Universidade de Aveiro Departamento de Ambiente e Ordenamento
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Carla Sofia Santos Ferreira

IMPACTES DA ALTERAÇÃO DO USO DO SOLO NOS PROCESSOS HIDROLÓGICOS E HIDROQUÍMICOS DE ÁREAS PERI-URBANAS

LAND-USE CHANGE IMPACTS ON HYDROLOGICAL AND HYDROCHEMICAL PROCESSES OF PERI-URBAN AREAS

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palavras-chave

Peri-urbano, uso do solo, propriedades do solo, escoamento superficial, connectividade hidrológica, qualidade da água superficial.

resumo

As áreas peri-urbanas representam uma das formas mais importantes de desenvolvimento urbano. Aprofundar o conhecimento dos impactes destas áreas ao nível dos processos hidrológicos e a sua influência na qualidade da água superficial, constitui o principal objetivo deste estudo. O trabalho foi desenvolvido numa bacia hidrográfica Portuguesa, com características peri-urbanas (Ribeira dos Covões), sob a influência do clima Mediterrâneo.

O estudo considera uma abordagem a várias escalas espaciais e temporais, envolvendo a realização de medições ao nível das propriedades do solo, ensaios em parcelas experimentais e a monitorização à escala da bacia hidrográfica e sub-bacias.

Solos associados a diferentes usos apresentam distintas propriedades físicas que determinam a capacidades de infiltração de água, bem como os mecanismos de geração de escoamento superficial ao longo do ano. Durante períodos secos, a natureza hidrofóbica dos solos florestais e dos campos agrícolas abandonados, localizados na zona de calcários, promove uma baixa capacidade de infiltração da matriz do solo, induzindo a suscetibilidade para a geração de escoamento do tipo Hortoniano. Contudo, a reduzida repelência nas áreas agrícolas (em zona de arenitos) e as características hidrófilas dos solos urbanos promovem uma maior capacidade de infiltração, o que revela o potencial destes solos para a infiltração do escoamento gerado em áreas a montante. Por outro lado, ao longo do período húmido, a repelência do solo vai desaparecendo, o que promove o aumento da capacidade de infiltração, principalmente nas áreas florestais. No entanto, o aumento da humidade do solo restringe a capacidade de infiltração nos solos agrícolas e urbanos, favorecendo a geração de escoamento superficial por saturação, principalmente em locais de fundo de vale e em encostas calcárias de solos pouco profundos.

As áreas florestais apresentam uma elevada capacidade de infiltração de água, mesmo quando a matriz do solo apresenta um elevado carácter hidrofóbico, promovida pela presença de macroporos. Todavia, densas plantações de eucaliptal são menos favoráveis à infiltração de água do que áreas de regeneração natural de eucalipto e zonas de carvalhos, devido à maior repelência do solo.

O padrão climático, nomeadamente a precipitação, determina o regime hidrológico das bacias hidrográficas e a qualidade da água superficial. As características físicas da bacia, tais como a litologia, também afetam os processos hidrológicos, uma vez que determinam a permeabilidade dos solos e o regime hídrico das linhas de água ao longo do ano.

Durante o verão, o escoamento de base representa uma componente relevante das linhas de água, mas o reduzido caudal promove uma baixa capacidade de diluição de poluentes, podendo colocar em causa a qualidade da água durante eventos de precipitação, principalmente devido a concentrações elevadas de carência química de oxigénio e nutrientes. Ao longo da época de chuvas, o aumento da conetividade hidrológica entre as fontes de escoamento superficial e de poluentes, origina maiores contribuições para as linhas de água. Elevadas cargas de poluentes, nomeadamente sólidos em suspensão, metais pesados e azoto, podem colocar em causa a qualidade da água superficial durante maiores eventos de precipitação.

De um modo geral, a expansão das áreas urbanas, e particularmente das superfícies impermeáveis, promove o aumento dos coeficientes de escorrência e origina concentrações médias elevadas de alguns parâmetros que afetam a qualidade da água, tais como nitratos e carência química de oxigénio. No entanto, os impactes nos recursos hídricos são determinados pela localização das fontes dentro da bacia hidrográfica. Fontes de escoamento superficial e poluentes localizadas em posições mais elevadas das encostas podem ter um efeito negligenciável nas linhas de água, devido às oportunidades de infiltração e retenção superficial promovidas pela passagem ao longo da encosta. Por outro lado, fontes de escoamento e de poluentes localizadas nas imediações das linhas de água originam maiores impactes nos ecossistemas ribeirinhos. A presença de sistemas de drenagem de águas pluviais aumenta de forma eficiente a conetividade hidrológica dentro da bacia.

Os agentes responsáveis pelo ordenamento do território e o planeamento urbano devem considerar a utilização de um mosaico paisagístico constituído por diversos usos do solo, de modo a maximizar a infiltração de água e limitar a conetividade hidrológica entre as fontes de escoamento e as linhas de água. A preservação de um regime hídrico mais aproximado ao de características naