison of the distribution of funneling ratios and the biotic factors of each tree (Figure 3.5) showed that pine trees with less than 25 cm DBH and with smaller crown volumes (P1, P2, P3 and P6) had funneling ratios that were greater than for larger trees (P4, P5 and P7), which had horizontal or downwards inclined branches and higher bark specific storage capacities. Tree lean (2º-5º) also increased funneling ratio, however, larger tree lean (>5º) decreased it. For oaks, tree Q7 had the highest funneling ratio, this tree had the smallest DBH, a voluminous crown, branch inclinations between 20º and 25º and the lowest bark storage capacity. But, on the other hand, trees Q1, Q2, Q5 and Q6, which had higher bark specific storage capacities (>0.50 mm), had low funneling ratios compared to Q7. Trees with the lowest funneling ratios (Q3 and Q4) were moderately sized trees (DBH 24.8 and 20.5 cm) and flow paths were obstructed (big nodules in the trunk observed *in situ*). A detailed response of each tree for each rainfall event can be seen in Figure A.1 in the Appendix A (Supporting information).

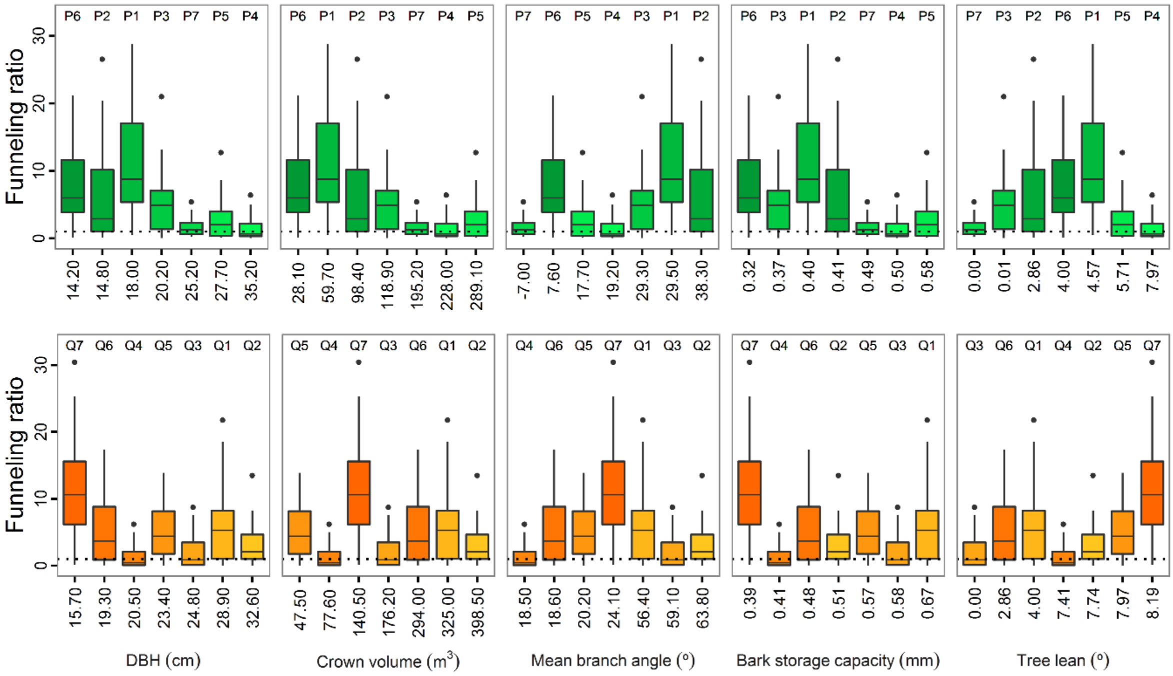


**Figure 3.5.** Box-plots of funneling ratios in relation to biotic factors for Scots pine (top) and downy oak (bottom). The horizontal black line indicates the median, boxes correspond to the first and third quartiles (the 25th and 75th percentiles), whiskers represent values that fall within 1.5 times the interquartile range and circles represent outliers. The dotted line indicates FR=1.

### 3.4.5. Interaction of biotic and abiotic factors that affect stemflow dynamics

Stemflow responses to the interaction between biotic and abiotic factors were analysed for 12 events with similar rainfall amount (30 mm on average). Among these events, six were of low intensity, with mean rainfall intensity of 6 mm $h^{-1}$ and mean duration of 17 hours and the other six events were of high intensity, with a mean rainfall intensity of 17 mm $h^{-1}$ and mean duration of 5 hours. In both stands, stemflow volumes increased with rainfall intensity ($F_{1, 132} = 8.68$; $p < 0.05$). Smaller pines produced slightly more stemflow than larger pines. In contrast, larger oaks produced more stemflow than smaller oaks, but without statistically significant differences ($F_{1, 10} = 0.50$; $p = 0.49$) (Figure 3.6a). There were not significant differences in funneling ratios due to the interaction between tree size and rainfall intensity ($F_{1, 132} = 1.54$; $p = 0.22$), although a greater variability was observed among pines depending on their size (i.e. lowest values for larger trees), especially for low intensity events (Figure 3.6b). Lag times were longer during high rainfall intensities for both species ($F_{1, 132} = 18.59$; $p < 0.01$), although slightly longer for oaks (Figure 3.6c). Stemflow duration at the end of the rainfall event was longer for bigger oaks, despite no significant differences were observed among trees ($F_{1,\,132} = 0.63$; $p = 0.42$) (Figure 3.6d).

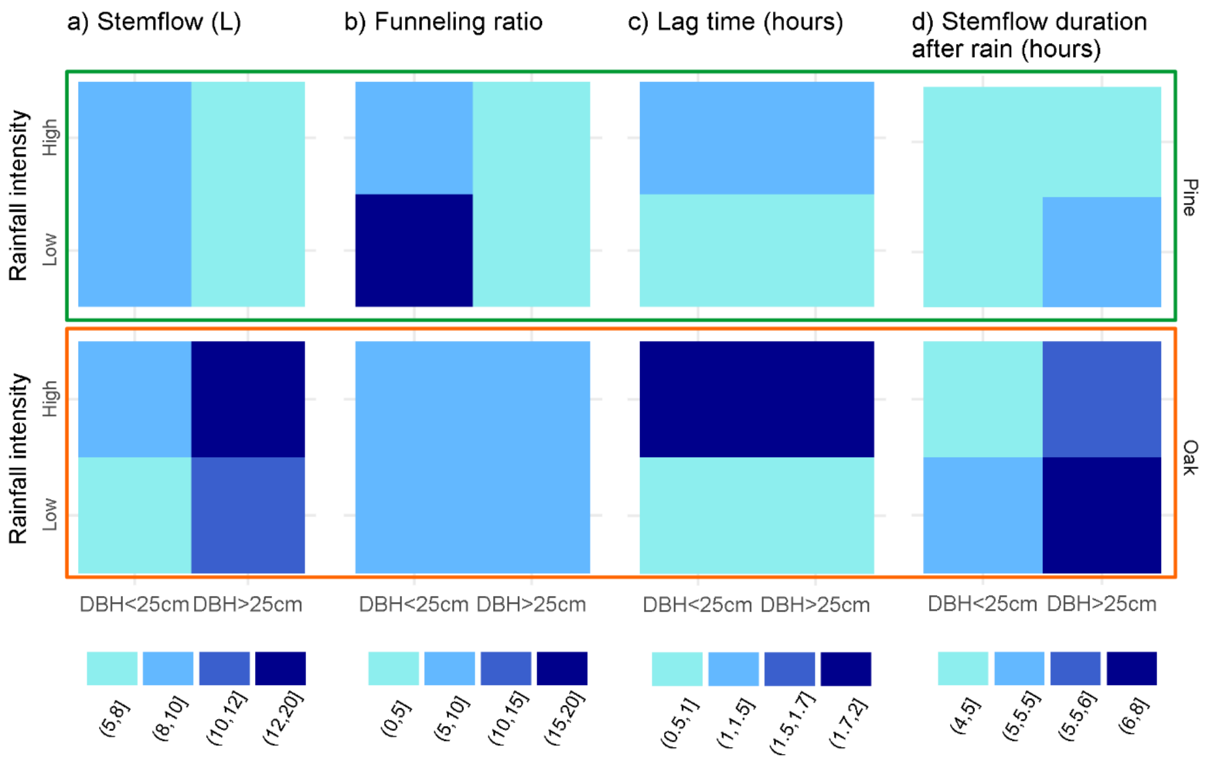


**Figure 3.6.** Relationship between rainfall intensity (Low/High), and (a) stemflow volume (litres), (b) funneling ratio, (c) lag time (hours) and (d) stemflow duration after rainfall (hours), for small (DBH < 25 cm) and large (DBH > 25 cm) pine and oak trees for events of rainfall amount ≈30 mm. From light to dark, colours represent the increase of each stemflow variable studied (volume, funneling ratio, lag time and duration), numbers in brackets indicate the range of values for each colour.

## 3.5. DISCUSSION

### 3.5.1. Stemflow production and funneling ratios

On average, stemflow produced by oak and pine represented only about 1% of the total gross rainfall over the study period. This percentage agrees with the previous values reported for Scots pine and downy oak under Mediterranean climate (Llorens and Domingo, 2007; Muzylo *et al.*, 2012b). In both stands similar stemflow volumes were produced, but different dynamics were observed. The different stemflow dynamics between species was attributed to a complex interaction of biotic and abiotic factors, similar to the observations by Levia *et al.* (2010).

### 3.5.2. Abiotic factors affecting stemflow and funneling ratios

Our study found that stemflow and funneling ratios were highly influenced by gross rainfall, duration of rainfall, rainfall intensity, vapour pressure deficit, and wind speed. The role of these factors in stemflow production has been previously described in other studies (e.g. Dunkerley, 2014; Reid and Lewis, 2009; Van Stan *et al.*, 2014), but the comparison between species and the high frequency of the stemflow measurements in this study revealed new insights into some of these factors. As pointed out by Herwitz (1987), high intensity rainfall events may agitate foliar surfaces, create splash, disrupt canopy interception and divert more rainfall into throughfall, resulting in a decrease of stemflow. In this sense, we observed that rainfall intensity greater than 5 mm in 5 minutes decreased the capacity of trees to funnel water. A similar effect was observed by Levia *et al.* (2010), who also linked this effect to a water in excess of the branches' flow capacity, causing water detachment and resulting in throughfall. This phenomenon was further reflected by a steady stemflow production and a decrease of the funneling ratio at increasing rainfall intensities. Moreover, we detected that stemflow volumes varied greatly depending on the position of the peaks of high intensity during the event. Similar to Dunkerley (2014), we observed that events with high rainfall peaks (but with intensities < 5 mm in 5 min) produced more stemflow than those of uniform rain and the lag time was reduced when the maximum peak intensity was at the onset of the event. When successive rainfall peaks occurred there was an increase of the stemflow volume and of the funneling ratio, which could be explained by a rapid diversion of water through the stemflow paths created earlier in the event. For these events, stemflow intensities could exceed almost in 100 times the intensity of open rainfall. As a consequence, and as observed by Spencer and van Meerveld (2016), during some moments throughout a rainfall event, the amount of water that reached the base of the tree as stemflow could enhance infiltration rates and groundwater recharge.

Unlike Van Stan *et al.* (2011), in this study, we observed that increasing wind speed resulted in lower stemflow volumes and lower mean funneling ratios. This effect was attributed to an increase of the VPD linked to higher wind speeds; in these conditions evaporative demand was enhanced and, as a consequence, interception loss increased, reducing stemflow volumes. Moreover, for the same evaporative demand, the evaporation of intercepted water in pine was higher because the canopy of pine is aerodynamically rougher than oak (Jarvis, 1976). Previous studies in the same study site (Llorens *et al.*, 1997; Muzylo *et al.*, 2012a) observed higher interception losses for pines (24%) than for oaks (15%). This higher interception loss in pines could explain why the synchronicity between rainfall and stemflow was weaker for pine than oak.

### 3.5.3. Biotic factors affecting stemflow and funneling ratios

As found in other recent studies (Germer *et al.*, 2010; Levia *et al.*, 2010; Siegert and Levia, 2014; Spencer and van Meerveld, 2016), we observed an effect of tree size on funneling ratios, trees with DBH between 15 and 25 cm had higher funneling ratios than larger trees. The higher funneling efficiency of small pine trees was attributed to a combination of different biotic factors: more branches tilted vertically, a smaller crown, and less bark surface. Smaller oaks, in general, also had higher funneling ratios, but the variability between trees was larger. For example, some small trees had flow paths obstructions, such as big nodules, or had a substantial tree lean, factors that would divert more water as throughfall and would reduce funneling ratios.

Canopy architecture, as observed by Reid and Lewis (2009), represented a dynamic storage where rainfall could be evaporated or diverted as stemflow during and after rainfall events. We observed a different effect depending on the species. For pine, larger stemflow volumes were observed for trees with smaller crowns. Those trees also had fewer branches that were tilted more vertically, thereby promoting the formation of preferential flow paths and a faster onset of stemflow. In this sense, McKee and Carlyle-Moses (2017) observed a higher water storage capacity for pines with a greater number of branches tilted vertically; for lower or negative branch angles more water dripped from the canopy. On the other hand, greater stemflow volumes were observed for oaks with big crowns, suggesting that bigger canopies could store and release more water as stemflow. For pine, we observed that a certain tree lean, between 2º and 5º, favoured the formation of flow paths and, therefore, increased funneling ratios; however, tree lean greater than 5º would divert more water to throughfall. Levia *et al.* (2015) also found that trunk lean was a factor affecting stemflow amount from European beech saplings. When flow paths were created, stemflow would wet the trunk and it could be enhanced or lessened depending on the bark storage capacity (Levia and Herwitz, 2005; Van Stan and Levia, 2010). Therefore, trees with thicker rough bark would produce less stemflow. In concurrence with these studies (Levia and Herwitz, 2005; Van Stan and Levia, 2010), we observed that oak, whose bark specific storage capacity was larger than pine, had longer lag times and required more rainfall to trigger stemflow, suggesting that water flowed slower along the stems of oak than pine.

### 3.5.4. Interaction of biotic and abiotic factors that affect stemflow dynamics

Biotic factors determined the funneling ratio of each tree, but abiotic factors determined the magnitude of the stemflow response for the event. In our study, biotic factors varied between trees, and abiotic factors varied between and within events. Stemflow, as described in previous literature (Levia and Frost, 2003), increased with gross precipitation, even though, we observed that for the same amount of rainfall, the response was different for small or big trees. Events of high rainfall intensity had a short duration, high wind speed and low VPD; during these events, more splash could be produced (Herwitz, 1987), higher evaporation rates would enhance the interception losses, and as observed by Reid and Lewis (2009), a higher retention of water in the bark would be possible. These conditions resulted in longer lag times in all trees regardless of their biotic characteristics. However, small pines, in contrast to oaks, had higher funneling ratios for all ranges of rainfall intensity, which demonstrate that the architecture of small pines is more efficient at collecting stemflow (McKee and Carlyle-Moses, 2017). On the other hand, the higher bark water storage capacity of oaks in combination with low intensity and long duration events increased the amount of water stored on their stems that was released slowly after the rainfall.

## 3.6. CONCLUSIONS

Stemflow in pine and oak forests in the Vallcebre research catchments represented only a small portion of the gross rainfall (~1%), although it may be a substantial source of water at the tree base (ranging from 0.5 ±0.6 litres to 25 ±16 litres per event). Stemflow volumes and funneling ratios varied greatly at the inter- and intra-storm time scales and was the result of a complex combination of biotic and abiotic factors. Stemflow increased with the event size but its variability depended on the duration of the event, the evaporative demand of the atmosphere, the rainfall intensity, the distribution of the rainfall intensity peaks during the event, and on the biometric characteristics of each tree. In general, smaller trees were more efficient in funneling stemflow per unit area and time, although bigger canopies enhanced stemflow volumes in oak. Moreover, lag times were longer and more rainfall was required to initiate stemflow for oak trees. These differences, between species and tree size, can partly be explained by the bark storage capacity and the effect of evaporation on stemflow. Stemflow should be taken into account when analysing infiltration processes, soil moisture dynamics, and groundwater recharge in forested catchments, because, as presented here, it can be a very large point source of water, with its amount varying with respect to biotic and abiotic factors. Thus, future work should consider the effect of stemflow in hydrological and biogeochemical processes that occur at the tree base during rainfall events, as well as the relevance of stemflow as a locally concentrated source of water at the catchment scale.

## ACKNOWLEDGMENTS

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# CHAPTER 4

## Particulate matter fluxes in a Mediterranean mountain forest: inter-specific differences between throughfall and stemflow in oak and pine stands

In forested areas, canopies play an important role in the partitioning of rainfall. During this process there is also a redistribution of particulate matter (PM) that is deposited from the atmosphere on vegetative surfaces and transported to soil layers by throughfall and stemflow. We collected samples of rainfall, throughfall and stemflow from two different forest plots (pine and oak) in a Mediterranean mountainous area and analysed the amount and size distributions of PM (0.45 µm < PM < 500 µm). The exploration of backward trajectories revealed that PM content varied significantly. This depended on the origin of the air mass, with Atlantic fronts transporting less PM in the atmosphere than North African dust intrusions, which added disproportionate inputs of PM. Overall, throughfall provided the largest proportion of incoming PM under trees, but, at the base of each tree, stemflow led to a localized input of water that was more PM-enriched than water through open precipitation or throughfall. Differences between species were determined by their differing interactions with respective vegetative surfaces. Pines retained more PM in their crowns than oaks; furthermore, the presence of leaves in oaks during the leafed season increased the size and the amount of particles released by throughfall. However, PM in stemflow was smaller and rounder than in throughfall. This study adds to our understanding knowledge on the processes that control the deposition and distribution of PM delivered to forest soils, a fraction that is often ignored in studies of nutrient and energy fluxes in ecosystems.

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## 4.1. INTRODUCTION

Atmospheric particulate matter (PM) is a mixture of physically and chemically diverse substances that exist in ambient air as discrete particles of widely differing sizes. Its source is diverse: it can be introduced to the atmosphere from natural sources (e.g. volcanic eruptions, sea salt, soil dust suspension, natural forest fires, biological elements such as pollen, bacteria, fragments of vegetal organisms or animals, etc.) or from multiple anthropogenic activities (e.g. transport, industry, biomass burning, etc.) (Weathers and Ponette-González, 2011; Lequy *et al.*, 2013). Depending on its size, PM can be transported over long distances: while coarse particles are rapidly removed from the air by sedimentation, fine PM can be easily transported by the wind up to thousands of kilometres from the area where they were formed (Perrino, 2010). Dust storms, originating primarily in drylands, play a particularly important role in PM distribution. They have numerous source areas, but the Sahara is undoubtedly the largest source of atmospheric desert dust (Middleton, 2017). For instance, Saharan dust has affected the nature of soils in the Canary Islands (Menéndez *et al.*, 2007; Castillo *et al.*, 2017) and Mount Cameroon (Dia *et al.*, 2006). Saharan micro-nutrients have also been detected as far away as northern Europe (Yaalon and Ganor, 1979; Franzén *et al.*, 1994; Avila *et al.*, 1997), the Caucasus Mountains (Kutuzov *et al.*, 2013), south-west USA (Prospero, 1999), Caribbean islands (Muhs *et al.*, 2007), the Amazon (Swap *et al.*, 1992) and the Andes (Boy and Wilcke, 2008). Numerous diameter classifications of PM have been proposed: for example, air quality standards (USEPA, 2004) regulate fine PM ($PM_{2.5}$: 0 – 2.5 μm aerodynamic diameter) and coarse PM (2.5 – 10 μm) due to its harmful effects on human health. However, less agreement exists on the classification of PM in ecological studies. Nevertheless, so as to be consistent with much of the scientific literature, this study focuses on PM diameter distributions of > 0.45 and < 500 μm (Levia *et al.*, 2013).

Forest canopies play an important role in the removal of PM from the atmosphere (McDonald *et al.*, 2007). PM can be deposited on vegetative surfaces via wet deposition, in the form of rain, snow or mist; via dry deposition, as direct particles and gases; or via occult deposition, as dissolved material in cloud droplets. Nevertheless, deposition rates respond to atmospheric conditions, vegetation properties and topography factors (Grantz *et al.*, 2003). In general, higher rainfall results in greater wet deposition (Weathers and Ponette-González, 2011) and high wind speed usually increases dry deposition due to enhanced particle impaction and turbulent transfer of gases and particles to forest canopies (Fowler *et al.*, 1989). The amount of PM deposited on forest canopies also depends on the structure of the crowns and bark roughness. For example, coniferous species, with needle-shaped leaves, enhance impaction and retention of PM (Beckett *et al.*, 2000; Dzierżanowski *et al.*, 2011; Song *et al.*, 2015). In addition, as they keep their leaves for several years, PM accumulates for longer periods (Beckett *et al.*, 1998). In contrast, deciduous forest canopies generally capture less PM. However, within deciduous broad-leaved trees, species with rough leaf surfaces capture PM more effectively than ones with smooth surfaces (Beckett *et al.*, 2000). Rainfall dynamics also play an important role; in general, the concentration of suspended and dissolved materials is highest at the onset of a precipitation event and decreases as an event progresses (Lindberg *et al.*, 1986). Long rainfall events, therefore, remove previously accumulated PM on vegetative surfaces much more effectively. In addition, intense rainfall may enhance the washing of PM deposited on leaves, whereas lower intensities may hydrate previously dry-deposited PM and facilitate the foliar uptake of the substances it contains (Lovett and Lindberg, 1984).

In forests, PM can be a source of essential macro- and micro-nutrients that reach the soil through the redistribution of rainfall as throughfall and stemflow (Weathers and Ponette-González, 2011). However, depending on the chemical composition and magnitude of the deposition, PM may affect plants, indirectly alter soil nutrient cycling and inhibit plant nutrient uptake (Grantz *et al.*, 2003). Although stemflow may be a low percentage of open rainfall, it can funnel >20-fold more water to near-stem soils than open rainfall in an equivalent area (Levia and Germer, 2015; Carlyle-Moses *et al.*, 2018). In addition, the longest path that a rain drop travels is as stemflow, which involves a prolonged interaction between intercepted rainfall and canopy surfaces (leaves, branches and stems) that causes a greater exchange of solutes and particulates (Michalzik *et al.*, 2016). Thus, soils near the stems reach a supply of water that can be more chemically enriched than water from rainfall or throughfall (Levia and Frost, 2003; Levia and Germer, 2015).

If the particulate matter fraction ($45\ \mu m < PM < 500\ \mu m$) is not taken into account, it can result in misleading inferences and budgeting gaps when nutrient and energy fluxes in ecosystems are studied (Levia *et al.*, 2013). Until now, only a few studies have focused on PM fluxes and their size distribution below the canopy (e.g. Levia *et al.*, 2013; Song *et al.*, 2015). As these PM fluxes provide essential information for understanding the dynamics of different forest covers in the removal of PM from the atmosphere, further research is required into biosphere-atmosphere interactions (Levia *et al.*, 2013). In this study, PM fluxes below the canopy (in throughfall and stemflow) and their size distribution for two tree species, downy oak (*Quercus pubescens* Willd.) and Scots pine (*Pinus sylvestris* L.), in a Mediterranean mountainous area are measured. We specifically aim to: (i) analyse how different tree species affect the PM content reaching the forest soil; and (ii) evaluate the differences in PM content and size distributions between throughfall and stemflow. This study will help to fill the gap in the understanding of the processes that control the deposition and distribution of PM on forest soils as well as measure their rates.

## 4.2. METHODOLOGY

### 4.2.1. Study area

Forest stands of downy oak and Scots pine located in the Vallcebre research area (NE Spain, 42º 12'N, 1º 49'E) in the eastern Pyrenees were chosen to analyse the deposition of PM. The climate in this mountainous area is Sub-Mediterranean, with a mean annual temperature of 9.1 ± 0.67ºC, mean annual reference evapotranspiration of 823 ± 26 mm and mean annual precipitation of 880 mm ± 200 mm (1989-2013). The precipitation regime is seasonal, with autumn and spring generally being the wet seasons, while summer and winter are drier. Summer rainfall is characterized by intense convective events, while winter precipitation is caused by frontal systems, with snowfall accounting for less than 5% of precipitation (Latron *et al.*, 2010a, 2010b; Llorens *et al.*, 2018).

The selected forest stands are less than 1 km from each other. There are neither high-polluting factories nor important motorways in the surroundings of the study area. The pine stand has an area of 900 $m^2$, a tree density of 1,189 trees $ha^{-1}$ and a basal area of 45.1 $m^2 ha^{-1}$, and is oriented northeast at an elevation of 1,200 m. The oak stand has an area of 2,200 $m^2$, a tree density of 518 trees $ha^{-1}$ and a basal area of 20.1 $m^2$ $ha^{-1}$, and is oriented southeast, at an elevation of 1,100 m.

### 4.2.2. Sampling design

A total of 10 throughfall and 4 stemflow collectors were deployed in each forest stand, covering different representative canopy coverages and all Diameter at Breast Height (DBH) distributions. Throughfall collectors were made of plastic funnels connected to a 1-litre bottle, funnels were held by a stake 0.5 m above the ground and the bottles were covered by an opaque PVC tube to minimize irradiation impact and algae growth. Stemflow collectors were made of cut plastic funnels sealed to the trees with silicone at breast height and connected to 60-litre opaque polyethylene bins. Bulk rainfall was collected by means of the same methodology as throughfall, but outside the forest stands. Funnels were equipped with a nylon sieve (1 mm mesh width) to prevent sample contamination with coarse matter. In addition, each stand was equipped with automatic tipping-bucket gauges to measure rainfall, throughfall and stemflow every five minutes.

### 4.2.3. Analysis of particulate matter fluxes

The sampling was conducted weekly (if rainfall occurred) between July 2015 and July 2016. Each sampled event included the total dry and wet deposition of the period between samplings. In total, 36 events were sampled, covering both the growing and the dormant season for oaks. Sampling of PM in December was not possible due to the lack of rain. For each sampled event, the origin of its air mass was identified through 10-day backward trajectories calculated using the HYSPLIT model (Stein *et al.*, 2015; Rolph *et al.*, 2017) with the one-degree meteorological GDAS (Global Data Assimilation System) dataset, downloaded from the available portal in the HYSPLIT interface.

For every rainfall event, single sub-samples of rainfall, throughfall and stemflow were prepared by pooling spatially distributed samples to one volume-weighted sample of 250 ml. Afterwards, sub-samples were filtered with nitrocellulose filters of 0.45 µm pore size (MF-Millipore HAWP04700) previously dried in a desiccator and weighed. After filtering, the filters were dried again in an oven at low temperature (~30ºC) to prevent the calcination of organic particles and then weighed again. Mean particulate matter flux per area (kg ha$^{-1}$) was calculated for each event by taking the weight of each filter ($f_i$) weighted by the volume of each corresponding sample ($w_i$), the area of the funnels for open rainfall and throughfall ($F_A$) (Equation 4.1), and the mean basal area for stemflow ($B_A$) (Equation 4.2).

$$PM_{P,T} = \frac{\frac{\sum_{i=1}^{n} w_i \cdot f_i}{\sum_{i=1}^{n} w_i}}{F_A} \tag{4.1}$$

$$PM_S = \frac{\frac{\sum_{i=1}^{n} w_i \cdot f_i}{\sum_{i=1}^{n} w_i}}{B_A} \tag{4.2}$$

Net deposition (ND) was calculated as the difference between the PM fluxes below the canopy (throughfall ($PM_T$) plus stemflow ($PM_S$)) and the PM fluxes in open rainfall ($PM_P$) (Equation 4.3).

$$ND = (PM_T + PM_S) - PM_P \tag{4.3}$$

In addition, the flux-based stemflow enrichment ratios compared to rainfall ($E_{P,B}$) (Equation 4.4) and throughfall ($E_{T,B}$) (Equation 4.5) were calculated following Levia and Germer (2015). This parameter is a flux-based ratio which seeks to quantify the extent to which trees concentrate solutes and particles at their base.

$$E_{P,B} = \frac{S_y \cdot C_S}{P \cdot B_A \cdot C_P} \tag{4.4}$$

$$E_{P,B} = \frac{S_y \cdot C_S}{T \cdot B_A \cdot C_T} \tag{4.5}$$

Where $C_S$, $C_P$ and $C_T$ are PM concentrations in stemflow, open rainfall and throughfall, respectively; P and T are depth equivalents of rainfall and throughfall, respectively (mm); and $S_Y$ is stemflow in volume (L). Finally, particulate matter fluxes for four selected events were analysed sequentially in the pine stand. For each selected event, samples of rainfall and throughfall were taken at every 5 mm of rainfall; and stemflow samples, at approximately every 2 litres. The sampling was carried out sequentially by three automatic water samplers (ISCO 3700C). Rainfall and throughfall automatic samplers were connected to a plastic funnel (160 mm diameter) and the stemflow automatic sampler was connected to a stemflow collar. Samples were filtered, dried and weighed as described above.

### 4.2.4. Analysis of particulate matter size distributions

Open rainfall, throughfall and stemflow filters of 7 rainfall events were selected for analysis by a Zeiss LSM 510 Meta-5 Live Duo confocal microscope. The selected events were representative of the range of rainfall events and took into account the leafed and leafless periods of oak. The confocal microscopy analyses were conducted at the BioImaging Centre at the University of Delaware. Each filter was scanned by means of a grid of 9x9 tiles and each individual tile was magnified by a 5x lens with a resolution of 1,536x1,536 pixels. ImageJ 1.51g software was used to stitch the tiles in a single image and to determine the number of particles and their diameter distribution. Maximum particulate diameters were calculated as the longest distance between any two points along the identified particulates.

In addition, the roundness of the PM was calculated as the ratio between the maximum and the minimum Feret diameters, which ranged between 1 (i.e. round or orthogonal) and infinity (i.e. a very thin wafer).

## 4.3. RESULTS

### 4.3.1. Particulate matter fluxes in open rainfall, throughfall and stemflow

For the 36 events analysed, throughfall represented 82% and 84% and stemflow represented 3.1% and 3.4% of the open rainfall for the pine and oak, respectively. The total annual (July 2015-July 2016) amount of PM collected below both tree canopies was higher than the 58 kg ha$^{-1}$ of PM collected in open rainfall. In the pine stand, the annual flux of PM was 69 kg ha$^{-1}$ in throughfall and 2.4 kg ha$^{-1}$ in stemflow. For oak, the annual flux of PM was 84 kg ha$^{-1}$ in throughfall and 1.5 kg ha$^{-1}$ in stemflow.

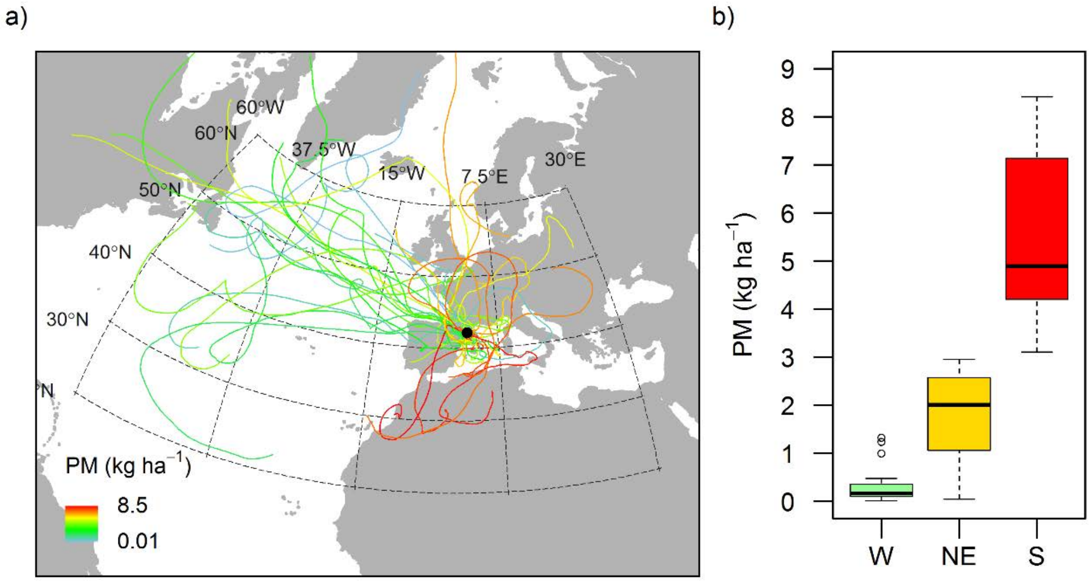


**Figure 4.1.** (a) Ten-day backward trajectories ending at the Vallcebre Research catchments (black dot) with the HYSPLIT dispersion model for the 36 events selected. Colour indicates the load of the PM flux. (b) Boxplots of the PM load for events grouped by origin: West (20 events, 476 mm), North-east (10 events, 468 mm) and South (6 events, 238 mm).

The load of PM in rainfall was related to the origin of the air mass (Figure 4.1a). Precipitation originating from air masses coming from the West (Atlantic sea) had the lowest content of PM in open rainfall, with median PM fluxes of 0.2 kg ha$^{-1}$. On the contrary, rainfall produced during Saharan air mass intrusions had the highest concentrations of PM, with median PM fluxes 25 times higher (4.9 kg $ha^{-1}$). High PM fluxes were also observed for air mass trajectories from the northeast crossing the European continent, with median PM fluxes of 2.0 kg $ha^{-1}$ (Figure 4.1b). Overall, the deposition of PM in the study area was dominated by Saharan dust intrusions. The 6 rainfall events that occurred during Saharan dust intrusions accounted for almost 60% of the total annual PM flux in rainfall. Throughfall and stemflow did not significantly differ for PM concentrations. Nevertheless, in both forest stands, the concentration of PM collected below the forest canopy was higher (median value of 7.8 g $l^{-1}$ in throughfall and 7.6 g $l^{-1}$ in stemflow) than the concentration of PM collected in open rainfall (median concentration of 3.4 g $l^{-1}$) (Figure 4.2)

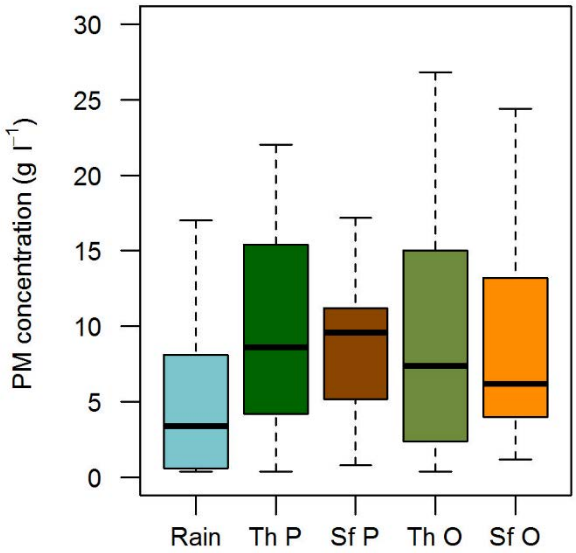


**Figure 4.2.** Boxplots of annual PM concentrations in g $l^{-1}$ for open rainfall, throughfall and stemflow in pines and oaks.

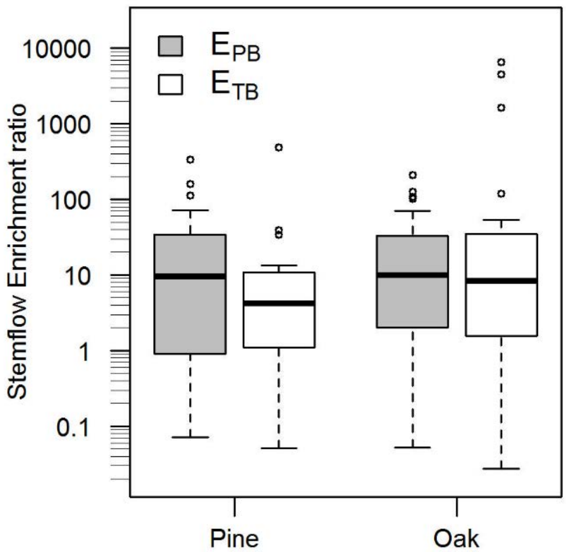


**Figure 4.3.** Boxplots of stemflow enrichment ratios for pine and oaks. $E_{PB}$ is enrichment ratio compared to precipitation flux, and $E_{TB}$ is enrichment ratio compared to throughfall flux. Note that the y-axis is in log scale.

Enrichment ratios revealed that stemflow funnelled larger amounts of PM per basal area than open rainfall and throughfall. As median, pines funnelled 9.5 times more PM than open rainfall and 4.2 times more PM than throughfall. Likewise, oaks funnelled 10.1 and 8.3 more PM than rainfall and throughfall, respectively (Figure 4.3). The rate of PM was not evenly distributed throughout the year. May was the month with the highest amount of PM per surface area in open rainfall (Figure 4.4b), coinciding with the rainiest month of the studied period (Figure 4.4a). However, throughfall in both species followed a similar distribution to open rainfall (Figures 4.4c).

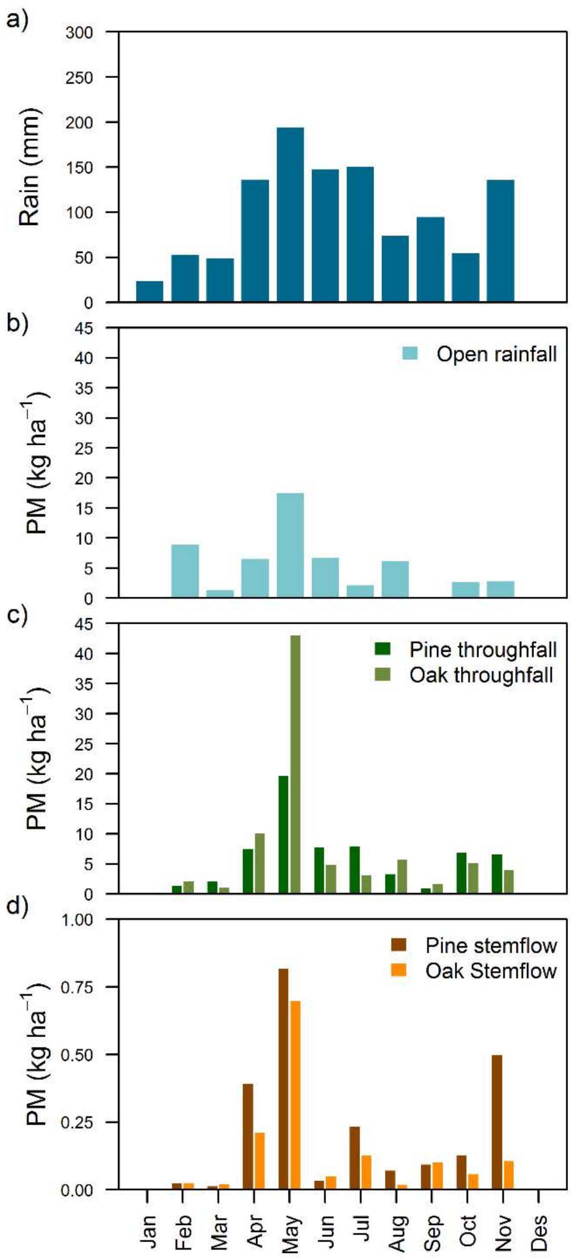


**Figure 4.4.** Monthly distribution of (a) Rainfall, (b) PM in open rainfall, (c) PM in throughfall for pines and oaks, (d) PM in stemflow for pines and oaks.

Differences between species were generally small, except during May, when PM for oaks was twice as high as for pine. The total contribution of PM in the study area due to stemflow was almost 10-fold lower than PM due to throughfall (Figures 4.4d). A significant correlation between monthly precipitation and monthly PM in rainfall (Figure 4.5a), throughfall (Figure 4.5b) and stemflow (Figure 4.5c) for both species ($p < 0.05$) was found. This correlation, however, was not significant when examined at the event scale.

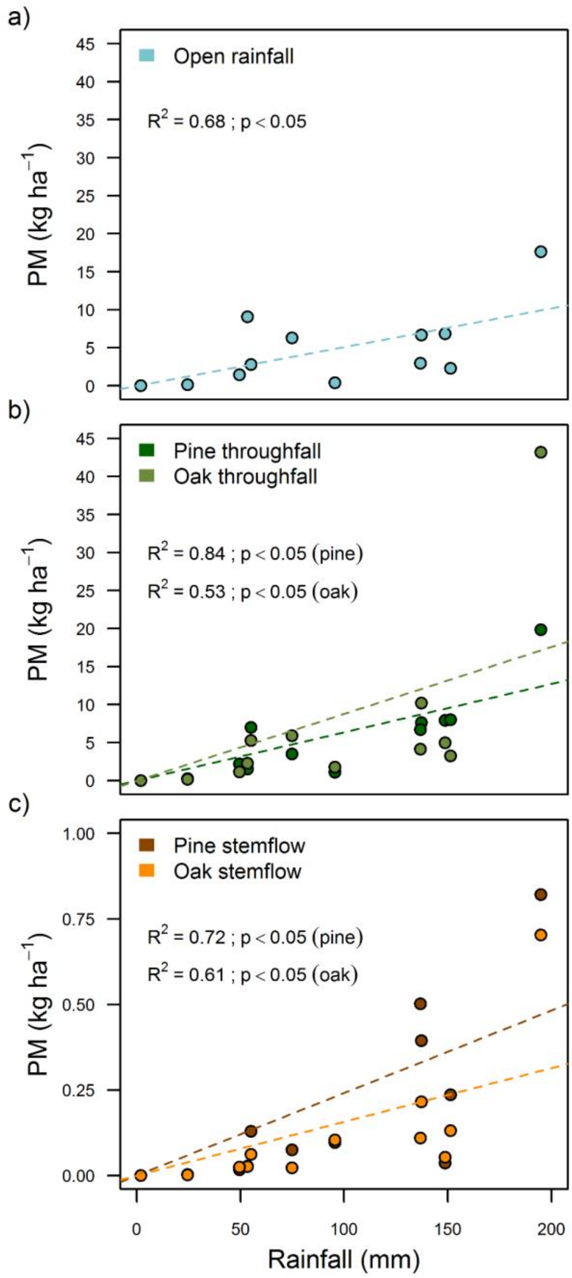


**Figure 4.5.** Correlations between monthly rainfall and monthly particulate matter for (a) open rainfall, (b) throughfall and (c) stemflow, in the pine and oak forest plots.

Overall, net deposition was positive throughout the year (Figure 4.6). Total net deposition into soil was higher in oaks than in pines; oaks released annually 27.4 kg ha$^{-1}$ to the soil layers via throughfall and stemflow, while pines released 12.7 kg ha$^{-1}$. The greatest differences between species occurred mainly during spring and summer, coinciding with the leafed season for oaks. Nevertheless, the highest retention of PM on leaves and stems of pines and oaks occurred during Saharan dust events, which were associated with low rainfall intensities (Figure 4.6 a, b and c).

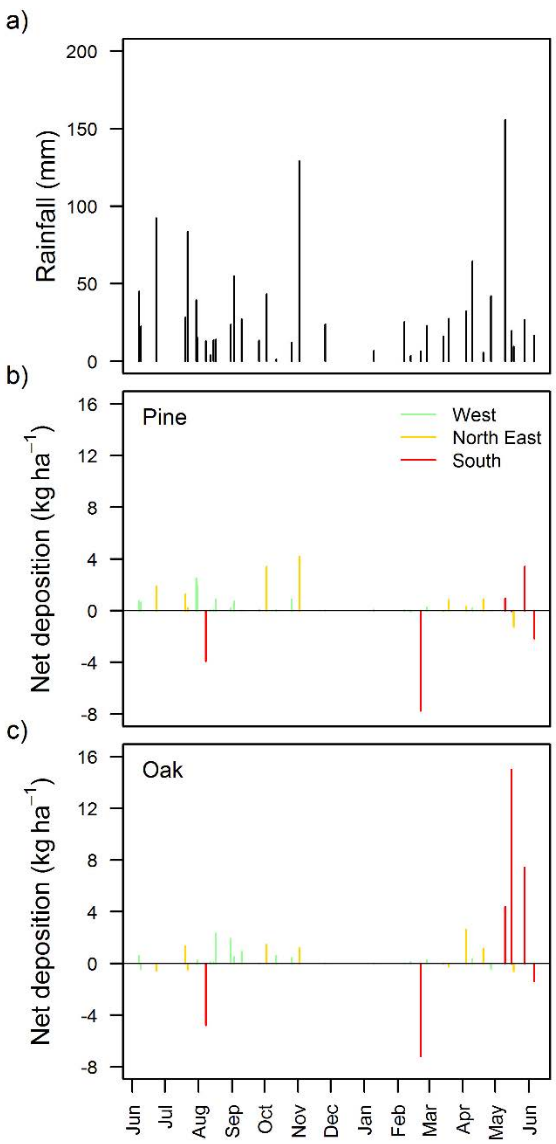


**Figure 4.6.** Time-series of (a) daily rainfall and event net deposition in (b) pine and (c) oak. Colours indicate the origin of the air mass.

### 4.3.2. Within-storm particulate matter fluxes

The analysis of intra-event fluxes in pines showed that particulate matter fluxes did not only vary between events, but also within the event. Overall, stemflow enrichment ratios of PM were higher when compared to rainfall ($E_{PB}$) than when compared to throughfall ($E_{TB}$). Rainfall intensity controlled enrichment ratios in different ways. For example, during low-intensity events (Figure 4.7a), enrichment ratios increased throughout the event and differences between $E_{PB}$ and $E_{TB}$ decreased, whereas high-intensity rainfall events resulted in peaks of enrichment ratios, mainly for $E_{PB}$, although this was also observable in $E_{PT}$. This trend was clearly seen in Figure 4.7c, when peak rainfall intensity coincided with maximum PM enrichment. Nonetheless, this tendency was also observed in events of varying intensity (Figures 4.7 b and d).

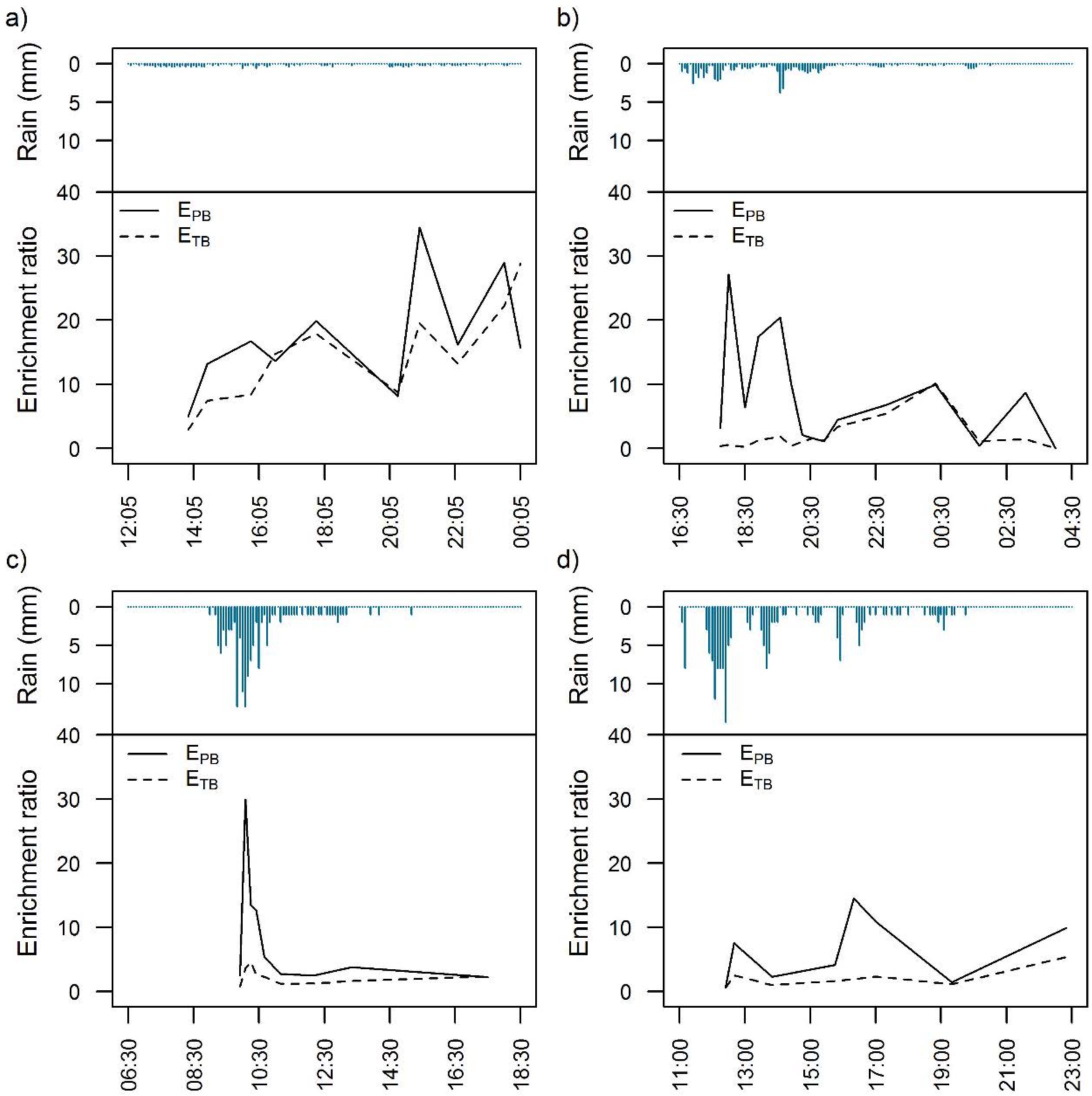


**Figure 4.7.** Intra-event time-series of stemflow enrichment ratios compared to rainfall ($E_{PB}$) and throughfall ($E_{TB}$) in the pine stand.

### 4.3.3. Particulate matter size distributions

The maximum diameters of 672,906 individual particulates were analysed to examine differences between open precipitation, throughfall and stemflow for pines and oaks. In general, median throughfall PM diameters were higher than open rainfall ones. The greatest diameters were observed for oak during the leafed period when the median PM size increased by 2 µm. The PM diameters in open rainfall and in throughfall in oaks during the leafless season were very similar. In contrast, stemflow PM diameters tended to be smaller than open rainfall ones, except for oak during the leafed period. Though the lower quantile of particulate diameters was similar in water fluxes, there was greater variability among the higher quantiles (Table 4.1).

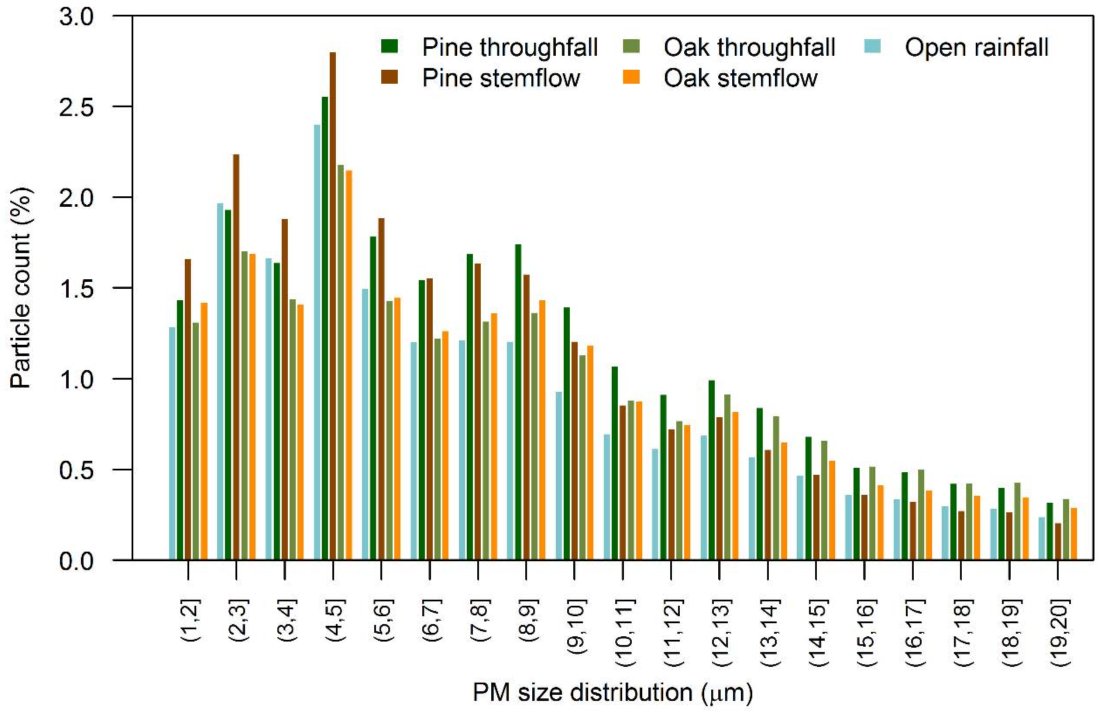


**Figure 4.8.** Particulate matter diameter frequency distributions of open rainfall, throughfall and stemflow in pine and oak for seven rainfall events. The frequency is relative to the total number of particles in each size class. For purposes of illustration, there are only 19 classes represented in the Figure, but PM of up to 500 µm diameter was found.

**Table 4.1.** Statistical summary of maximum particle diameters for open rainfall, stemflow and throughfall in pines and oaks during leafed and leafless periods.

| | Maximum particulate diameter (µm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Median** | **Lower Quantile** | **Higher Quantile** | **Mean** | **Standard Deviation** | **Max/Min Feret Ratio** | **Skewness** |
| *Open rainfall* | 7.2 | 4.2 | 13.6 | 12.7 | 20.9 | 1.66 | 8.1 |
| *Stemflow* | | | | | | | |
| Pine | 6.7 | 4.1 | 11.4 | 10.0 | 13.2 | 1.70 | 7.2 |
| Oak leafed | 8.1 | 4.5 | 13.0 | 10.7 | 12.0 | 1.69 | 8.9 |
| Oak leafless | 5.4 | 3.6 | 9.8 | 8.2 | 9.8 | 1.60 | 7.1 |
| *Throughfall* | | | | | | | |
| Pine | 8.1 | 4.5 | 13.6 | 11.8 | 15.6 | 1.65 | 8.3 |
| Oak leafed | 9.4 | 5.0 | 17.0 | 15.6 | 22.9 | 1.75 | 6.3 |
| Oak leafless | 7.2 | 4.2 | 12.8 | 11.0 | 15.0 | 1.63 | 7.5 |

All particulate diameter frequency distributions were skewed to the right (Figure 4.8) and the highest number of particles was found in throughfall and stemflow for pine fluxes. Stemflow had a higher proportion of small particles (0.45 < PM < 2.5 µm) than throughfall, but a lower proportion of coarse PM for both pines and oaks (Figure 4.9). Results showed that, in general, PM tended to be round; the less round particles were found in stemflow for pine and in throughfall for oak during the leafed period. A negative exponential relationship was observed between roundness and PM size ($r^2 = 0.70$, $p < 0.05$); in general, the coarse PM of water fluxes tended to be less round than fine PM.

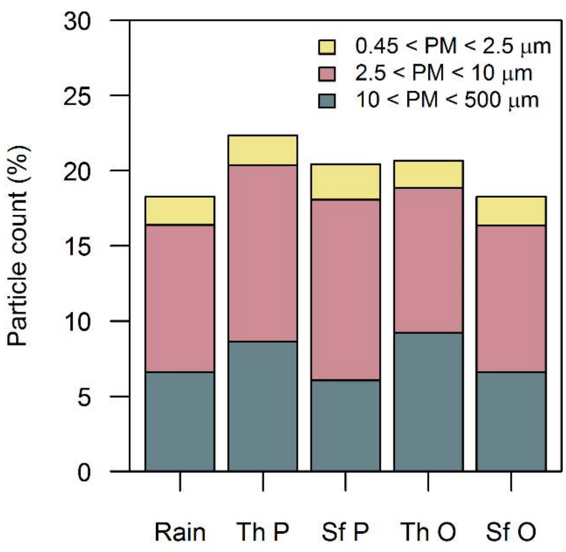


**Figure 4.9.** Relative number of particles by flux and diameter class.

## 4.4. DISCUSSION

### 4.4.1. Spatio-temporal variations of particulate matter fluxes

The load of particulate matter arriving at the study site varied significantly, depending on the origin of its air mass. Like Castillo *et al.* (2017), we found that rain-laden Atlantic advections cleaned the atmosphere, leading to the lowest content of PM in open rainfall. On the contrary, the load of PM increased for rainfall coming from the Mediterranean basin or from other regions of the European continent. These air masses would have been more affected by pollutants that build up during long dry spells. Particularly important were the air masses coming from North Africa. They represented more than half of the total PM reaching the study area, even though they only accounted for 16% of the events. On the Iberian peninsula, African intrusions usually occur in spring-summer (Castillo *et al.*, 2017), but, as observed here, sporadic intrusions may occur throughout the year, leading to disproportionate outbursts of PM on specific days with significant inputs of minerals such as phyllosilicates, quartz or calcite (Lequy *et al.*, 2018) and nutrients, particularly phosphorous, which in some ecosystems could be a limiting factor (Morales-Baquero and Pérez-Martínez, 2016). We also observed that the rainiest months coincided with the highest PM fluxes, but this correlation was not significant when analysed at the event scale. This lack of correlation might be related to the accumulation of PM by dry-deposition processes in the period between rains.

### 4.4.2. Particulate matter fluxes below the canopy

Throughfall is the dominant flux of water below trees, which is why studies analysing PM fluxes in forested areas have often focused on this water flux (e.g. Lovett and Lindberg, 1984; Lindberg *et al.*, 1986; Cape, 2008). When expressed by area, throughfall PM inputs were 1.2- and 1.4-fold greater than open rainfall and 28- and 56-fold greater than stemflow ones in pines and oaks, which is similar to the findings of Lequy *et al.* (2014). However, despite representing only a small proportion of rainfall, the higher enrichment ratios of stemflow than rainfall and throughfall, underline the importance of stemflow as a localized input source of water and PM to soil near the trunks. These findings corroborate previous work on stemflow (e.g. Levia and Germer, 2015; Michalzik *et al.*, 2016; Carlyle-Moses *et al.*, 2018), which highlighted the importance of stemflow as a preferential flow path of chemically enriched water to the soil that facilitates the release of nutrients previously bound in plants. Higher enrichment ratios are most probably due to the longer path that stemflow has to take before reaching the soil. The increase of the contact time of water with leaves and stems may enhance the enrichment of water with PM, especially during high rainfall intensities when the mobilization of previously dry-deposited PM and greater scouring of the bark surface increase input of particles to the soil, causing short-term changes in the rates of nutrient cycling due to the prompt availability to PM (Lovett and Ruesink, 1995).

Canopy, bark structure and leaf characteristics partly explained the differences between the species studied. Like other researchers (Beckett *et al.*, 1998; Grantz *et al.*, 2003; Sæbø *et al.*, 2012), we found that, overall, pines accumulated more particles than broad-leaf species, although this did depend strongly on rainfall amount and intensity. Low rainfall and low-intensity events were less effective when removing PM previously deposited on leaves. In addition, higher enrichment ratios in stemflow for oaks suggested a higher mobilization of PM through the stems of oaks, which increased the availability of particles and nutrients at the base of oak trees. On the contrary, as pines retained more PM and as they keep their needles for several years, the recycling of PM accumulated on their needles is more limited (Dzierżanowski *et al.*, 2011).

### 4.4.3. Particulate matter size distributions

As in other studies (Levia *et al.*, 2013; Song *et al.*, 2015), PM size distributions were skewed to the right, with a larger amount of fine particles (< 6 µm), confirming that our study site corresponded to a rural area far from busy roads, where the proportion of coarse PM retained in leaves would be higher (Beckett *et al.*, 2000). Seasonality was also found to influence particulate matter size distribution between species. In general, maximum PM diameters were higher for throughfall in pines and oaks during the leafed period, whereas, during the leafless period, the size of PM in oaks become closer to that in open rainfall, indicating that leaves were able to retain and enhance the interaction and aggregation between PM. This aggregation could happen between the plant surfaces and the wax layer (Dzierżanowski *et al.*, 2011). Likewise, due to the higher aggregation capacity of PM in leaves, larger PM diameters were observed in stemflow for oaks, despite the size of the PM content in stemflow for both pines and oaks being smaller than in throughfall. The smaller PM diameter in stemflow than in throughfall may be the result of its scouring with the bark during its pathway to the soil. Consequently, the smaller particles found in stemflow than in open rainfall and throughfall, along with a high volume of water reaching the base of the trees, could enhance the input of soil nutrients, energy flows and the spatial patterning of biogeochemical processes (Lovett and Ruesink, 1995; Michalzik *et al.*, 2016).

## 4.5. CONCLUSIONS

Particulate matter content below the canopy of a Scots pine and a downy oak stand was almost 1.5 times higher than in open rainfall. Overall, the content of PM in rain, throughfall and stemflow correlated with rainfall amount, although Saharan dust events increased PM content disproportionately: only 16% of rainfall events occurred during Saharan dust intrusions, but these represented almost 60% of the total PM in the study area. Overall, the concentration of PM was similar between throughfall and stemflow, yet the higher flux-based enrichment ratios measured in stemflow confirmed its importance as the preferential flow path of chemically enriched water to the soil, facilitating the release of nutrients previously bound in plants. Within an event, rainfall intensity enhanced the mobilization of PM to the soil. Further, the interaction between PM and vegetative surfaces was found to be a key factor determining the amount and size of PM. The presence of leaves on oaks increased the diameter and the content of PM released by throughfall. On the other hand, the diameter of PM in stemflow was smaller than in open rainfall and throughfall, indicating a possible scouring of the particles by the bark during their pathway to the soil. This study highlights the importance of considering stemflow in nutrient and energy flux studies, as it is the major source of PM at the base of trees. Future research will need to look at the elemental analysis of PM content, as this will provide valuable information about nutrients and pollutants reaching forests.

## ACKNOWLEDGEMENTS

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# CHAPTER 5

## Modification of the isotopic composition of rainfall by throughfall and stemflow: the case of Scots pine and Downy oak forests under Mediterranean conditions

Most hydrological studies based on stable water isotopes ($^{18}O$ and D) use the isotopic composition of rainfall as input signal. Although stable water isotopes are conservative tracers, previous studies have shown that canopies modify the isotopic composition of rainfall. At present, there is scientific agreement about the factors involved in isotopic modification, but the effect of each factor and the magnitude of the isotopic shift are still not clear. In this study, we analyse at an inter- and intra-event basis the spatio-temporal differences between the isotopic composition of rainfall, throughfall and stemflow for two different species (*Pinus sylvestris* L. and *Quercus pubescens* Willd). The aim of the study is to analyse the isotopic modification that takes place in throughfall and stemflow and how meteorological variables and structural forest characteristics influence the observed changes. Rainfall and throughfall were sampled by a combination of bulk and sequential collectors, whereas stemflow was collected only by bulk collectors. Results showed that the isotopic modification occurred in both directions, although stemflow was consistently more enriched than throughfall. Despite the contrasting canopy structures, no significant differences between species were found. Moreover, the intra-event analysis suggested that all fractionation factors could occur during one event, but evaporation or isotopic exchange would have a higher impact at the beginning of rainfall, whereas canopy selection processes would be more important at the end of rainfall. Our results emphasise the importance of considering the isotopic composition of throughfall and stemflow in isotope-related studies in forested catchments.

**Original work:** Cayuela, C., Llorens, P., Sánchez-Costa, E., Latron, J. 2018. Modification of the isotopic composition of rainfall by throughfall and stemflow: the case of Scots pine and Downy oak forests under Mediterranean conditions. *Ecohydrology*, e2025. https://doi.org/https://doi.org/10.1002/eco.2025

## 5.1. INTRODUCTION

In recent decades, the isotopic composition of rainfall ($^{18}O$ and D) has increasingly been used as an input signal to trace the source and movement of water in a catchment (Kendall and McDonnell, 1998). However, in forested or partly forested catchments, throughfall and stemflow have seldom been considered when defining the catchment input signal, although previous studies have shown that there may be a shift in their isotopic composition.

Saxena (1986) was one of the first to observe that throughfall was in general more enriched in heavy isotopes of Oxygen ($\delta^{18}O$) than open rainfall, even though depletion was also found on some occasions. Enrichment was attributed to isotopic fractionation in non-equilibrium conditions, whereas depletion was associated with the retention in the canopy of the last portion of rain during events of varying isotopic composition. This process was named selective canopy storage by Dewalle and Swistock (1994). In addition, these authors, noting the lack of relationship between interception loss and the isotopic composition of throughfall, and also because samples fell on the local meteoric water line, suggested that selective canopy storage was more important than fractionation caused by evaporation. Friedman (1962) also showed that isotopic fractionation could be achieved by the isotopic exchange between vapour and liquid during high-humidity atmosphere conditions. Molecular exchange could result in enrichment or depletion, preferably enrichment, except under conditions of relative humidity close to 100% and a high difference in $\delta^{18}O$ between rain water and water vapour (Brodersen *et al.*, 2000). More recently, Allen *et al.* (2014) suggested that the isotopic composition of throughfall could also be influenced by the presence of residual water from previous rainfall, retained within the canopy and mixed with the new rainfall input, resulting in either enrichment or depletion. However, their results were for a location with high mean annual precipitation (2000 mm year$^{-1}$), high mean relative humidity (99%) and inter-event rain-free periods shorter than 2 days.

The isotopic composition of stemflow is generally assumed to undergo similar processes as throughfall. However, Kubota and Tsuboyama (2003) observed that stemflow samples were in general more enriched in $\delta^{18}O$ than throughfall samples, although no specific reasons for such differences were discussed by the authors. Ikawa *et al.* (2011), based on the different isotopic dynamics of stemflow rather than open rainfall and throughfall, suggested that the isotopic composition of stemflow could be affected more by mixing with rain water previously stored in the canopy and the stems. All these processes occur in the canopy and result in isotopic offsets of throughfall and stemflow from rainfall. Offsets can be different depending on the canopy characteristics, usually being greater in coniferous forests than in broadleaf forests, possible due to their higher storage capacity (Allen *et al.*, 2017). Until now, research efforts have tried to understand the factors that produce the modification of the isotopic composition of water that falls through the canopy, but no clear temporal or spatial patterns have yet been found (Allen *et al.*, 2017). Moreover, most recent studies have focused on throughfall (e.g. Brodersen *et al.*, 2000; Kato *et al.*, 2013; Allen *et al.*, 2014, 2015; Qu *et al.*, 2014; Xu *et al.*, 2014; Hsueh *et al.*, 2016), whereas shifts in the isotopic composition of stemflow have been much less widely studied (e.g. Kubota and Tsuboyama, 2003; Ikawa *et al.*, 2011) despite recent studies have highlighted its importance as a preferential flow-path of water to the soil (Levia and Germer, 2015). In the study area, stemflow accounted for ~1% of the incident rainfall; however, stemflow reaching the base of a tree (expressed as l $m^{-2}$) could represent more than 10 times the volume of rainfall, therefore, its influence on the isotopic composition of soil water should not be underestimated (Cayuela *et al.*, 2018b).

The analysis of the intra-event variability of the isotopic composition of throughfall and stemflow has proved to be a useful tool (Allen *et al.*, 2017), although there are only a few studies (Kubota and Tsuboyama, 2003; Ikawa *et al.*, 2011; Qu *et al.*, 2014) and these have no strong concluding remarks. Therefore, there is still an important challenge to understand how and why the isotopic composition of rain is modified during rainfall partitioning processes (Hsueh *et al.*, 2016; Allen *et al.*, 2017) and what implications this has for the identification of water sources and paths through a forested or partly forested catchment. Low resolution samplings of soil water (weekly or monthly) may dampen the propagation of any interception effect in the soil (Stockinger *et al.*, 2016) and reduce the isotopic spatial variability of soil water. Despite this fact, Stockinger *et al.* (2015) found that changes in the isotopic composition of open rainfall due to canopy interception were relevant and had to be considered for isotope-based transit time studies. In addition, other studies using higher sampling resolution (event sampling) like Kubota and Tsuboyama (2003) also found differences when incorporating the isotopic composition of throughfall; in that case they found differences of 5-10% in the contribution of pre-event water for hydrograph separation. These studies show up the importance of considering throughfall and stemflow in hydrological studies.

In this study, we examine the paired isotopic differences of throughfall-rainfall and stemflow-rainfall, using a combination of bulk and sequential samples. The main objectives of the study are (i) to analyse the spatio-temporal differences between the isotopic composition of rainfall, throughfall and stemflow for two different species: *Pinus sylvestris* L. (Scots pine) and *Quercus pubescens* Willd. (downy oak) and (ii) to relate these differences to different meteorological conditions and structural forest characteristics to gain some knowledge on the fractionation factors that occur in the canopy.

## 5.2. METHODOLOGY

### 5.2.1. Study area

The study area is located in the Vallcebre research catchments (NE Spain, 42º 12'N, 1º 49'E) in the eastern Pyrenees at 1100 m asl (meters above sea level). These catchments have been monitored for various hydrological purposes since 1988 (Llorens *et al.*, 2018). The climate is Sub-Mediterranean, with a mean annual temperature of 9.1 ± 0.67ºC, a mean annual precipitation of 880 ± 200 mm and a mean annual evapotranspiration of 823 ± 26 mm (1989-2015). The precipitation regime is seasonal; autumn and spring are usually wetter, while summer and especially winter are often dryer seasons. Summer rainfall is characterized by intense convective events, whereas during the rest of the year precipitation is generally caused by frontal systems.

The original oak forest (*Quercus pubescens* Willd.), in the sunny aspects, and Scots pine (*Pinus sylvestris* L.), in the shady ones, were deforested in the past and most of the area was terraced for agricultural production. After the abandonment of agricultural activities in the sixties, most of the terraces underwent spontaneous afforestation by Scots pines (Poyatos *et al.*, 2003). Two forest plots were selected for the study, a pine and an oak stand. The pine stand is oriented towards the northeast at an elevation of 1,200 m and has an area of 900 $m^2$, a tree density of 1,189 trees $ha^{-1}$ and a basal area of 45.1 $m^2$ $ha^{-1}$. The oak stand is oriented towards the southeast at an elevation of 1100m and has an area of 2,200 $m^2$, a tree density of 518 trees $ha^{-1}$ and a basal area of 20.1 $m^2$ $ha^{-1}$ (Figure 5.1).

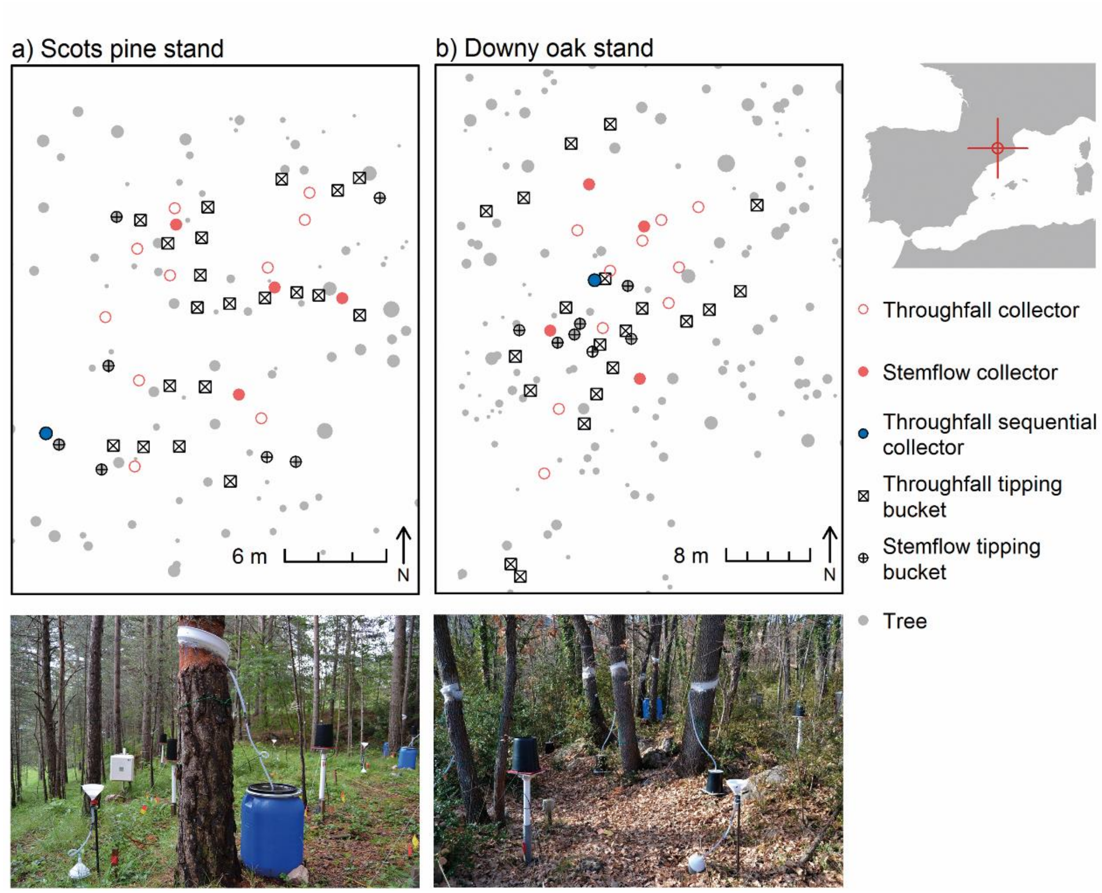


**Figure 5.1.** Location and maps of the monitored stands in the Vallcebre research catchments. (a) Scots pine stand and (b) Downy oak stand. Grey dots represent the distribution of trees. The size is proportional to the diameter at breast high (DBH).

### 5.2.2. Hydrometric and meteorological monitoring

In each stand, rainfall was measured with a tipping bucket rain gauge located in a clearing less than 100 m from each stand. Throughfall was measured with 20 tipping bucket rain gauges (Davis Rain Collector II, Davis Instruments) spatially distributed according to canopy cover distribution. The tipping buckets were placed at the 20 most representative locations. Canopy cover was determined from 50 hemispherical photographs taken at each stand. A complete description of the method to determine the canopy cover can be found in Llorens and Gallart (2000). Stemflow was measured in seven trees, representing the range of diameter at breast height (DBH) distributions, with stemflow rings connected to tipping bucket rain gauges. Meteorological data were obtained from 15 and 18 m towers at the oak and pine stands, respectively. Each station monitored air temperature, relative humidity, net radiation, wind speed and wind direction 1 m above the canopy. Wet canopy evaporation was calculated by the Penman–Monteith equation with a stomatal resistance set to zero (Stewart, 1977). All data were recorded at 5-min intervals by a datalogger (DT80, Datataker Inc.).

### 5.2.3. Isotopic sampling

Sampling was carried out from May 2015 to May 2016 on an event basis. To take into account seasonal changes in canopy cover, as well as possible temporal differences due to air temperature, two time-periods were considered: the growing season from May 15$^{th}$ to October 15$^{th}$, which covered the period of higher air temperature; and the dormant season for the remaining months, which covered the period of lower temperature. To ensure the dryness of the canopy between successive rainfall events, the inter-event period was set to be at least 6 hours (without any rainfall) during the day and 12 hours during the night (Llorens *et al.*, 2014). As a result, 22 individual rainfall events that had not been mixed with previous or following events, were analysed.

In each study plot, throughfall was sampled with 10 collectors consisting of plastic funnels 130 mm in diameter positioned 50 cm above ground and connected to a plastic bin by looped tubing. The plastic bin had 1 litre capacity and was placed in the ground to prevent heating and evaporation. The location of each throughfall collector was selected to represent all ranges of canopy cover in each stand (from 30 to 88% in the pine stand, and from 30 to 95% in the oak stand). In addition, throughfall was sampled automatically, at 5 mm rainfall intervals, using a plastic funnel (340 mm diameter) connected to an automatic water sampler (ISCO 3700C). Stemflow was sampled on 4 trees with different DBH (~ 15, 20, 25 and 30 cm) representative of the DBH distributions in each stand, using a stemflow ring connected to a 60 litre polyethylene bin by looped tubing. Rainfall was sampled in a clearing near each stand by means of a bulk collector and an automatic sampler (5 mm rainfall intervals) in the same way as for throughfall.

To ensure the reliability of the collectors in preventing evaporation, one additional collector was filled with water of a known isotopic composition and was sampled once a week. After 5 weeks, water in this collector showed a mean fractionation of 0.05‰ for $\delta^{18}O$ and 0.30‰ for $\delta D$. Nonetheless, all samples used in this study were collected within 1 to 4 days after each storm; and funnels and bins were cleaned and dried before the following rainfall.

### 5.2.4. Isotopic analysis

Stable water isotopes ($^{18}O$ and D) were analysed by a Cavity Ring-Down Spectroscopy Picarro L2120-i isotopic water analyser at the Scientific and Technological Services of the University of Lleida. Accuracy of the L2120-i, based on the repeated analysis of four reference water samples, was < 0.1‰ and < 0.4‰ for $\delta^{18}O$ and $\delta D$, respectively. All isotope data are expressed in terms of δ-notation as parts per mil (‰). Moreover, deuterium excess (d-excess) which relates $\delta D$ and $\delta^{18}O$ (Equation 5.1) was calculated and used as an indicator of kinetic or equilibrium fractionation (Dansgaard, 1964).

$$d\text{-}excess = \delta D - 8 \cdot \delta^{18}O \qquad (5.1)$$

### 5.2.5. Data analysis

The isotopic modification of throughfall ($\Delta\delta^{18}O_{TF\text{-}RF}$) was calculated as the difference between $\delta^{18}O$ of throughfall and $\delta^{18}O$ of rainfall; and the isotopic modification of stemflow ($\Delta\delta^{18}O_{SF\text{-}RF}$), as the difference between $\delta^{18}O$ of stemflow and $\delta^{18}O$ of rainfall. The modification of the d-excess of throughfall ($\Delta$d-excess$_{TF\text{-}RF}$) and stemflow ($\Delta$d-excess$_{SF\text{-}RF}$) was expressed similarly. The combination of the isotopic and d-excess differences was used to speculate about the operating mechanisms in the canopy (Brodersen *et al.*, 2000). To analyse the isotopic modification of throughfall and stemflow at the event scale, a linear mixed model (LMM) with repeated measurement structure was set. After checking for collinearity among measured variables, the model included rainfall depth, maximum wind speed, canopy cover, DBH, season and species, as fixed factors; and the location of each collector, as a random effect. Results of the model are expressed according to the Fisher distribution ($F_{dfn,\ dfd}$), indicating the degrees of freedom in the numerator (dfn) and degrees of freedom in the denominator (dfd). Finally, to analyse possible temporal persistent stability patterns of throughfall depth, $\Delta\delta^{18}O$ and $\Delta$d-excess, time-stability plots (Keim *et al.*, 2005) with standardized data were performed.

## 5.3. RESULTS

### 5.3.1. Isotopic composition of rainfall, throughfall and stemflow

The rainfall depth of the analysed events ranged from 2.3 mm to 69.1 mm; and mean rainfall intensities, from 0.4 mm $h^{-1}$ to 23.0 mm $h^{-1}$. Overall, mean rainfall intensity increased with rainfall depth ($F_{1,\ 428} = 566.6$; $p < 0.01$). For these events, mean relative throughfall was 77%

in the pine stand and 76% in the oak stand. Mean relative stemflow accounted for 1.5% and 0.9% of the incident rainfall in the pine and oak stands; four events did not produce enough stemflow to measure its isotopic composition.

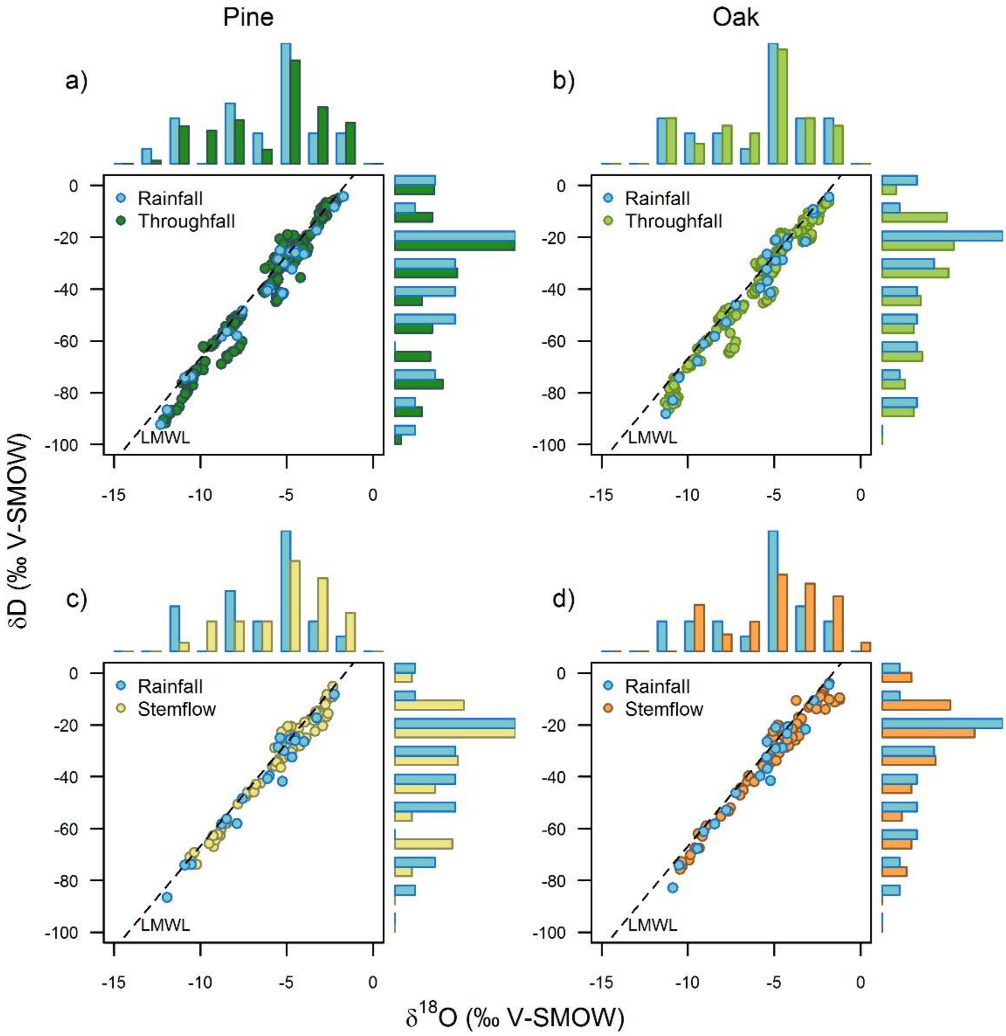


**Figure 5.2.** $\delta^{18}O$ and $\delta D$ values of rainfall, throughfall and stemflow for the pines and oaks. The histogram borders show partitioning of the data sets at 10 equivalent intervals. The dashed line shows the local meteoric water line (LMWL). V-SMOW, Vienna-Standard Mean Ocean Water.

$\delta^{18}O$ values in bulk rainfall of both stands ranged from -12.32‰ to -1.72‰; and $\delta D$ values, from -92.30‰ to -4.18‰. Rainfall samples fell on the Local Meteoric Water Line (LMWL) of the Vallcebre Research Catchments, $\delta D = 7.96\ \delta^{18}O + 12.89$, which was determined by the least squares method for $\delta^{18}O$ and $\delta D$ measured in bulk rainfall samples during the period 2011-2016. Throughfall and stemflow samples also fell on the LMWL; values of $\delta^{18}O$ of throughfall in the pine stand ranged from -12.13‰ to -2.03‰ and in the oak stand from -11.33‰ to -1.83‰. For stemflow, $\delta^{18}O$ values ranged from -10.61‰ to -2.33‰ in the pine stand and from -10.46‰ to -1.22‰ in the oak stand (Figure 5.2).

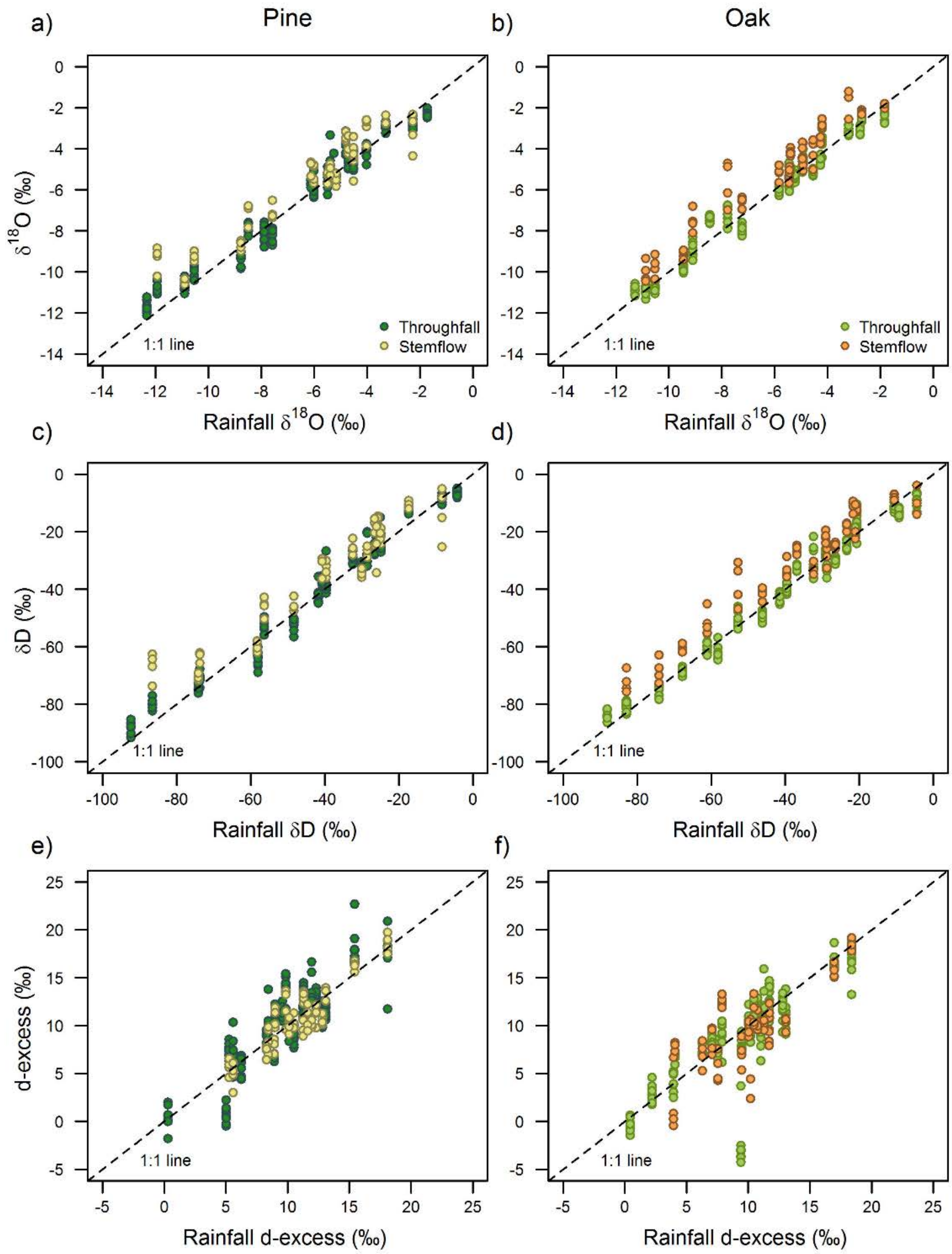


**Figure 5.3.** Relationship between $\delta^{18}O$ of rainfall and throughfall for the pines (a) and oaks (b), between δD of rainfall and throughfall (c, d) and between d-excess of rainfall and throughfall (e, f).

In general, the isotopic composition of throughfall and stemflow followed similar distribution to rainfall but with heavier isotopic composition for $\delta^{18}O$ ($F_{2, 26} = 129.24$; $p < 0.01$) (Figure 5.3 a and b) and for $\delta D$ ($F_{2, 26} = 90.74$; $p < 0.01$) (Figure 5.3 c and d). For both isotopes, throughfall was more enriched than rainfall and stemflow was more enriched than throughfall. In the pine stand, 55% of throughfall and 81% of stemflow samples were enriched in $\delta^{18}O$. In the oak stand, enrichment occurred for 50% of throughfall and 94% of stemflow samples. Similar trends were observed for $\delta D$.

Between stands, however, there were no statistically significant differences in $\Delta\delta^{18}O_{TF-RF}$ ($F_{1, 16} = 2.91$; $p = 0.11$) and $\Delta\delta^{18}O_{SF-RF}$ ($F_{1, 4} = 1.53$; $p = 0.28$); the $\Delta\delta^{18}O_{TF-RF}$ in the pine stand ranged between -1.13‰ and 2.05‰, and in the oak stand between -1.02‰ and 1.25‰. On the other hand, $\Delta\delta^{18}O_{SF-RF}$ ranged between -2.1‰ and 3.08‰ in the pine stand, and between -0.52‰ and 3.07‰ in the oak stand. From Figure 5.3e and f, it can be inferred that not all samples enriched in $\delta^{18}O$ and $\delta D$ corresponded with a decrease of d-excess and not all depleted samples in $\delta^{18}O$ and $\delta D$ corresponded with an increase of d-excess, as would be expected from non-equilibrium fractionation processes. Indeed, from the enriched samples in the Scots pine stand, only 35% of throughfall and 37% of stemflow samples had negative d-excess. In the oak stand, this was the case for 28% of throughfall and 51% of stemflow samples; similar percentages were found for $\delta D$.

### 5.3.2. Spatio-temporal patterns in the modification of the isotopic composition of rainfall

Rainfall with heavier $\delta^{18}O$ was more common in events occurring at the end of spring and in summer, when air temperature was higher. In general, a seasonal pattern linked to air temperature was observed in the isotopic composition of rainfall throughout the year (Figure 5.4a and b). Results showed that depleted throughfall (negative $\Delta\delta^{18}O_{TF-RF}$) was more common during the growing season ($F_{1, 404} = 4.39$; $p < 0.05$) (Figure 5.4 c and d). Moreover, $\Delta\delta^{18}O_{TF-RF}$ decreased for rainfall depths higher than 20 mm ($F_{1, 404} = 4.22$; $p < 0.05$) in both stands (Figure 5.5a). For rainfall depths lower than 20 mm (corresponding with rainfall intensities lower than 5 $mmh^{-1}$), differences between throughfall and rainfall were higher. In addition, a greater spatial variability between throughfall collectors was observed during these events, with $\delta^{18}O$ coefficients of variation (CV) up to 10% in the pine stand and 15% in the oak stand. For higher rainfall depth (>20 mm), CV were in general lower than 5% (Figure 5.5b). On the other hand, stemflow was more enriched (positive $\Delta\delta^{18}O_{SF-RF}$) during the growing season ($F_{1,\ 127}$ = 13.13; $p$ < 0.01) (Figure 5.4e and f) and isotopic differences were marginally less for higher rainfall amounts ($F_{1,\ 127}$ = 3.02; $p$ = 0.08) (Figure 5.5c). The spatial variability of $\delta^{18}O$ among collectors was also higher for low rainfall amounts, with CV up to 20% in the oak stand and 30% in the pine stand. Higher rainfall amounts decreased CV among collectors (Figure 5.5d).

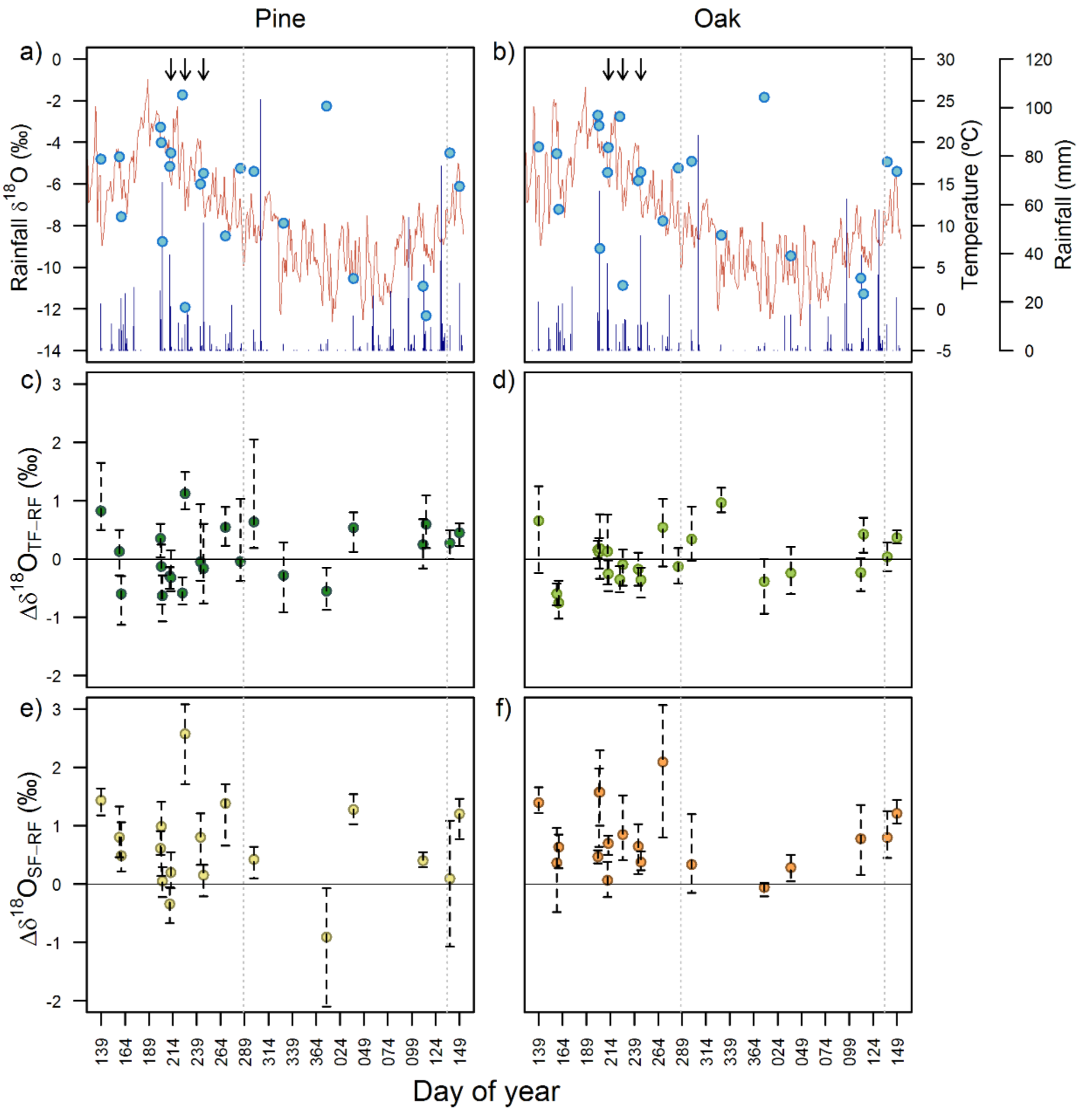


**Figure 5.4.** Time series of daily rainfall, daily temperature and event $\delta^{18}O$ of rainfall in the pine (a) and oak (b) stands. Time series of the isotopic $\delta^{18}O$ differences between throughfall and rainfall (c, d). Time series of the isotopic $\delta^{18}O$ differences between stemflow and rainfall (e, f). Black dashed lines represent the range of observed differences for each event (from 10 samples for throughfall and 4 samples for stemflow). Grey vertical dashed lines mark the growing and dormant seasons; and black arrows indicate the events analysed at the intra-event scale.

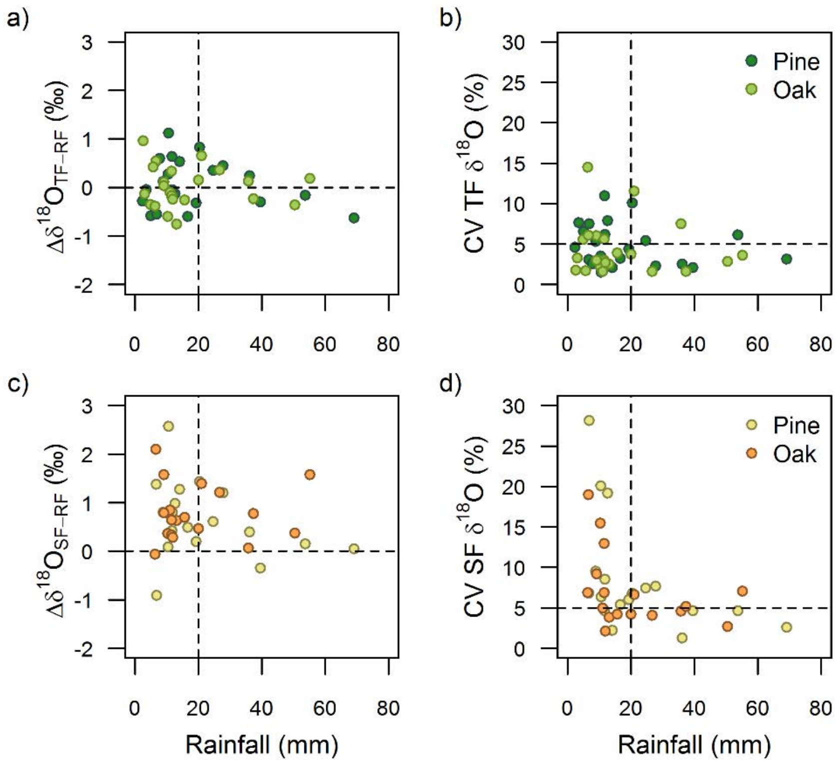


**Figure 5.5.** Mean event $\delta^{18}O$ differences between thoughfall and rainfall (a) and stemflow and rainfall (c) as a function of event rainfall depth. Spatial variability of $\delta^{18}O$ in throughfall (b) and stemflow (d), expressed as the coefficient of variation (CV) among collectors.

The spatial distribution of throughfall depth measured in each collector from event to event showed a persistent temporal stability (Figure 5.6a) that neither $\Delta\delta^{18}O_{TF\text{-}RF}$ (Figure 5.6b) nor $\Delta$d-ecxess$_{TF\text{-}RF}$ (Figure 5.6c) had in pines or oaks. However, a marginal relationship ($F_{1,\,16}$ = 3. 52; $p$ = 0.07) between the $\Delta\delta^{18}O_{TF\text{-}RF}$ and the canopy cover was found (Figure 5.6e). This effect was more clearly seen in the pine stand, where the most covered collectors had higher $\Delta\delta^{18}O_{TF\text{-}RF}$. However, throughfall volume and $\Delta$d-excess$_{TF\text{-}RF}$ did not show persistent temporal stability patterns (Figures 5.6d and 5.6f) when ranked by canopy cover. No stable patterns could be observed for throughfall in oaks during the dormant season neither for stemflow (data not shown).

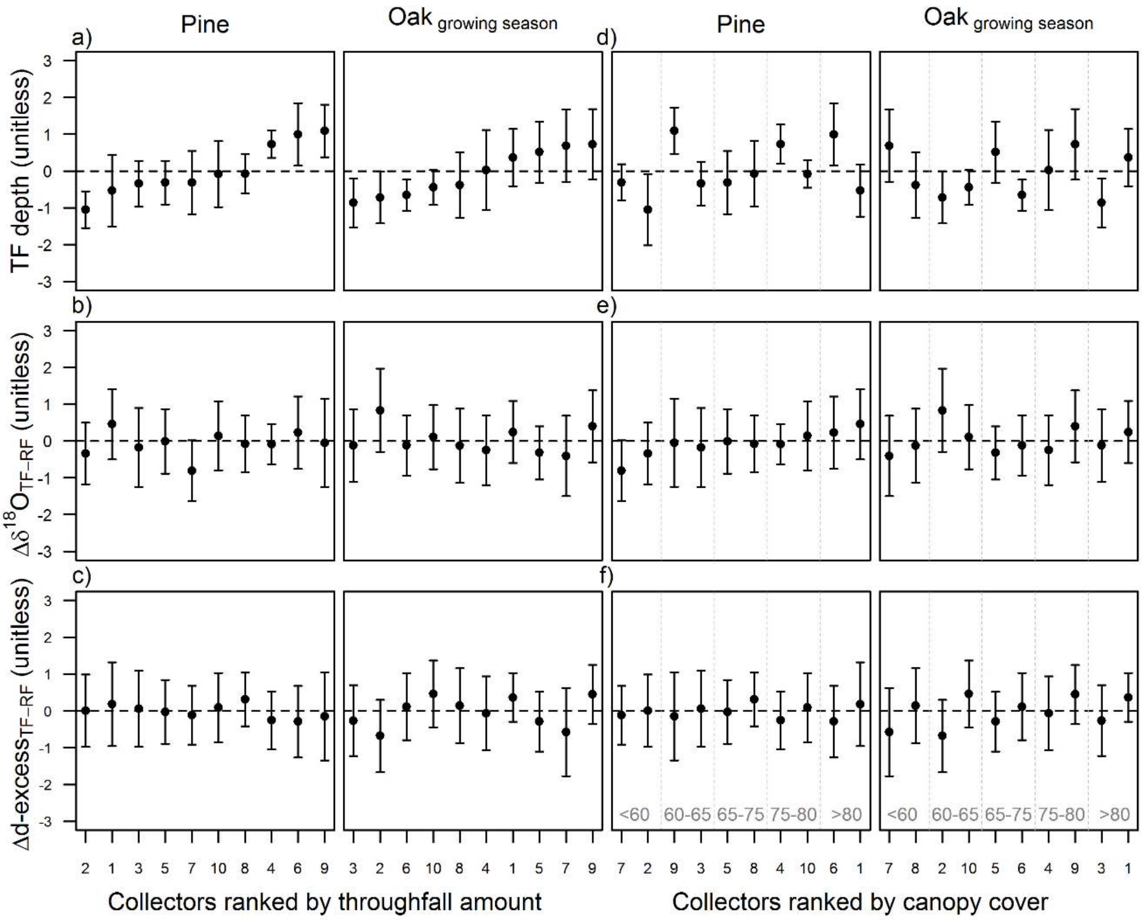


**Figure 5.6.** Time stability plots of normalized throughfall depth (a, d) in the pine (during the dormant and growing seasons) and oak (only during the growing season) stands; normalized $\delta^{18}O$ differences between throughfall and rainfall (b, e) and normalized d-excess differences between throughfall and rainfall (c, f). In (a, b, c) collectors are ranked according to throughfall amount; in (d, e, f) collectors are ranked by canopy cover. The grey number at the bottom of the Figure indicates the canopy cover percentage.

### 5.3.3. Intra-storm isotopic composition of rainfall and throughfall

The intra-storm isotopic modification of rainfall was analysed for 10 events that were sequentially sampled. Mean rainfall depth for those events was 29.8 mm in the pine stand and 27.2 mm in the oak stand, and ranged between 10 mm and 67 mm. From the 10 analysed events, seven corresponded to the growing season, thus the dormant season was less represented in the analysis. Selected events were divided into three stages of the storm: initial, representing the first 5 mm of each event; middle, representing all samples between the first and the last sample; and final, representing the last sample collected. Each consecutive stage had a statistically significant difference in the d-excess of rainfall ($F_{2, 61}$ = 3.98; $p < 0.05$) and throughfall ($F_{2, 52}$ = 3.94; $p < 0.05$).

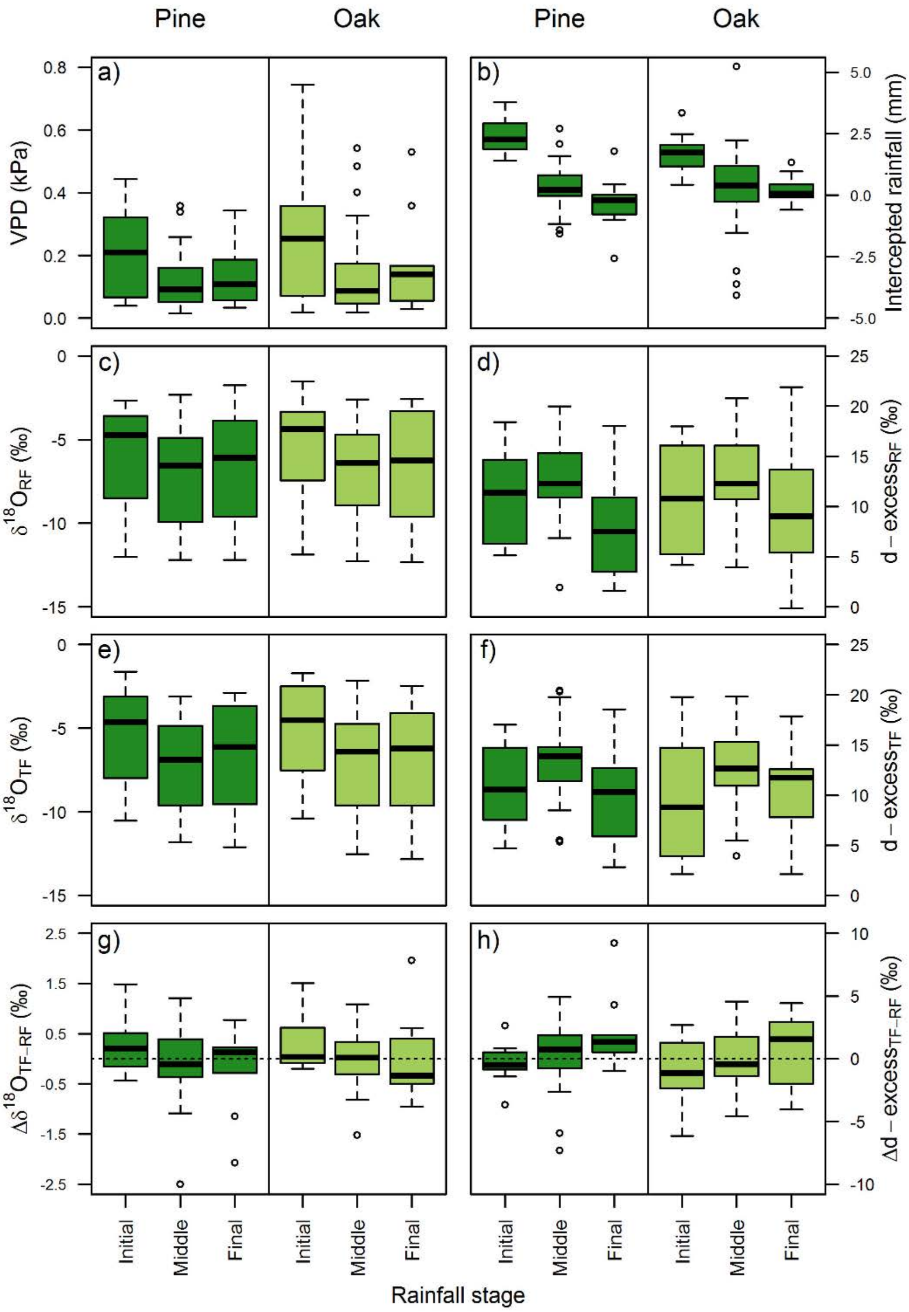


**Figure 5.7.** Boxplots of the intra-event dynamics of 10 rainfall events (> 10mm) in the pine and oak stands. VPD (a), Intercepted rainfall (b), rainfall $\delta^{18}O$ (c), rainfall d-excess (d), throughfall $\delta^{18}O$ (e), throughfall d-excess (f), $\delta^{18}O$ differences between throughfall and rainfall (g) and d-excess differences between throughfall and rainfall (h). Each boxplot represents a different phase (initial, middle and final) of the event. Initial represents the first 5 mm of each event; middle, all samples between the first and the last sample; and final, the last sample collected.

Results showed similar trends between forest stands. In general, the isotopic compositions of rainfall and throughfall were heavier at the beginning of the event (Figures 5.7c and e). These heavier values coincided with the highest values of vapour pressure deficit (VPD) and intercepted rainfall (difference between rainfall and throughfall) (Figures 5.7a and b). d-excess increased during the middle stage and decreased during the final stage (Figures 5.7d and f). The $\Delta\delta^{18}O_{TF\text{-}RF}$ was also higher at the beginning of the event (mean $\delta^{18}O$ difference of 0.32 ± 0.61‰ in pines and 0.27 ± 0.55‰ in oaks) and decreased during the rainfall event (mean $\delta^{18}O$ difference of -0.14 ± 0.86‰ in pines and -0.02 ± 0.86‰ in oaks at the final stage) (Figure 5.7g). On the contrary, $\Delta$d-excess$_{TF\text{-}RF}$ tended to increase during the event (Figure 5.7h), with mean differences ranging from lower values at the beginning of the event (-0.40 ± 1.62‰ in pines and -1.05 ± 2.61‰ in oaks) to higher values at the end (2.04 ± 2.85‰ in pines and 0.58 ± 2.95‰ in oaks).

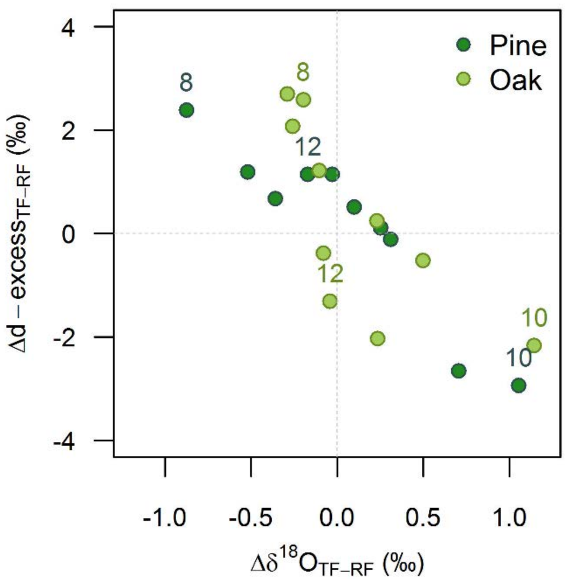


**Figure 5.8.** Relationship between the mean isotopic modification of throughfall ($\Delta\delta^{18}O_{TF\text{-}RF}$) and the change in d-excess ($\Delta$d-excess$_{TF\text{-}RF}$) for the sequentially analysed events in the pine and oak stands. Mean $\delta^{18}O$ and d-excess for each event are weighted by the volume of each sample.

For each sequentially sampled event, there was a negative relationship between the mean $\Delta\delta^{18}O_{TF\text{-}RF}$ and the mean $\Delta$d-excess$_{TF\text{-}RF}$ at the pine stand ($F_{1,\,8}$ = 54.51, $p < 0.01$) and at the oak stand ($F_{1,\,8}$ = 9.13, $p < 0.05$) (Figure 5.8) (both mean $\delta^{18}O$ and d-excess for each event were weighted by the volume of each sample). According to this relationship, the isotopic dynamic of three different events was analysed: event 8 had negative $\Delta\delta^{18}O_{TF\text{-}RF}$ and positive $\Delta$d-excess$_{TF\text{-}RF}$; event 10 had positive $\Delta\delta^{18}O_{TF\text{-}RF}$ and negative $\Delta$d-excess$_{TF\text{-}RF}$; and event 12 had differences in $\delta^{18}O$ and d-excess close to zero. Meteorological and isotopic characteristics of each event are shown in Table 5.1.

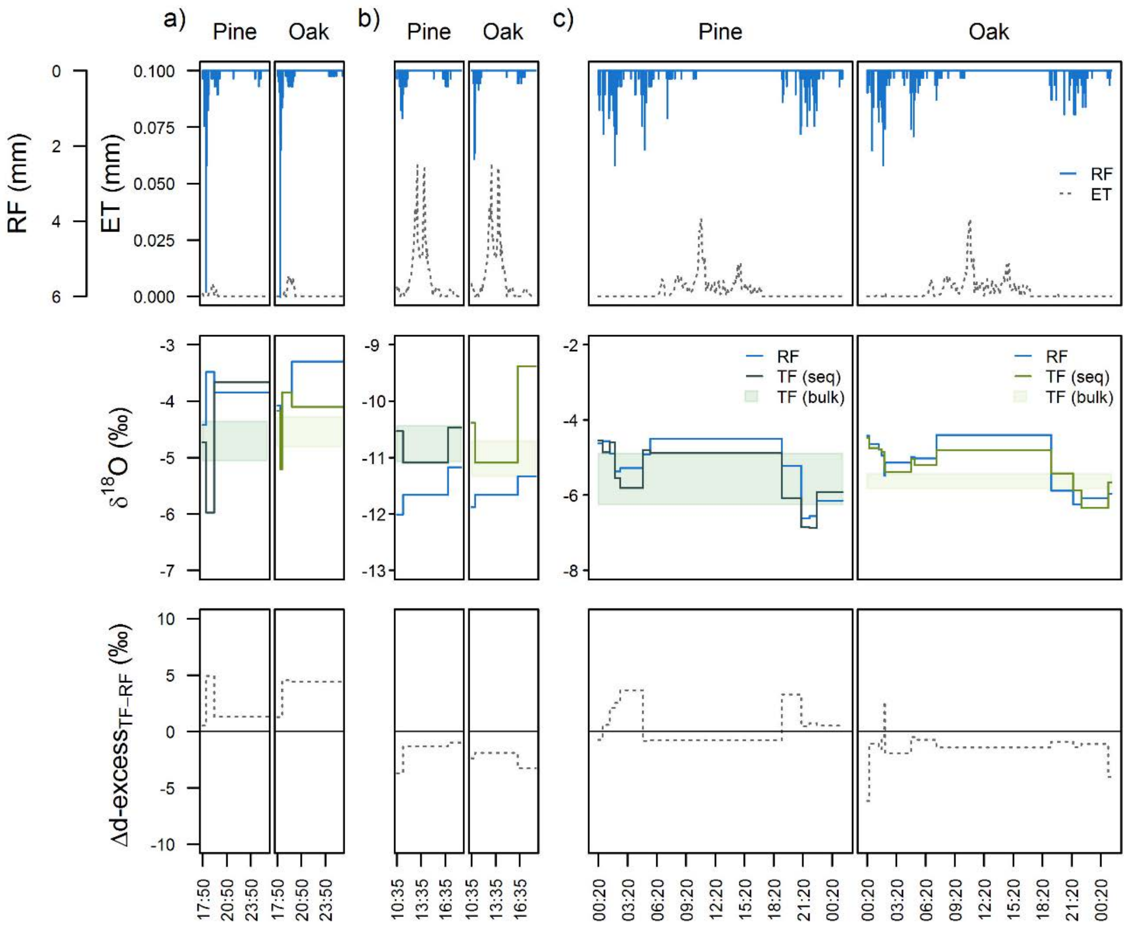


**Figure 5.9.** Comparison of the intra-event dynamics for three events: (a) Event 8 (July 31st), (b) Event 10 (August 15th) and (c) Event 12 (September 3rd). From top to bottom: time series of rainfall and wet canopy evaporation (5 min time step); $\delta^{18}O$ in rainfall and in throughfall collected by the sequential sampler (highlighted area represents the range of $\delta^{18}O$ of throughfall collected by the different bulk collectors in the forest plots); and d-excess difference between sequential throughfall and sequential rainfall samples.

The isotopic composition of throughfall showed similar dynamics to the isotopic composition of rainfall. d-excess was always positive during event 8 (Figure 5.9a), always negative during event 10 (Figure 5.9b) and variable during event 12 (Figure 5.9c). Nonetheless, in both stands the dynamics of $\delta^{18}O$ and d-excess were similar. The representation of the sequential samples of rainfall and throughfall in the dual space ($\delta^{18}O$ and $\delta D$) showed the space of mixing waters (Figure 5.10). In this space the isotopic composition of throughfall and rainfall had in general greater differences during the short events.

**Table 5.1.** Meteorological characteristics of 3 events analysed at the intra-event temporal resolution in Figures 5.9 and 5.10 in the Scots pine and downy oak stand.

| | | | Meteorological characteristics | | | | | Sequential samples | | Spatial samples |
|---|---|---|---|---|---|---|---|---|---|---|
| **Event** | **Date** | **Stand** | **Rainfall (mm)** | **Throughfall (mm)** | **Duration (hours)** | **Max Intensity in 30 min ($mmh^{-1}$)** | **Total ET (mm)** | **Mean weighed rainfall $\delta^{18}O$ (‰) (mean ± SD)** | **Mean weighed throughfall $\delta^{18}O$ (‰) (mean ± SD)** | **Mean bulk throughfall $\delta^{18}O$ (‰) (mean ± SD)** |
| 8 | 31st of July | Pine | 19.3 | 13.9 | 7.2 | 10.4 | 0.03 | -4.41 ± 0.46 | -4.94 ± 1.16 | -4.83 ± 0.16 |
| | | Oak | 21.7 | 14.0 | 7.2 | 9.5 | 0.08 | -4.41 ± 0.69 | -4.32 ± 0.60 | -4.51 ± 0.18 |
| 10 | 15th of August | Pine | 10.5 | 7.3 | 6.6 | 4.2 | 0.84 | -12.02 ± 0.41 | -10.80 ± 0.34 | -10.81 ± 0.21 |
| | | Oak | 13.9 | 9.3 | 6.6 | 5.3 | 0.85 | -11.41 ± 0.36 | -10.69 ± 0.95 | -10.96 ± 0.18 |
| 12 | 3rd of September | Pine | 53.8 | 46.1 | 25.1 | 7.6 | 0.71 | -5.85 ± 0.89 | -5.71 ± 0.99 | -5.65 ± 0.35 |
| | | Oak | 48.3 | 42.4 | 25.1 | 7.1 | 0.71 | -5.84 ± 0.95 | -5.48 ± 0.77 | -5.79 ± 0.16 |

For event 8 (Figure 5.10a) throughfall was depleted in both stands; however, the distance between mixing spaces was much greater in the Scots pine stand (the mean $\Delta\delta^{18}O_{TF\text{-}RF}$ was -0.87‰ for pines and -0.20‰ for oaks). Event 10 (Figure 5.10b) had enriched throughfall in comparison to rainfall, with mean $\Delta\delta^{18}O_{TF\text{-}RF}$ of 1.05‰ in the pines and 1.14‰ in the oaks. For event 12, the mixing spaces overlapped (Figure 5.10c). Bulk throughfall samples (dots in Figure 5.10) showed some spatial variability in their isotopic composition. However, these samples were mostly distributed within the throughfall mixing spaces defined by the sequential samples.

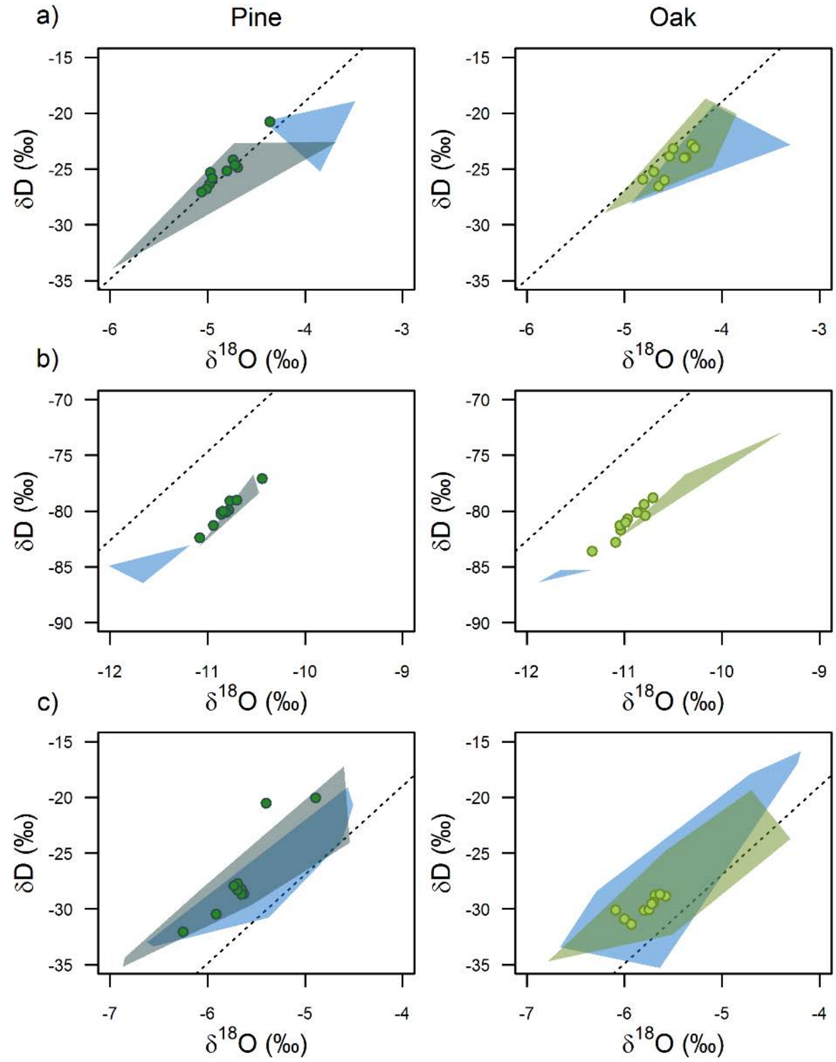


**Figure 5.10.** Dual plots for the rainfall events shown in Figure 5.9: (a) Event 8, (b) Event 10, and (c) Event 12, in the pine and oak stands. Dots represent bulk throughfall samples, blue areas represent the space created by the union of sequential rainfall samples and green areas represent the space created by sequential throughfall samples.

## 5.4. DISCUSSION

### 5.4.1. Temporal variability of the isotopic composition of rainfall, throughfall and stemflow

The isotopic composition of throughfall and stemflow was in general more enriched than that of rainfall. However, all samples fell along the LMWL, indicating that, in general, fractionation happened in both isotopes ($\delta^{18}O$ and $\delta D$). The isotopic composition of rainfall showed a seasonal effect related to air temperature. In general, higher $\delta^{18}O$ in rainfall was observed in summer and lower $\delta^{18}O$ in winter. According to Gat (1996), higher $\delta^{18}O$ is consistent with rainfall that contains more water condensed at higher temperature and that evaporates more during its descent.

As observed by others (e.g. Saxena, 1986; Dewalle and Swistock, 1994; Xu *et al.*, 2014; Stockinger *et al.*, 2017), our data also showed an enrichment pattern, with lighter throughfall than rainfall more common during the growing season (at higher temperatures), and heavier throughfall than rainfall more common during the dormant season (at lower temperatures). This pattern corroborates that fractionation is temperature-dependent and that molecular bonds between lighter isotopes are more easily broken than molecular bonds between heavier isotopes (Majoube, 1971).

Positive and negative $\Delta\delta^{18}O_{TF\text{-}RF}$ happened almost in the same proportion; no significant differences were found between stands regardless of the different canopy structures. The highest isotopic differences between throughfall and rainfall, in either direction, were found for events with fewer than 20 mm of rainfall. In that sense, higher enrichment was observed for low rainfall volumes and intensities in a boreal Scots pine forest in northern Scotland (Soulsby *et al.*, 2017). These events did not completely saturate the canopy, resulting in a non-uniformly wet canopy that might have increased the variability of throughfall amount and also of its isotopic composition. In some locations below the canopy, the proportion of free throughfall could be higher than throughfall striking the canopy. However, in other locations the proportion of dripping throughfall could be higher, and it would have been affected more by fractionation processes due to interaction with a dryer canopy, increasing the isotopic differences between throughfall and rainfall. On the contrary, beyond 20 mm of rainfall, the homogenization of canopy saturation promotes the creation of canopy flow-paths that might reduce the residence time of water in the canopy and lead to a decrease in the isotopic differences between throughfall and rainfall.

Stemflow had more enriched $\delta^{18}O$ than throughfall, which is similar to results described by Kubota and Tsuboyama (2003), but the reasons for this remain unclear. Ikawa *et al.* (2011) highlighted how the isotopic composition of stemflow was strongly affected by the mixing of waters in the canopy and stems, with secondary effects of evaporation and isotopic exchange with ambient vapour. Although in our study most of the stemflow samples showed enriched $\delta^{18}O$, d-excess differences were not consistently negative. This suggests that, as proposed by Ikawa *et al.* (2011), evaporation, isotopic exchange, selection processes or a combination of all of them could affect the isotopic composition of stemflow. However, in contrast to throughfall, evaporation or isotopic exchange may have a greater impact on stemflow, as previous studies found that the residence time of water stored in branches and stems is longer than water stored in the canopy (Pypker *et al.*, 2011). For Scots pine, Llorens and Gallart (2000) found that the specific storage capacity of stems was 6 times higher than for needles. Cayuela *et al.* (2018) found that, above 20 mm of rainfall, funneling ratios for both species no longer increased. Above this threshold, stems funnelled water at their maximum capacity, reducing the exposure time of stored water to the atmosphere and reducing the effects of evaporation or isotopic exchange. In addition, stemflow in oaks had more negative d-excess values and 13% more enriched samples than pines. These differences between species could be related to the higher specific storage capacities of downy oak, which would enhance the impact of evaporation on their stems.

### 5.4.2. Spatial variability of the isotopic composition of throughfall and stemflow

At the intra-event scale, some spatial variability of the $\delta^{18}O$ was observed between throughfall collectors. This variability was higher for events with fewer than 20 mm of rainfall. Other studies that analysed the spatial variability of the isotopic composition of throughfall led to somewhat contradictory conclusions. Some of them observed an enrichment pattern due to the canopy cover (Brodersen *et al.*, 2000; Kato *et al.*, 2013), increasing the differences between throughfall and rainfall from the crown periphery to the crown centre. Other studies observed a lack of temporal stability in the spatial patterns of enrichment (Allen *et al.*, 2014, 2015; Hsueh *et al.*, 2016). Allen *et al.* (2014) related this lack of temporal stability with the existence of pre-event moisture retained in the canopy. But there is little justification of this process at our study site, as this is a plausible explanation only at very rainy and humid locations.

We found a positive relationship between the $\Delta\delta^{18}O_{TF\text{-}RF}$ and the canopy cover. This relationship was stronger for pines than for oaks. Greater canopy cover would imply a longer residence time of rain water moving through the leaves and stems in the canopy, which would increase the effect of fractionation processes. The lower spatial variability of the isotopic composition of throughfall associated with large rainfall events is probably related to the fact that for such events the canopy can easily reach saturation. On the contrary, for events of low magnitude, evaporation, isotopic exchange or canopy selective storage, along with a higher proportion of free throughfall, would have a greater impact on the spatial variability of the isotopic composition of throughfall, because of the unsaturated canopy. However, we observed that bulk samples were distributed mostly within throughfall mixing spaces, indicating that, at the event scale, the isotopic spatial variability of throughfall was in general lower than its isotopic temporal variability. A few exceptions were observed, possibly due to a higher effect of fractionation factors on some locations below the canopy during some rainfall events.

Stemflow also had marked isotopic variability for events of fewer than 20 mm of rainfall, suggesting that the isotopic modification of the stemflow was more variable between trees when their stems were not completely saturated and flow paths were not completely connected.

### 5.4.3. Rainfall intra-event isotopic modification

The greatest differences between $\delta^{18}O$ of throughfall and rainfall were observed at the beginning of the rainfall event, simultaneously with a decrease in d-excess. The greater isotopic enrichment in throughfall at the beginning of the event was consistent with a dryer atmosphere with high VPD, suggesting that evaporation in the canopy at this initial stage of rainfall could be important, as corroborated by higher interception losses. During the rainfall event, $\delta^{18}O$ differences between throughfall and rainfall tended to decrease, whereas d-excess tended to increase. Ikawa *et al.* (2011) suggested that differences between the $\delta^{18}O$ of throughfall and rainfall tended to disappear because the wetter the canopy becomes, the more flow paths are created, decreasing the lag time between rainfall and throughfall and reducing evaporation impact. In general, at the end of the event, throughfall had higher d-excess than rainfall, possibly because of the selection process. Therefore, the retention in the canopy of the final portion of rainfall, which usually had low d-excess values, would imply that throughfall measured during the final interval corresponded to rainfall lagged in earlier time intervals with higher d-excess. As observed by Kubota and Tsuboyama (2003), intra-storm isotopic trends in rainfall and throughfall may also vary depending on rainout effects or on changes in the origin of the vapour masses (Dansgaard, 1964). However, the general patterns observed in the three rainfall events analysed in detail suggest that evaporation, isotopic exchange or canopy selection are the drivers of the shift observed in the isotopic composition of rainfall when it passes through the canopy.

For large rainfall events, the activation of flow paths through the saturated canopy increases the amount of throughfall less affected by evaporation, equilibrium exchange or canopy selection, thus reducing the differences between throughfall and rainfall and resulting in an overlapping of the mixing spaces of throughfall and rainfall. On the contrary, for some small rainfall events, the final isotopic composition of throughfall is more greatly affected by fractionation factors. In this case, we speculate that temperature and relative humidity may have a big impact, leading to an enrichment in throughfall for high evaporation rates due to non-equilibrium fractionation. This process would be stronger in isotopically lighter rainfall events or it could lead to either depletion or enrichment during low evaporation rates due to equilibrium fractionation. These processes could explain why the mixing spaces of throughfall and rainfall for some events did not overlap and why sometimes the mixing space of throughfall was above or below the mixing space of rainfall.

## 5.5. CONCLUSIONS

This study showed that, though mean isotopic differences between rainfall, throughfall and stemflow can occur in both directions, there was greater throughfall enrichment at low air temperatures, and stemflow was more enriched than throughfall. Overall, no significant differences were found between species. Fractionation could be achieved by the mixture of factors previously described in the literature: evaporation, isotopic exchange and canopy selection processes. Although all processes probably occurred during the same rainfall event, evaporation seemed to have a higher impact at the beginning of rainfall. However, under low evaporation conditions, isotopic exchange may acquire more relevance. Fractionation caused by canopy selection processes appeared to be more important at the end of the event, when part of the final portion of rainfall was retained on the leaves and stems. All fractionation factors had a lower impact for events larger than 20 mm of rainfall because canopies were saturated and the lag time between rainfall, throughfall and stemflow was reduced.

Further research, to assess the movement of water through the canopy and to discern fractionation factors better, should consider an even higher temporal resolution of sampling collection for throughfall and stemflow. Measurement of the isotopic composition of the atmospheric vapour under the canopy could also shed light on possible enrichment or depletion under equilibrium conditions. Finally, complementary measurements like drop size distributions and velocities or stem flow velocities could help us to understand observed variations in the isotopic composition of throughfall and stemflow when compared with rainfall.

## ACKNOWLEDGMENTS

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# CHAPTER 6

## Spatio-temporal variability of the isotopic input signal in a partly forested catchment: implications for hydrograph separation

The isotopic composition of precipitation (D and $^{18}O$) has been widely used as an input signal in water tracer studies. Whereas much recent effort has been put into developing methodologies to improve our understanding and modelling of hydrological processes (e.g. transit-time distributions or young water fractions), less attention has been paid to the spatio-temporal variability of the isotopic composition of precipitation, used as input signal in these studies. Here, we investigate the uncertainty in isotope-based hydrograph separation (IHS) due to the spatio-temporal variability of the isotopic composition of precipitation. The study was carried out in a Mediterranean headwater catchment (0.56 $km^2$). Rainfall and throughfall samples were collected at three locations across this relatively small catchment and stream water samples were collected at the outlet. Results showed that throughout an event, the spatial variability of the input signal had a higher impact on hydrograph separation results than its temporal variability. However, differences in IHS determined pre-event water due to the spatio-temporal variability were different between events and ranged between 1 and 14%. Based on catchment-scale isoscapes, the most representative sampling location could also be identified. This study confirms that even in small headwater catchments, spatio-temporal variability can be significant. Therefore, it is important to characterise this variability and identify the best sampling strategy to reduce the uncertainty in our understanding of catchment hydrological processes.

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## 6.1. INTRODUCTION

Much of our understanding of the hydrological process relies on the relationship between precipitation and a predictor (e.g. runoff, soil moisture, etc.). Precipitation is indeed the main input driving many if not most models of hydrological processes (Seibert and McDonnell, 2002; McDonnell and Beven, 2014). However, while we know that precipitation varies greatly in time and even over short distances in space (Goodrich *et al.*, 1995; Girons Lopez *et al.*, 2015; Vieux, 2016), uniformity is often still assumed for small areas. This assumption applies not only to the precipitation amount, but also to its isotopic composition (D and $^{18}$O), which has become a common tool in tracer hydrological investigations (McGuire and McDonnell, 2015). As such, this could have serious implications for our understanding of a catchment functioning.

At a specific location, the isotopic composition of precipitation is the result of the combination of multiple and complex processes. These processes have been studied and described over the years, particularly in large-scale studies (i.e. Dansgaard, 1964; Smith *et al.*, 1979; Araguás-Araguás *et al.*, 2000; Seeger and Weiler, 2014; Bowen and Good, 2015). These studies concluded that major factors controlling the isotopic composition of precipitation include its vapour source, air mass trajectory, and fractionation that occurs as water evaporates into the air mass and during precipitation formation. Based on correlation or geostatistical relationships, spatially continuous maps of the isotopic composition of precipitation ("isoscapes") have often been constructed from long-term mean annual or monthly observations (Bowen *et al.*, 2009). However, precipitation is greatly influenced by geographic and temporal variations, most of which are not captured when analysed on a larger scale. For example, higher elevation landforms usually cause disproportionately high rainfall on their windward side, a rain-out of heavier isotopes and lower evaporation rates of falling raindrops that lead to a more depleted precipitation (Dansgaard, 1964). Siegenthaler and Oeschger (1980) and Holdsworth *et al.* (1991) reported that elevation effects varied from -0.15 to -0.5‰ per 100 m increase in elevation for $^{18}$O, and from -1 to -4‰ for D. Moreover, within a rainfall event, changes in air mass temperature can modify significantly the isotopic composition of precipitation. As such, higher rainfall intensities, coinciding with maximum air mass lift and cooling, result in more depletion (Dansgaard, 1964; Celle-Jeanton *et al.*, 2004). Furthermore, the isotopic composition of rainfall can also be affected by canopy interception processes that, in general, lead to more enriched net precipitation (sum of throughfall and stemflow inputs) than open rainfall, although depletion is also possible (Allen *et al.*, 2017). The isotopic shift produced in the canopy is mainly due to evaporation of falling water (Saxena, 1986), equilibrium exchange between vapour and liquid (Friedman, 1962) and the retention in the canopy of the last portion of precipitation (Dewalle and Swistock, 1994). Therefore, to better understand rapid hydrological responses (event scale processes), spatial and temporal isotopic variations at smaller scales need to be taken into account (Von Freyberg *et al.*, 2017; Allen *et al.*, 2018).

Over the last few decades, isotope-based hydrograph separation (IHS) has been widely used in hydrology as a useful tool to gain insights into catchment runoff processes (i.e. Sklash *et al.*, 1976; Pearce *et al.*, 1986; McDonnell *et al.*, 1990; Kubota and Tsuboyama, 2003; Fischer *et al.*, 2017). These, among many other hydrological studies that aim to clarify water origin and movements, relied on the conservative behaviour of water stable isotopes and used D and $^{18}O$ as tracers. The common practice for small headwater catchments (<10 km$^2$) is to sample rainfall at one location and assume that rainfall amount and its isotopic composition are uniform (McDonnell and Beven, 2014; Fischer *et al.*, 2017). Nevertheless, the few studies that explored the effect of different sampling locations or temporal resolutions actually found large differences in hydrograph separation. For instance, Lyon *et al.* (2009) found differences in pre-event water larger than 50% when using rainfall collected at different locations within a catchment. Likewise, Fischer *et al*. (2017) observed that the spatial variability of rainfall was almost as large as its temporal variability in its isotopic composition, and that it varied from event to event, producing differences up to 60% in the pre-event water contribution. In addition, Kubota and Tsuboyama (2003) used throughfall instead of rainfall as input signal and found differences that ranged between 5 and 10% in pre-event water contributions. Finally, Von Freyberg *et al.* (2017), by comparing results of different sampling frequencies, found that sampling at time intervals longer than 3h resulted in an underestimation of the event-water fraction. However, studies in small headwater catchments, where effects of elevation, forest cover and both spatial and temporal variations are all evaluated simultaneously, are still required. This is particularly relevant in areas where factors like high climate seasonality, spatially distributed forest cover or temporally varying runoff generation processes add even more complexity. Such understanding would also be needed towards finding effective sampling strategies in order to decrease the spatio-temporal uncertainties in the understanding of IHS-deduced hydrological processes.

Here, we analyse the spatio-temporal variability of precipitation in a small, partly forested Mediterranean headwater catchment in order to address the following questions: i) what is the spatio-temporal variability in the isotopic composition of rainfall and its relation to elevation and forest cover? ii) what is the uncertainty associated with isotope-based hydrograph separation due to the spatio-temporal variability of rainfall? and iii) how can we identify the best sampling strategy to obtain a representative input signal for the entire catchment? Answers to these questions will ultimately improve the understanding of dominant hydrological processes in seasonal mid-latitude small headwater catchments.

## 6.2. METHODOLOGY

### 6.2.1. Study area

The study was conducted in the Can Vila catchment (0.56 km$^2$) located within the Vallcebre research area (NE Spain, 42º 12'N, 1º 49'E). The catchment drains into the River Llobregat, which supplies most of the surface water for the city of Barcelona. The climate is Sub-Mediterranean, characterised by a marked water deficit in summer. Mean annual temperature (1989-2013) is 9.1 ± 0.67ºC, mean annual precipitation is 880 ± 200 mm and mean annual evapotranspiration, calculated by the method of Hargreaves and Samani (1982) is 823 ± 26 mm. Precipitation is seasonal, with autumn and spring usually being wetter seasons, and summer and winter often drier. Summer rainfall is characterised by intense convective events, while winter precipitation is caused by frontal systems, with snowfall accounting for less than 5% of precipitation (Latron *et al.*, 2010a, 2010b; Llorens *et al.*, 2018).

In the past, most of the hillslopes were deforested and terraced for agricultural purposes (Poyatos *et al.*, 2003). However, at present, the catchment is mostly covered by Scots Pine *(Pinus sylvestris* L.*)* forests (58.3%) that cover all elevations. In addition, grasslands (31.9%) and shrubs (4.1%) are also found within the catchment (Figure 6.1a). Despite the human impact on the landscape, the primary stream network in the catchment is mostly natural: it is one to three meters wide and not very deeply incised. Stream runoff responses have a clear seasonal pattern, with an alternation between wet periods, when the catchment is hydrologically responsive and produces larger runoff coefficients and gentle recessions, and dry periods, when the catchment is much less reactive to precipitation and produces low runoff coefficients (Latron *et al.*, 2008). The high spatio-temporal variability of the hydrological responses is related to the extent of saturated areas, that are very relevant for runoff generation in the catchment (Latron and Gallart, 2007). On average, the stream dries out in summer once every two years for a period ranging from 15 to 40 days (Latron *et al.*, 2010b).

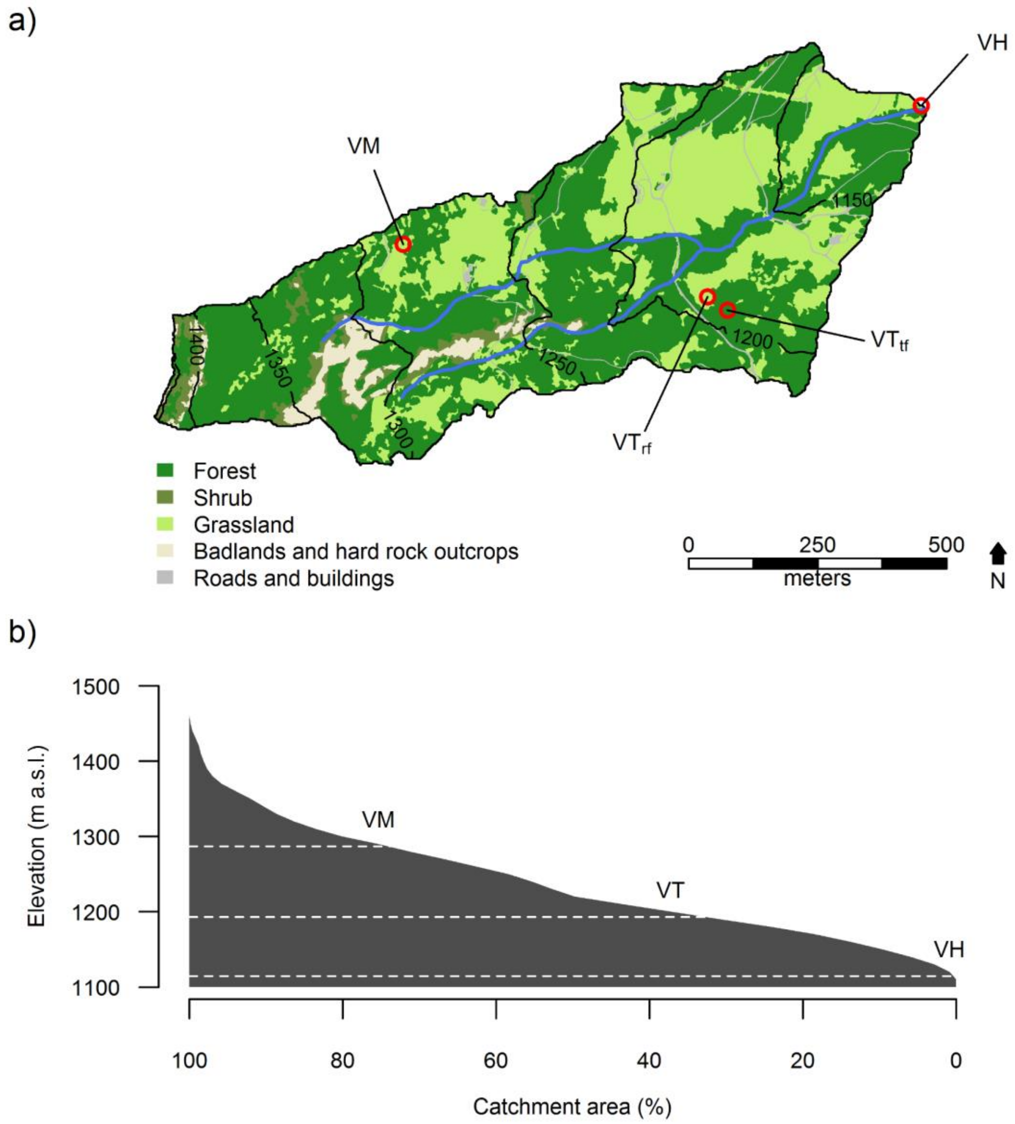


**Figure 6.1.** (a) Land use map of the Can Vila catchment. Red circles indicate the sampling locations for rainfall (rf): VM (1,287 m a.s.l.), $VT_{rf}$ (1,193 m a.s.l.) and VH (1,115 m a.s.l.); and for throughfall (tf): $VT_{tf}$. (b) Elevations represented by the catchment area. Dashed lines indicate the elevation of the sampling locations.

The catchment area is almost entirely situated on clayey bedrock, with soils predominantly of silt-loam texture. Soil depth is variable, mainly because of the changes induced by terracing, with typical depth between 0.5 and 3 m. Topsoil is rich in organic matter, but this decreases with increasing depth from 15.3% in the top layer to 0.33% in the deepest one. In addition, soils are well-structured and with high infiltration capacity, although this decreases rapidly with depth (Rubio *et al.*, 2008). The altitude of the catchment ranges between 1,108 and 1,462 m a.s.l. (Figure 6.1b). Slopes vary between 0 and 20% in most of the catchment, except in its upper part, characterised by a limestone cliff with slopes steeper than 40%.

### 6.2.2. Hydrometric monitoring

Hydrometric monitoring was conducted from May 2015 to May 2016. Rainfall was measured at three locations representing 75% of the area-proportional elevation range (Figure 6.1b): VH (1,115 m a.s.l.), $VT_{rf}$ (1,193 m a.s.l.) and VM (1,287 m a.s.l.). These involved 0.2 mm tipping-bucket rain gauges (Casella CEL, Casella, UK), which were all placed in open areas and located 1 m above the ground. Throughfall was measured under a Scots pine forest ($VT_{tf}$) by 20 0.2 mm tipping-bucket rain gauges (Davis Rain Collector II, Davis Instruments, USA), distributed to cover all ranges of canopy cover, which were previously determined by hemispherical photographs (Llorens and Gallart, 2000). Finally, runoff data were obtained from the catchment outlet gauging station (VH) equipped with a 90º V-notch weir and a water pressure sensor. Runoff was determined using established stage discharge rating curves, calibrated by manual discharge measurements. All hydrometric data were stored every 5 minutes by dataloggers (DT 50/80 Datataker, Datataker Inc., USA).

### 6.2.3. Sampling design

For the same period, rainfall, throughfall and stream water samples were collected for isotope analyses on an event basis by bulk and sequential collectors. Rainfall and throughfall bulk collectors consisted of plastic funnels (130 mm diameter) positioned 50 cm above ground and connected to a 1 litre plastic bin. Sequential collectors of stream water and rainfall consisted of plastic funnels (340 mm diameter) connected to an automatic water sampler (24 500-ml bottles, ISCO 3700C). To minimize evaporation, both bulk and sequential collectors were buried beneath the soil surface and connected to the funnels by looping drainage tubes.

Open rainfall was collected bulkily and sequentially (every 5 mm of rainfall) at the top part (VM) and at the outlet of the catchment (VH). Throughfall was collected in the forest stand ($VT_{tf}$) with 10 bulk collectors representative of all ranges of canopy cover (Cayuela *et al.*, 2018a). In addition, one sequential sampler collected throughfall samples every 5 mm of rainfall. The isotopic composition of rainfall at $VT_{rf}$ was calculated by means of the linear regression between elevation and δD (using VM and VH samples for each event). Results were compared and validated with 7 samples of rainfall collected at $VT_{rf}$ during the study period. The regression parameters showed a good fit between estimated and real values (slope 1.01, intercept 1.06 and $r^2 = 0.99$).

Finally, stream water samples were collected at VH by two automatic water samplers (24 1,000-ml bottles, ISCO 3700C). Each collector sampled stream water at different time frequencies. One sampled once every 12 hours and the other sampled at higher resolution intervals during events to ensure the sampling of the rising and falling limb of the hydrograph. In addition, a manual stream water sample was collected weekly during days of data and sample collection.

### 6.2.4. Isotope analysis

All water samples were analysed at the Scientific and Technological Services of the University of Lleida, using a Cavity Ring-Down Spectroscopy Picarro L2120-i isotopic water analyser (Picarro Inc., USA). The precision of the measurements, based on the repeated analysis of four reference water samples, was < 0.1‰ and < 0.4‰ for $\delta^{18}O$ and δD, respectively. All isotope data are expressed in terms of δ-notation as parts per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW).

### 6.2.5. Catchment-scale isoscapes

Finer-scale isoscapes were constructed for events in which IHS was calculated. The isoscapes represented the catchment-scale isotopic input signal for different time-intervals within the event. The interpolation was based on a 2-meter resolution digital elevation model (DEM), the point scale precipitation amount (5 min data from the rain gauges) and δD values in VH, VM and $VT_{rf}$ (samples every 5 mm of rainfall). Among predictor variables (elevation, latitude and longitude), elevation was used to estimate δD at each pixel of the DEM. Afterwards, for each elevation, the effect of the forest cover was incorporated to pixels with forest. Thus, for each event, time interval and pixel with forest, the amount of precipitation and its isotopic signature were modified according to canopy interception losses and isotopic differences between throughfall ($VT_{tf}$) and rainfall ($VT_{rf}$). Finally, an incremental weighted mean catchment-scale isotopic input signal was calculated for each time interval (McDonnell *et al.*, 1990). The resulting interpolation was then evaluated by comparing the estimated δD values at VH, VM and $VT_{tf}$, with the measured values. Regression parameters showed a good fit (slope 0.99, intercept 0.11 and $r^2 = 0.99$).

With this information, three scenarios were analysed for the catchment-scale isotopic input signal: i) a catchment with the current land cover, with 58% of forest (Scenario 1) that resulted from the original interpolation, ii) a catchment completely covered by forest (Scenario 2), where all pixels of the DEM had to be forest, and iii) a completely deforested catchment (Scenario 3), where all pixels were considered grassland. From these scenarios we hypothesize that the catchment-scale input signal calculated for the actual land uses (Scenario 1) was the most representative input signal for the entire catchment. Scenarios 2 and 3 represent a hypothetical catchment input signal in which precipitation measurements and isotopic sampling would take into account the elevation effect, but only under forest (Scenario 2) or in an open area (Scenario 3).

### 6.2.6. Data analysis and isotope-based hydrograph separation

Rainfall events were defined as periods with more than 1 mm of precipitation. To ensure canopy dryness between events, the inter-event period was set to be at least 6 hours during the day and 12 hours during the night (Llorens *et al.*, 2014). Following Latron and Gallart (2007), runoff event duration as well as stormflow depth and coefficient were derived for each rainfall–runoff event selected, using the "constant slope" method of Hewlett and Hibbert (1967) with a modified slope value of 1.38 l $s^{-1}$ $km^{-2}$ $day^{-1}$, once a discharge increment in the stream higher than 5.6 l $s^{-1}$ $km^{-2}$ was identified.

In total, the spatio-temporal variability of the input signal was analysed for 29 rainfall events. For each event, differences between the isotopic composition of bulk samples of rainfall at VM, rainfall at VH and a volume-weighted mean of throughfall in $VT_{th}$ were analysed by a linear mixed model (LMM) with repeated-measurement structure. In the model, elevation, rainfall amount, rainfall interception loss and season were included as covariate fixed effects, and the factor "event" was used as a random effect. Isotope-based hydrograph separation (IHS) was performed only for those 7 runoff events that met the following two criteria: (1) enough runoff was generated at the outlet to collect several samples (more than 4) during the flood, and (2) the required assumptions for IHS proposed in Pearce *et al.* (1986) and Sklash *et al.* (1986) were all met. The isotope-based hydrograph separation used two components to quantify the contribution of pre-event ("old") and event ("new") water into the stream during the duration of the runoff event, using different input signals. The pre-event water contribution was calculated by solving the mass balance equations (Eqs. (6.1) and (6.2)) (Pinder and Jones, 1969).

$$Q_S = Q_E + Q_{PE} \qquad (6.1)$$

$$C_S Q_S = C_E Q_E + C_{PE} Q_{PE} \qquad (6.2)$$

Where Q is discharge, C refers to the isotopic signature, and the subscripts S, PE and E indicate the stream, the pre-event water and the event water, respectively. Equations (1) and (2) are used to find the contribution of the pre-event water in the streamflow (Eq. (6.3)).

$$X = (C_S - C_E) / (C_S - C_{PE}) \qquad (6.3)$$

Where X is the ratio of $Q_{PE}/Q_S$.

The isotopic signature of the stream sample prior to the event was used as the pre-event water component. Nine different input signals were used as event water: rainfall at the top of the catchment (VM) (bulk and sequential); rainfall at the bottom of the catchment (VH) (bulk and sequential); throughfall at the centre of the catchment ($VT_{tf}$) (bulk and sequential); and the catchment-scale input signal for the three proposed scenarios. δD for sequential samples of rainfall and throughfall was adjusted by means of the incremental mean technique (McDonnell *et al.*, 1990), which took into account the temporal variability of the rainfall amount.

Uncertainty in the hydrograph separation due to the variability of the input signal was analysed with a Monte Carlo approach, following an adaptation by Bazemore *et al.* (1994). For each event and time step, the Monte Carlo approach solved equation (3) 50,000 times. The isotopic composition of the input signal was randomly chosen within the range of its spatial variability, which was obtained by calculating normal distributions of the isotope signature for each time step. Finally, 95% confidence intervals were calculated.

## 6.3. RESULTS

### 6.3.1. Isotopic composition of rainfall, throughfall and streamflow

Total rainfall during the studied period (~12 months) was 1,102 mm. Rainfall amount from the 29 analysed rainfall events ranged between 3 and 129 mm and accounted for 71% of total rainfall. Total runoff was 379 mm, with the seven events selected for IHS accounting for 36% of total runoff (Figure 6.2). Nevertheless, as seen in Table 6.1, the hydrological response of these events was representative of the different types of runoff responses that occurred in the catchment during the period studied.

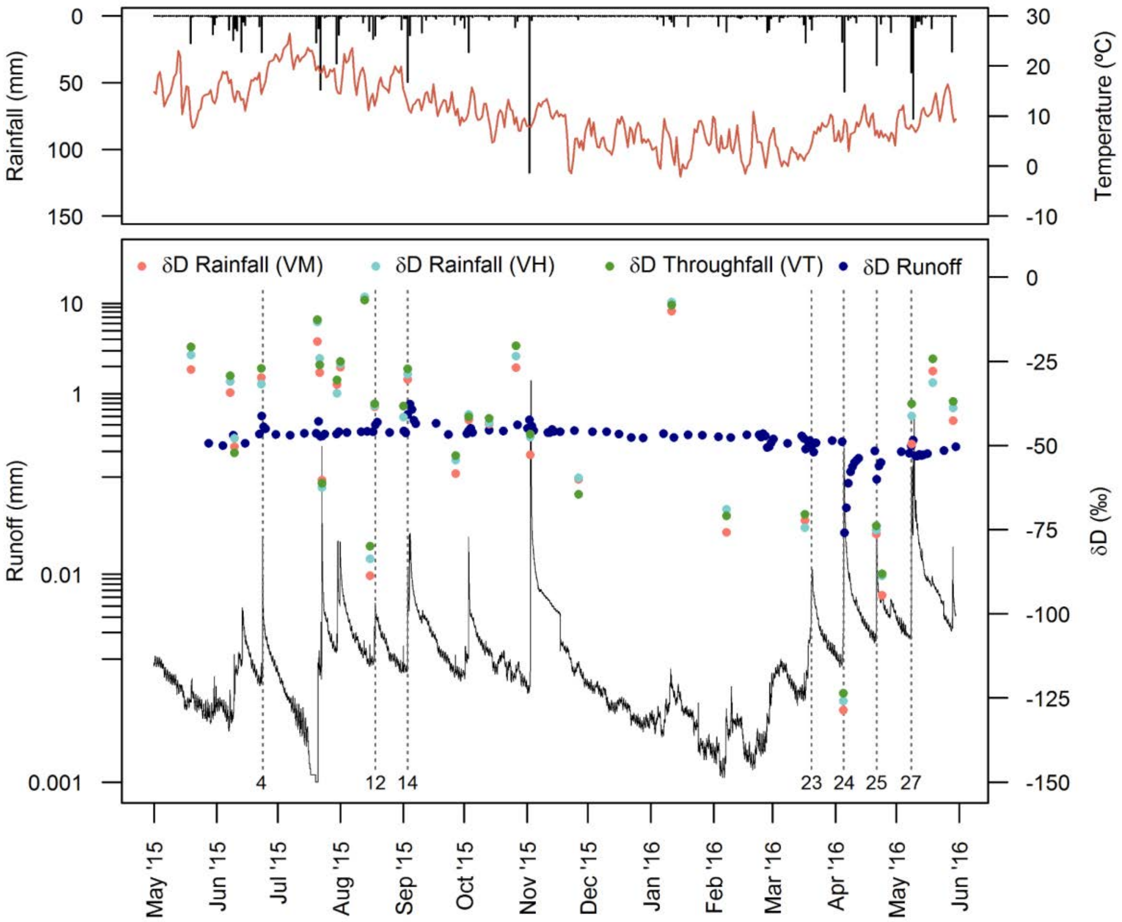


**Figure 6.2.** Daily rainfall and temperature time-series during the studied period (top). Daily runoff and isotopic composition (δD) of rainfall, throughfall and runoff (bottom). Dashed lines indicate the runoff events analysed with IHS.

The isotopic composition of rainfall at VM ranged from -128.62 to -6.02‰ for δD and from -17.04 to -2.12‰ for $\delta^{18}O$. At VH, the isotopic composition of rainfall ranged from -125.82 to -5.84‰ for δD and from -17.03 to -2.05‰ for $\delta^{18}O$. On the other hand, the isotopic composition of throughfall in $VT_{tf}$ ranged from -123.64 to -6.85‰ for δD and from -16.44 to -2.3‰ for $\delta^{18}O$. Significant differences were found between the isotopic composition of summer and winter rainfall ($F_{1,\,56}$ = 14.88; $p$ < 0.01), whereby rainfall was more enriched during summer and more depleted during winter. The median of stream water was -46.97‰ for δD and -7.29‰ for $\delta^{18}O$ (Figure 6.2). The inter-quartile ranges were -40.65 to -56.34‰ and -6.31 to -8.40‰, respectively. For conciseness, further data analysis is shown for δD only. Even though the choice of isotope may also slightly influence hydrograph separation results (Lyon *et al.*, 2009), evaluating the uncertainty related to that is beyond the scope of this work. Moreover, covariation between Oxygen-18 and Deuterium suggested that fractionation due to non-equilibrium factors was negligible ($r^2 = 0.97$, $p<0.05$). Figure 6.2 shows the rainfall and runoff time series for δD, including the spatial variability observed in rainfall.

### 6.3.2. Elevation effect

Rainfall measured in the upper part of the catchment (VM) was significantly more depleted ($F_{1, 28} = 14.96$; $p<0.01$) than in the lower part (VH) (Figure 6.3). The mean change in δD was -1.25‰ per 100 m increase in elevation. This decreasing trend with elevation was observed for 24 of the 29 analysed events.

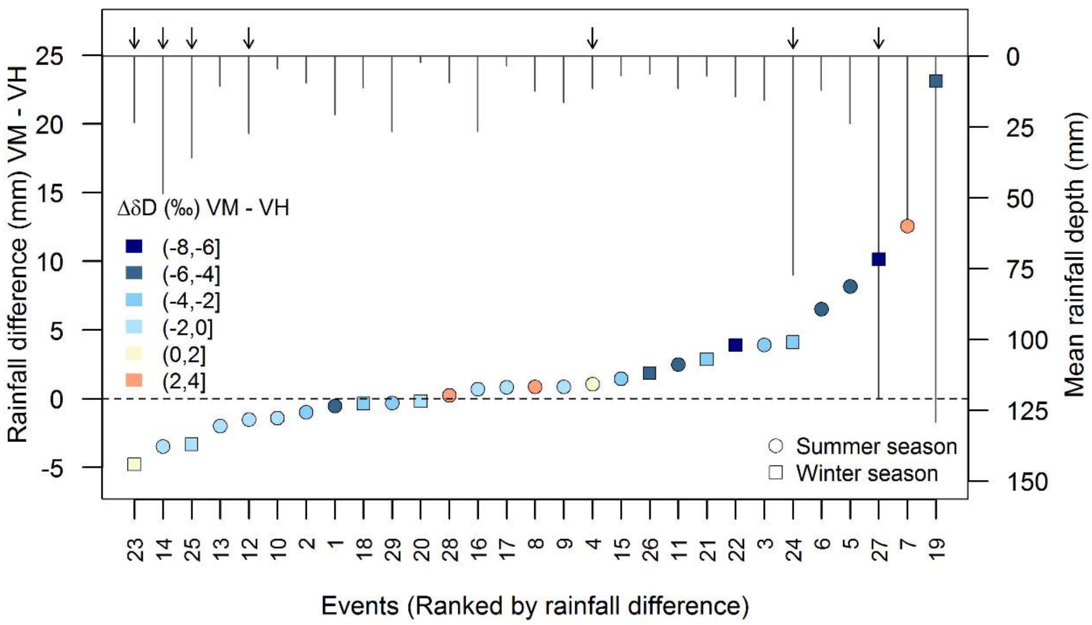


**Figure 6.3.** Rainfall isotopic differences (ΔδD) in relation to rainfall amount differences. Events are ranked by increasing rainfall amount differences between the upper (VM) and the lower (VH) parts of the catchment. Rainfall events with more depleted isotopic composition in VM than in VH are in blue; and those more enriched in VM than in VH are in red. Catchment mean event rainfall is represented by vertical lines. Circles and squares indicate the season and arrows indicate the events with runoff responses analysed by IHS.

In addition, at the event scale and during the entire period under study, depletion at the upper part of the catchment coincided (Figure 6.3) with more rainfall ($F_{1, 26} = 4.97$; $p<0.05$), with no statistically significant differences between seasons ($F_{1, 26} = 2.08$; $p = 0.16$). Mean event rainfall was only 2 mm greater at VM than at VH, representing 8% more rainfall at VM. However, the range of the differences was highly variable depending on the rainfall event. For example, event 19, with more rainfall and greater intensity than the average (more than 100 mm of rainfall in under 24 hours), had the highest rainfall amount difference (23 mm) between the upper and lower parts of the catchment. Overall, during the period studied 66 mm more rainfall was measured at VM.

### 6.3.3. Forest cover effect

Mean throughfall collected below the forest canopy was lower than the volume of open rainfall (Figure 6.4). Greater variability in the amount of throughfall was found for rainfall events under 20 mm, for which loss due to canopy interception ranged between 10 and 50% of the open rainfall.

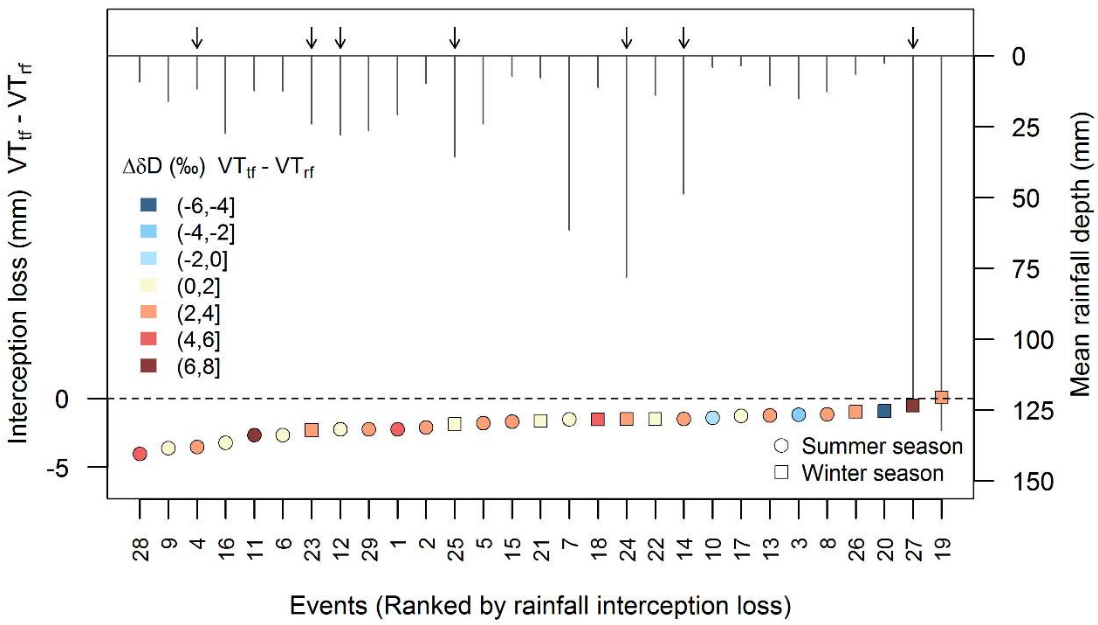


**Figure 6.4.** Rainfall isotopic differences (ΔδD) in relation to rainfall interception loss. Events are ranked by increasing rainfall interception (differences between throughfall ($VT_{tf}$) and rainfall ($VT_{rf}$)). Rainfall events with more depleted isotopic composition in throughfall than in rainfall are in blue; and those more enriched in throughfall than in rainfall are in red. Catchment mean event rainfall is represented by vertical lines. Circles and squares indicate the season and arrows indicate the events with runoff responses analysed by IHS.

For larger rainfall events (>20 mm), however, differences in volume between open rainfall ($VT_{rf}$) and throughfall ($VT_{tf}$) were reduced, with canopy interception between 0 and 10%.

The mean isotopic composition of throughfall was, in general, heavier than open rainfall (Figure 6.4), with a mean enrichment of 2.95‰, although differences tended to decrease for events larger than 20 mm. No relationship could be found between the isotopic composition of throughfall and rainfall interception losses ($F_{1,\ 26}$ = 0.41; $p$ = 0.53). Nor were there differences between seasons ($F_{1,\ 26}$= 0.31; $p$ = 0.58), although mean isotopic differences appeared slightly higher during the winter season.

### 6.3.4. Catchment-scale isoscapes for hydrograph separation

Figure 5 shows the different bulk and sequential isotopic input signals used in the IHS for the largest analysed event (event 27), as well as the isotopic composition of the stream. The patterns observed in Figure 6.5 serve as a general example, as these are common to most of the events, with more rainfall measured in the upper part of the catchment (VM) along with more depleted rainfall than in the lower part (VH); throughfall ($VT_{tf}$) was also generally more enriched than rainfall and its volume was lower. Each event is shown in Figure B.1 (Appendix B Supporting information).

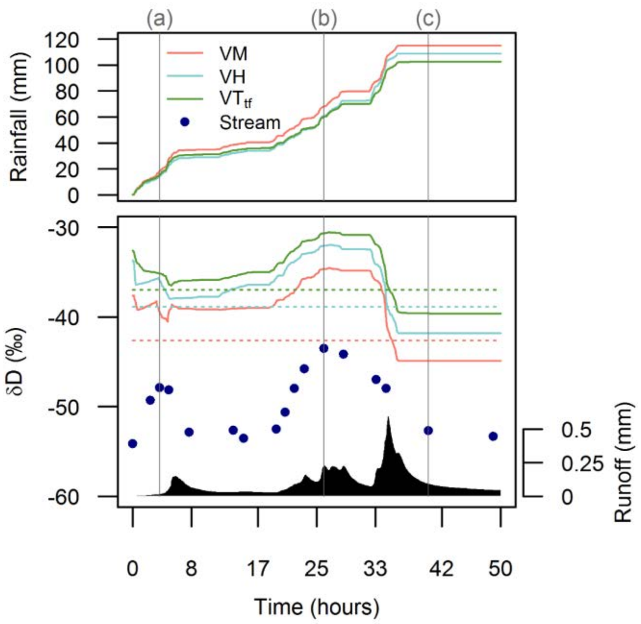


**Figure 6.5.** Cumulative rainfall in VM and VH along with cumulative throughfall in $VT_{tf}$ throughout event 27 (top). Runoff and isotopic composition (δD), in VM, $VT_{tf}$, VH and in the stream during the event (bottom). Continuous lines represent volume-weighted incremental mean isotopy (from sequential samples) and dashed lines represent the mean value (from bulk samples). Vertical lines (a, b and c) refer to three moments of the event, for which the spatio-temporal variability of the catchment-scale input signal is shown in Figure 6.6.

The spatial and temporal information was integrated to obtain catchment-scale isoscapes at each 5 min time step. Figure 6.6 shows the weighted mean catchment-scale isotopic input signal during three moments of event 27 for Scenarios 1, 2 and 3. Maps for Scenario 1 show how the isotopic composition of the input signal tends to be more enriched under forested areas and, along the elevation gradient, upper areas tend to be more depleted. Scenarios 2 and 3 reflect the elevation effect, though the input signal in Scenario 2 is more enriched than in Scenario 3 due to the effect of the forest cover. All scenarios captured temporal variability, showing different mean δD for each time step. However, maximum differences between methods occurred at the end of the event, when the incremental weighted mean had accumulated the δD differences throughout the event. In addition, comparison of temporal variability with the spatial range of δD for the seven events analysed showed that it was, in general, lower or the same as spatial variability.

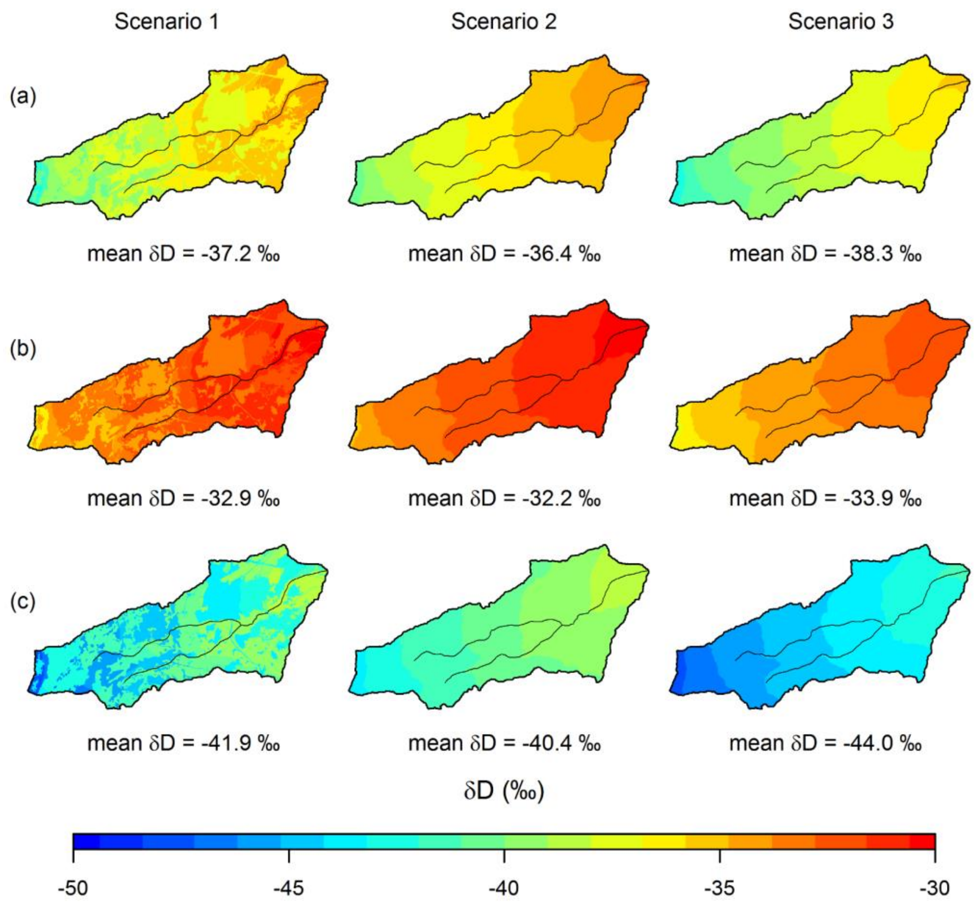


**Figure 6.6.** Maps of the catchment-scale input signal during three moments of event 27 (a, b and c). Scenario 1 represents the isotopic input signal for the catchment with the current land use information; Scenario 2 represents the isotopic input signal for a hypothetical catchment completely covered by forest; and Scenario 3 represents the isotopic input signal for a hypothetical catchment completely covered by grassland.

**Table 6.1.** Rainfall and hydrological characteristics of the seven runoff events used for IHS. The last row of the table shows the ranges measured during all events and runoff responses (larger than 0.003 mm of runoff) that occurred during the period studied. Rainfall intensity is calculated as maximum intensity in 30 minutes. Response time is the time interval between the peak flow and the time when half the precipitation has fallen. Specific discharge increment is the difference between peak-flow discharge and base-flow discharge.

| Event | Rain (mm) | Intensity (max 30) (mm $h^{-1}$) | Runoff duration (hours) | Response time (hours) | Runoff (mm) | Specific discharge increment (l $s^{-1}$ $km^{-2}$) | Stormflow coefficient (%) |
|---|---|---|---|---|---|---|---|
| 4 | 11.6 | 8.3 | 24.0 | 1.3 | 1.7 | 48.2 | 4.5 |
| 12 | 27.4 | 14.2 | 37.5 | 6.2 | 0.6 | 6.8 | 2.2 |
| 14 | 48.5 | 16.2 | 26.0 | 26.6 | 8.9 | 51.7 | 14.5 |
| 23 | 23.7 | 9.3 | 8.5 | 73.5 | 4.5 | 20.5 | 11.5 |
| 24 | 77.4 | 10.7 | 65.1 | 2.1 | 32.4 | 465.7 | 39.6 |
| 25 | 35.9 | 8.7 | 32.6 | 4.2 | 5.0 | 66.3 | 13.8 |
| 27 | 120.6 | 19.6 | 83.3 | 9.3 | 82.3 | 1111.3 | 59.7 |
| | 3-129 | 2-71 | 8.5-83.3 | 0.9-73.5 | 0.6-82.3 | 6.8-2620.0 | 2.2-59.7 |

When performing IHS, significant differences in pre-event water contributions were found, depending on the input signal used ($F_{2,\ 32} = 3.34$; $p < 0.05$) (Figure 6.7). However, for a given sampling location, no significant differences in pre-event water contributions were caused by sampling methodology (bulk or sequential collection of samples) ($F_{1,\ 32} = 0.08$; $p = 0.77$). Nevertheless, all runoff events were dominated by pre-event water, regardless of the hydrological conditions. Out of all the other input cases, the pre-event water contributions most similar to the catchment-scale input signal (Scenario 1) were when rainfall was sampled (bulkily or sequentially) at the lower part of the catchment (VH) (Figure 6.7). When using rainfall sampled at the upper part of the catchment (VM) or using Scenario 3 (deforested catchment), the contribution of pre-event water was underestimated. On the contrary, when using only measured throughfall ($VT_{tf}$) or using Scenario 2 (forested catchment), the pre-event water contribution was generally overestimated (Figure 6.7).

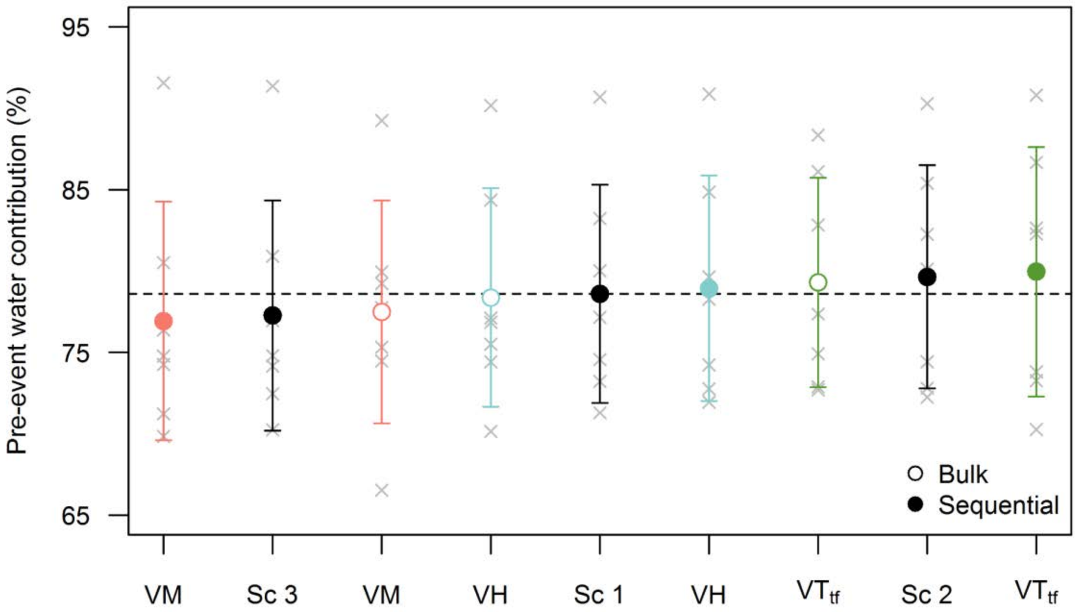


**Figure 6.7.** Comparison of the mean pre-event water contribution (for the 7 events analysed) as function of the input signal used in the isotope-based hydrograph separation ("Sc" on the x-axis is the abbreviation of "Scenario"). Vertical lines indicate the standard deviation of the mean pre-event water contribution and grey crosses represent the value of pre-event water contribution for each event. The dashed line represents the pre-event water contribution, using the catchment-scale input signal for Scenario 1 (58% of forest).

Although mean uncertainty in pre-event water contribution between sampling locations and sampling methods was 8.5%, it varied from event to event, ranging from 1 to 14% (Figure 6.8). In general, uncertainty was lower for events with little spatial variability, such as event 24, in which the contribution of pre-event water was similar regardless of the input water used. On the other hand, uncertainties increased for events with large spatial differences, such as event 12, and for events with similar isotopic composition between rainfall and the stream, such as event 27. Hydrographs of each event with the mean pre-event water contribution and uncertainty ranges can be seen in Figure B.2 (Appendix B Supporting information).

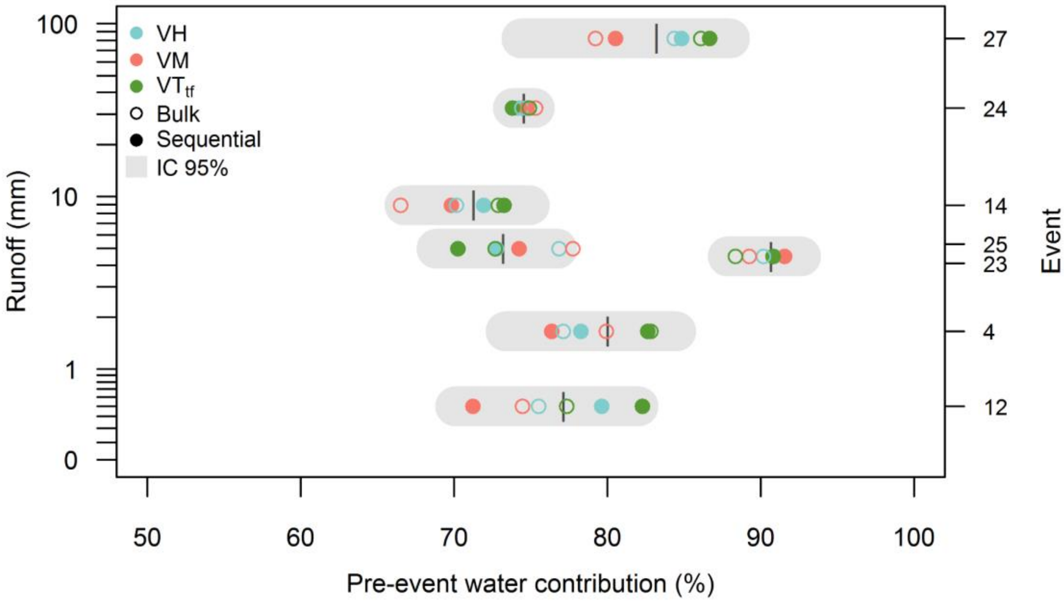


**Figure 6.8.** Pre-event water contribution for the seven events analysed. Vertical black lines and grey areas represent the pre-event water contribution for Scenario 1 with a 95% confidence interval.

## 6.4. DISCUSSION

### 6.4.1. Spatio-temporal variability of the input signal

Results obtained in this study highlight the high spatio-temporal variability of rainfall amount and isotopic signature, even over short distances. The precipitation pattern in the Can Vila catchment had an elevation effect, with higher rainfall amounts accumulated in the upper part of the catchment. These rainfall differences could be attributed to a topographic effect caused by the general increase in elevation topped by a high limestone cliff that forced orographic precipitation. Simultaneously, this process may force rain-out of heavier isotopic water as a consequence of Rayleigh condensation, with steadily higher condensation levels and lower condensation temperatures (McGuire and McDonnell, 2007). This would explain why most rainfall events produced lighter rainfall at the upper part of the catchment along with higher rainfall depths. Likewise, elevation could also increase the spatial variability of rainfall due to evaporation of falling raindrops (Dansgaard, 1964). On this, Siegenthaler and Oeschger (1980) pointed out that evaporation of falling raindrops is expected to be greater in summer than in winter as it depends on the prevailing vapour pressure. Nonetheless, we did not find significant differences between seasons for spatial variability. The observed enrichment pattern was comparable to other patterns found in previous studies (i.e. Dansgaard, 1964; Friedman and Smith, 1970; Holdsworth *et al.*, 1991; McGuire *et al.*, 2005), although it corresponded to the lower range (-1.25‰ per 100 m increase in elevation for δD). One possible explanation for this is the location of the catchment, for which precipitation may originate from different moisture sources, mainly the Mediterranean and Atlantic areas (Camarero and Catalan, 1993). These different air masses have different trajectories that may also reduce the effect of elevation, as already observed by Fischer *et al.* (2017) in the Zwäckentobel catchment (4.3 $km^2$), where rainfall enhancement and mountain shading effects for precipitation coming from different air trajectories resulted in an absence of elevation effect in its isotopic composition.

Similarly to what was previously reported by Llorens *et al.* (1997) for a study site close to the Can Vila catchment, pines reduced the amount of rainfall reaching the soil, especially during events of low magnitude. For events of less than 20 mm, interception could be almost half of the incident precipitation. It was for these events when the isotopic differences between throughfall and open rainfall were higher and with higher coefficients of variation. Cayuela *et al.* (2018a) attributed this greater variability to a greater impact of fractionation factors on unsaturated canopies. For events larger than 20 mm, as the canopy became saturated, interception loss and isotopic differences decreased. In the same study, a higher enrichment pattern was found for samples collected under denser canopy coverage, although the spatial variability of the isotopic composition of throughfall was usually lower than its temporal variability. Similar trends were observed in a boreal Scots pine forest in northern Scotland, where greater enrichment was observed for low rainfall volumes and intensities (Soulsby *et al.*, 2017). Therefore, the effect of throughfall in IHS may have a higher impact on runoff events responding to low rainfall amounts. In the Can Vila catchment, the highest runoff responses occurred mainly for events larger than 20 mm. Thus, for these events the forest cover effect could be reduced, due to the homogenisation of the canopy's saturation, and have a relatively lower impact on the IHS results.

### 6.4.2. Catchment-scale isotopic input signal

Significant differences in the isotopic composition of the input signal were found between the three sampling locations, which gave rise to the following questions: which is the most representative input signal for the entire catchment? Given limitations in resources, is it better to take multiple spatially distributed bulk samples or is it better to sequentially sample one location? and is it necessary to take into account the forest effect in the input signal?

On comparing the results from the IHS performed with samples collected at single locations (VH, VM and $VT_{tf}$) with the catchment-scale input signal for the actual land uses (Scenario 1), it was observed that the closest results to Scenario 1 were obtained when the input rainfall was collected at VH, suggesting that VH was the most representative location for the entire catchment. This happened because precipitation at VH was more enriched than at VM and more depleted than at $VT_{tf}$. This combination eventually triggered a similar isotopic composition between VH and the catchment-scale input signal. As such, this does not imply that a similar location in space (i.e. near the catchment outlet) should be examined in other studies, but that the most representative location will most likely depend on the (balance between) the elevation gradient and the spatial organisation of the forested areas within the catchment.

Regarding the spatio-temporal variability of the input signal, at our study site no significant differences between bulk or sequential sampling methods were found in the IHS. Therefore, the results indicate that it may be more important to cover spatial variability than temporal variability when calculating the catchment input signal. Similar results were found in Fischer *et al.* (2017), who suggested that to perform robust IHS it is not only necessary to account for the temporal variability in the isotopic composition of rainfall, but also for its spatial variability. Therefore, multiple rain samplers should be used to characterise the isotopic composition of the input water to perform event-based IHS. Nevertheless, once the spatial variability of a catchment is known and a representative location has been found, sampling at this location at a higher resolution may have some benefits over using multiple bulk samples. For example, sequential samplers allow consecutive events to be distinguished, without the need to collect the samples immediately after the rain. In addition, if placed at different locations and under the forest cover, they allow to characterise the time intervals when the isotopic differences are most extreme. Moreover, a study by Von Freyberg *et al.* (2017) showed that 6 h or 12 h bulk precipitation samples failed to reflect the large isotopic variability revealed by higher sampling frequencies, and were inadequate to represent the signature of the event-water end member. Nevertheless, as they suggested, a robust IHS is also highly dependent on a correct capture of the short-term responses in the streamflow, including peak response.

Our results confirmed the importance of taking into account the effect of forested areas on the isotopic input signal, especially in events with less than 20 mm of rainfall depth, as forest affects both the incident volume of water reaching the soil and its isotopic composition, as shown in this catchment (Cayuela *et al.*, 2018a) and elsewhere (Kubota and Tsuboyama, 2003; Allen *et al.*, 2017; Stockinger *et al.*, 2017).

### 6.4.3. Uncertainty in isotope-based hydrograph separation due to input signal selection

Uncertainty in pre-event water contribution increased for events with high spatial variability in the input signal. Thus, the more uniform the input signal within the catchment was, the lower the uncertainty associated with the IHS. On the other hand, despite significant differences between the mean isotopic composition of rainfall and stream water, uncertainty also increased for events with varying intra-storm isotopic composition when, at a time step and location, the isotopic composition of the input signal was closer to that of the stream. Under such circumstances, differences between pre-event water contributions using different input signals increased. On the contrary, when bulk samples were used, this temporal variability was masked and, therefore, the uncertainty was not affected by the temporal variations of the input signal.

Uncertainty in pre-event water contribution due to the variability in the input signal ranged between 1 and 14% and varied from event to event. Uncertainty in the IHS results due to the spatio-temporal variability of the input signal was of the same order of magnitude as other sources of uncertainty, for example those related to the determination of different end members (Bazemore *et al.*, 1994; Genereux, 1998; Uhlenbrook and Hoeg, 2003). In order to assess the uncertainty in the pre-event water contribution to runoff and to find the most representative input signal across the catchment, it is also important to account for spatial variability by sampling rainfall at different locations, including forested areas. Nevertheless, not all areas within the catchment contribute to runoff generation in the same proportion and runoff-contributing areas can expand and contract seasonally, depending on prior wet conditions (Dunne *et al.*, 1975; Latron and Gallart, 2007). Therefore, future work to identify runoff contributing areas and their corresponding isotopic input signal could further improve our hydrological processes understanding and reduce uncertainties for IHS studies and other types of analyses that require the characterisation of isotope input.

## 6.5. CONCLUSIONS

The spatial variability of rainfall amount and its isotopic composition has often been overlooked in hydrological studies conducted in small headwater catchments. In this study we found that even for a small catchment (<1 km$^2$), 83% of events during one year had more depleted rainfall in the upper part of the catchment. The analyses demonstrated the existence of an elevation effect that increased rainfall amount and, for this study's catchment, induced a mean change in δD of -1.25‰ per 100 m increase in elevation. In addition, below forested areas, the amount of rainfall was reduced and its isotopic composition was, on average, 2.95‰ more enriched in δD than open rainfall. Via the use of elevation and the isotopic gradient in rainfall and throughfall measured in three locations of the catchment, isoscapes were obtained to estimate a catchment-scale input signal representative of the spatio-temporal variability within the catchment. This methodology was used to identify the most representative sampling location within the catchment. Finally, while the isotope-based hydrograph separations showed that runoff was controlled by pre-event water, results could differ significantly, depending on the location of the precipitation input signal collector used. On the contrary, no significant differences were found between using bulk or sequential collectors. This suggests that, in general, resources might be best spent on capturing spatial rather than temporal variability in precipitation isotopic composition within an event. Overall, uncertainty introduced by not capturing spatio-temporal variability varied from event to event and ranged between 1 and 14%.

## ACKNOWLEDGMENTS

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# CHAPTER 7

## General Discussion

From precipitation to streamflow water moves through multiple compartments, changing its properties and isotopic signature. The ability to measure water fluxes and trace their movement is an important challenge for hydrologists. This knowledge provides information about the hydrological functioning of catchments and is fundamental to predict hydrological responses to landscape or climate changes.

This chapter synthesizes the most relevant results obtained in this dissertation, and presents some future research opportunities.

## 7.1. STEMFLOW AS A "HOT SPOT" OF WATER AND PARTICULATE MATTER TO SOIL NEAR STEMS DURING "HOT MOMENTS"

Even though stemflow has been traditionally underrepresented in the literature, during the last decade an increase on stemflow interest has brought to new worldwide and relevant information. Stemflow is a significant water flux that reach the base of trees and can exert considerable effects on the hydrology, biogeochemistry and ecology of forested ecosystems. Nevertheless, research is still unevenly distributed among locations (Figure 7.1), and much of the existent knowledge only provides information on the stemflow percentages (Carlyle-Moses *et al.*, 2018). New research lines are mainly focused on understanding (i) the interrelationship among stemflow and meteorological conditions, (ii) the dynamic interplay between stemflow and canopy structure, (iii) the cycling of solutes and transport of particulate matter in stemflow, (iv) the interactions of stemflow and canopy fungi or bark lichens, and (v) the stemflow-soil interactions (Levia and Germer, 2015).

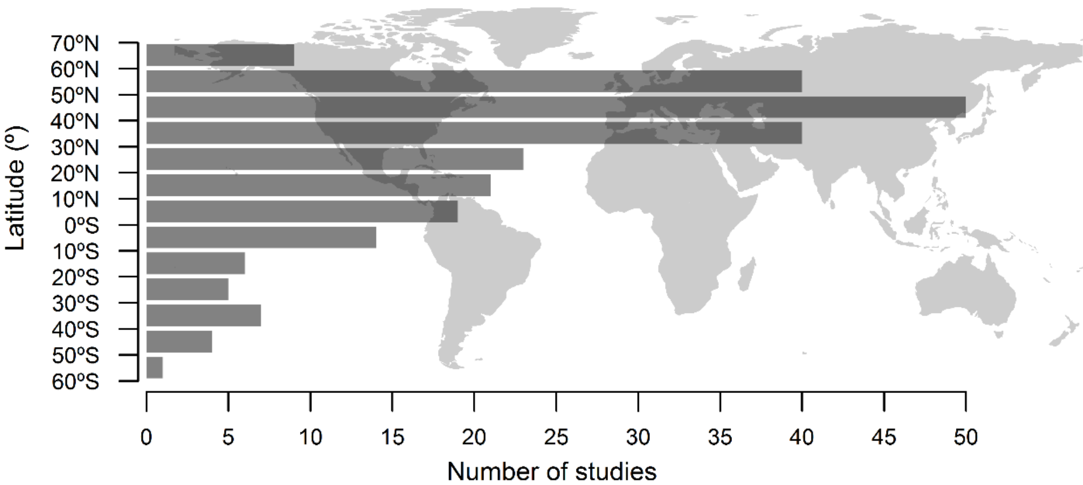


**Figure 7.1.** Latitudes where stemflow has been studied between 1986 and 2017. Elaborated from supplementary data listed in Van Stan and Gordon (2018).

Global observations of canopy interception processes have shown that stemflow can be highly variable between and within types of vegetation (Levia and Frost, 2003). Some species can concentrate more than 30% of the incident precipitation as stemflow (Llorens and Domingo, 2007). However, those are exceptional cases, and usually stemflow represents < 2% (Levia and Germer, 2015). Nonetheless, as pointed out by McClain *et al.* (2003), due to the concentration of water over small areas near tree stems during rainfall, it represents a "hot spot" that enhances hydrological and biogeochemical processes during "hot moments". As pointed out by Levia and Germer (2015) and Carlyle-Moses *et al.* (2018), stemflow may cause localized overland flow and erosion (e.g., Herwitz, 1986; Keen *et al.*, 2010), contribute to preferential and subsurface flow as well as perched water table development (e.g., Johnson and Lehmann, 2006; Germer, 2013; Bialkowski and Buttle, 2015) and groundwater recharge (e.g., Tanaka *et al.*, 1996; Taniguchi *et al.*, 1996). In addition, in certain catchments, stemflow may by-pass flow promoting storm runoff (e.g., Crabtree and Trudgill, 1985), and in the case of dryland ecosystems, it can lead to elevated fluxes of nutrients in soils of the proximal area surrounding the base of trees, contributing to the formation of "fertile islands" (e.g., Whitford *et al.*, 1997; Wang *et al.*, 2011; Michalzik *et al.*, 2016).

In our study area, despite that the two compared species differed significantly in their biotic characteristics (e.g. canopy structure and bark roughness), results showed that stemflow production was more variable among individuals of the same species than between species. For the studied species, stemflow represented < 2% of the incident precipitation. Nevertheless, during specific events it could reach up to 6%. To compare stemflow amounts and dynamics between species, funneling ratios (Herwitz, 1986) were used, which emphasized the role of rainfall intensity and the size of trees as controlling factors of stemflow production. Higher intensities reduced the amount of stemflow, and larger trees were less efficient in producing stemflow. Recent work by Carlyle-Moses *et al.* (2018) proposed new metrics to express stemflow in a more realistic way. For instance, if all the stand area would be occupied by tree stems, stemflow would greatly exceed throughfall that would have fallen on those areas in the absence of tree cover. This index, called stand-scale funneling ratio, was 2.7 in pines and 5.5 in oaks in our study site, representing an input that averaged 3.3 and 6.5 times the average throughfall for pines and oaks respectively. In addition, the examination of stemflow enrichment ratios (Levia and Herwitz, 2000) through the analysis of the fluxes and diameter distribution of particulate matter, confirmed the importance of stemflow in enhancing biogeochemical process in the near-stem area. Generally, stemflow added to the soil 4.2 times more particulate matter (PM) than throughfall for pines and 8.3 more PM for oaks.

Overall, the analysis of stemflow in this dissertation provides a novel piece of knowledge on the rainfall partitioning in Mediterranean mountain forests. The intra-event measurements of stemflow dynamics for different trees has not only shown the complexity of stemflow response, but also has highlighted its role in concentrating water and particulates at the base of trees. With this background, future research in the study area should focus on the infiltration patterns of stemflow within soils as well as on the implications of such concentrated water and particulate matter recharge compared the one associated to throughfall or open precipitation. This research would improve further our knowledge on the relevance of stemflow in the hydrology of forested ecosystems. In addition, research on the chemistry of the particulate matter reaching the soil would also help to understand the processes that are taking place in the canopy and how they relate with the soil chemistry.

## 7.2. LINKING ECOHYDROLOGICAL PROCESSES AND CATCHMENT RESPONSES

Within the water cycle, the isotopic composition of water can change due to fractionation and mixing processes, resulting in a recognizable isotopic signature. Identifying and linking these isotopic signatures with different phases of the water cycle allows to trace the movement of water through a catchment (Gat, 1996). Therefore, the stable isotopes of water are perfect tracers to better understand hydrological processes at different spatio-temporal scales. Nowadays, the cost of isotopic analysis has been reduced to the point that it is easily affordable, and a boom of hydrologic studies using isotopes has occurred in the last decades. However, the lack of understanding of the isotopic fractionation that occurs since water enters into a system can result in misleading information and increasing uncertainties (e.g. Bazemore *et al.*, 1994; Genereux, 1998; Uhlenbrook and Hoeg, 2003; Fischer *et al.*, 2017).

At the catchment scale, the isotopic composition of rainfall is usually used as the reference input signal of water in most hydrological studies (Kendall and McDonnell, 1998). Nevertheless, some studies with the aim to better constrain this input signal, assumed that during canopy interception processes, water could be isotopically enriched due to the evaporation of the intercepted water (e.g. Dewalle and Swistock, 1994; Kubota and Tsuboyama, 2003; Stockinger *et al.*, 2017). However, as pointed out by Allen *et al.* (2017), different factors are involved in the isotopic shift of throughfall and stemflow. These factors include fractionation (Saxena, 1986), exchange between liquid and vapour (Friedman, 1962) and selective transmittance of temporally varying rainfall along varying canopy flowpaths (Dewalle and Swistock, 1994). In spite of the frequent attribution of canopy effects on isotopic composition of throughfall to evaporative fractionation, data suggest that exchange and selection are more likely the dominant factors. In our study site, we analysed spatio-temporal differences between the isotopic composition of throughfall, stemflow and open rainfall. Results showed that throughfall and stemflow were either enriched or depleted, confirming that the canopy affected the isotopic composition of the intercepted water in both directions, enrichment and depletion. Some spatial and temporal trends were observed, for example, in the pine stand, the isotopy of samples collected below denser covered areas was generally more enriched. In addition, throughout the analysis of event time-series, we evaluated how different factors affected intercepted rainfall at different stages of a storm, providing evidences about the effects of evaporation, isotopic exchange and canopy selection processes.

We also observed that the modification of the isotopic composition of rainfall by forest canopy (i.e. in throughfall and stemflow) was not the only source of variability of the input signal. The isotopic composition of rainfall also varied greatly in time and over short distances in space due to multiple and complex processes related to the vapour source, the air mass trajectory, or the fractionation that occurred as water evaporates into the air mass and during precipitation formation (Dansgaard, 1964). In our study area, particularly significant changes occurred due to the elevation gradient that triggered the rain-out of heavier isotopes, resulting in more depleted rainfall at the upper part of the catchment.

The effect of the spatio-temporal variability of the input isotopic signal throughout the Can Vila catchment on hydrograph separation results was tested along several runoff events. Overall, despite a large variability among events, the uncertainty associated with the spatio-temporal variability of the input isotopic signal at the catchment scale ranged between 1 and 14% in terms of pre-event water contribution in the hydrograph. Nevertheless, a smart sampling strategy can help to improve the representativeness of the catchment scale input isotopic signal. As seen in this dissertation, capturing the spatial variability was more important than assessing the temporal variability within a rainfall event for a better characterisation of the catchment scale input isotopic signal. Multiple factors affected the isotopic composition of the input water (e.g. rainfall partitioning, elevation or rainfall amount). However, assuming that all rainfall reaching the catchment contribute to runoff, we were able to identify the location in the catchment with the isotopic input signature closest to catchment scale input isotopic signal. Using this location as the reference for sampling input water, instead of the mean of multiple locations is a cost-effective strategy to account for spatial uncertainties. This approach could be used in small mountain catchments with an isotopic elevation gradient, or with a partial forest cover. However, we know that in many catchments there is a spatio-temporal variability of the runoff contributing areas (Dunne *et al.*, 1975; Ambroise, 2004). Thus, future work aiming to reduce uncertainties in hydrograph separation results for a better process understanding, should focus on the identification of runoff contributing areas and on the specific input isotopic signal associated to these areas.

## 7.3. THE VALUE OF FIELD STUDIES

Fundamental questions in hydrology are usually investigated through empirical observations to understand the involved processes. Indeed, long-term datasets enable the possibility to understand temporal changes and linkages among rainfall, soil moisture, groundwater and runoff, facilitating the understanding of flood and drought risk in different types of landscapes. The Vallcebre research catchments are "outdoor laboratories" that have enabled scientists of all over to world to test their hypothesis during more than 30 years (Llorens *et al.*, 2018) and improve the understanding of hydrological processes. In these and similar "outdoor laboratories", working at different scales: tree, stand and catchment scales, provide a benchmark to better understand the water cycle and to hypothesize and model what would happen in other species, landscapes, catchments, or in different climatic conditions. Nevertheless, in the present context, the future of experimental sites is at risk, as they need continuous economic and technical maintenance. Consequently, experimental sites with long-term data sets are becoming scarce (Tetzlaff *et al.*, 2017). Thus this dissertation contributes with a grain of sand to highlight the scientific benefits of maintaining these sites. However, it is also fundamental to attract the interest of stakeholders, politicians and even a wider public by doing high-quality research, effectively communicating the results, and promoting the work done and its value to society.

# CHAPTER 8

## Conclusions

## 8.1. GENERAL CONCLUSIONS

The studies included in this dissertation guided us to the following conclusions.

### CHAPTER THREE

- Stemflow in pine and oak forests in the Vallcebre research catchments represented only a small portion of the gross rainfall (< 2%), nevertheless it supposed a substantial source of water at the tree base.
- Stemflow volumes and funneling ratios varied greatly at the inter- and intra-storm time scales and was the result of a complex combination of biotic and abiotic factors.
- Stemflow increased with the event size but its variability depended on the duration of the event, the evaporative demand of the atmosphere, the rainfall intensity and the biometric characteristics of each tree.
- Differences among stemflow dynamics between species were related to the different bark storage capacity and the effect of evaporation on stemflow.

### CHAPTER FOUR

- Particulate matter content below the canopy of a Scots pine and a Downy oak stand was almost 1.5 times higher than in open rainfall.
- The content of particulate matter in rain, throughfall and stemflow was correlated with rainfall amount; nevertheless, Saharan dust events increased disproportionately the particulate matter content.
- The concentration of particulate matter was similar between throughfall and stemflow, yet the higher flux-based enrichment ratios measured in stemflow confirmed its importance as preferential flow path of chemically enriched water to the soil.
- The interaction between particulate matter and vegetative surfaces was found to be a key factor determining the amount and size of particulate matter.

## CHAPTER FIVE

- Isotopic differences among rainfall, throughfall and stemflow can occur in both directions.
- Greater throughfall enrichment was observed at low air temperatures, and no significant differences were found between species. Stemflow was consistently more enriched than throughfall.
- Fractionation could be achieved by the mixture of factors: evaporation, isotopic exchange, and canopy selection processes. All processes probably occurred during the same rainfall event; however, evaporation had a higher impact at the beginning of rainfall, but under low evaporation conditions, isotopic exchange may acquire more relevance. Fractionation caused by canopy selection processes appeared to be more important at the end of the event, when part of the final portion of rainfall was retained on the leaves and stems.
- All fractionation factors had a lower impact for events larger than 20 mm of rainfall because canopies were saturated and the lag time between rainfall, throughfall, and stemflow was reduced.

## CHAPTER SIX

- An elevation effect on rainfall volumes and isotopic composition was observed in the Can Vila catchment. This effect induced a mean change in δD of −1.25‰ per 100 m increase in elevation.
- Below forested areas, the amount of rainfall was reduced and its isotopic composition was, on average, 2.95‰ more enriched in δD than open rainfall.
- Although the Isotope Hydrograph Separations showed that runoff was controlled by pre-event water, results could differ significantly, depending on the location of the precipitation input signal used.
- No significant differences were found between using bulk or sequential collectors. Suggesting that, in general, resources might be best spent on capturing spatial rather than temporal variability in precipitation isotopic composition within an event.
- Uncertainty introduced by not capturing spatio-temporal variability varied from event to event and ranged between 1 and 14%.

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# SUPPORTING INFORMATION

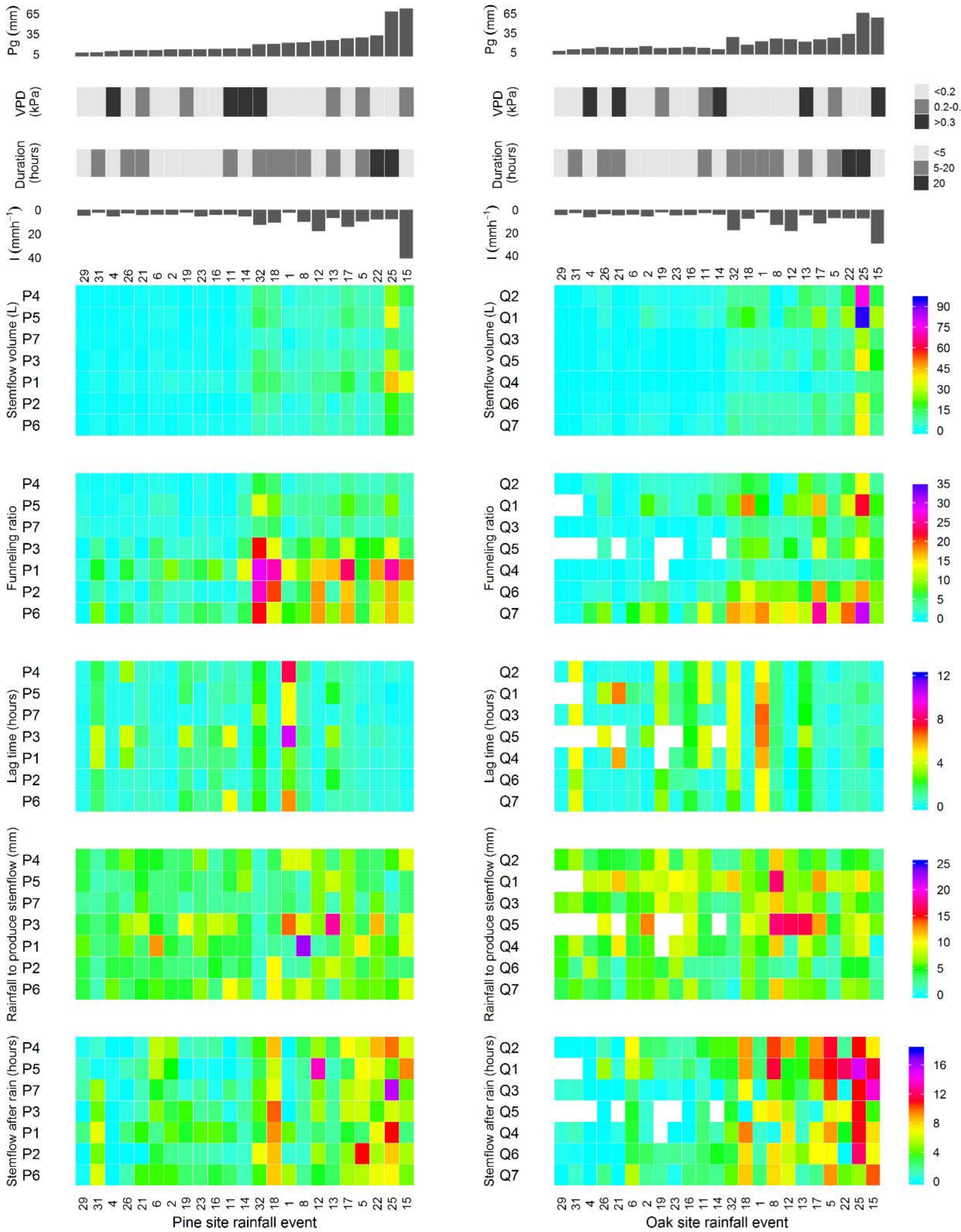
This section comprises supporting information for Chapter 3 and Chapter 6.

**Appendix A** provides a detailed figure with information about all the data available to examine stemflow at the event scale (Chapter 3).

**Appendix B** provides the figures with the time-series of the isotopic data available for each analysed event and of the hydrograph separation (Chapter 6).

## APPENDIX A

**Figure A.1.** Tile plots for all trees and events with more than 6 mm of gross rainfall. From top to bottom: gross rainfall (Pg, mm), vapour pressure deficit (VPD, kPa), rainfall duration (hours), rainfall intensity (mm h$^{-1}$), stemflow volume (litres), funneling ratio, lag time between rainfall and stemflow (hours), rainfall needed to produce stemflow (mm) and stemflow duration after rainfall ceased (hours). Trees are ordered by DBH and events by the rainfall volume measured in the pines stand. White colours represent NA values.



## APPENDIX B

**Figure B.1.** Representation of the intra-event dynamics of the analysed events. Top panel shows the relation between rainfall and runoff (mm) and lower panel shows the isotopic composition of δD for rainfall and throughfall in VM, VH and VT (bulk and sequential) and the isotopic composition of the stream water at the outlet of the catchment.

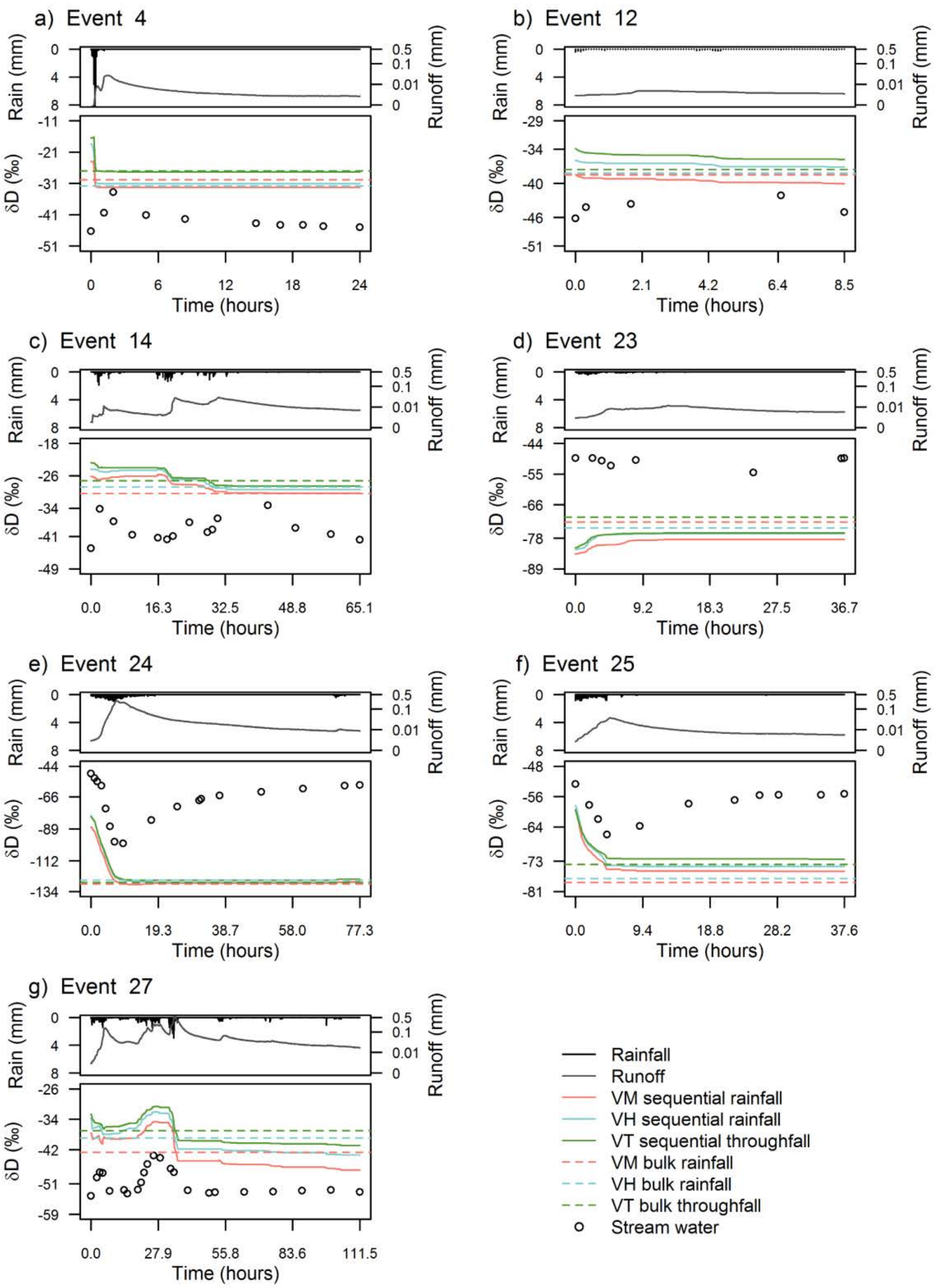


**Figure B.2.** The hydrograph separation for the 7 analysed events. Blue areas represent the mean pre-event water contribution; and dashed lines, uncertainty with a 95% confidence interval.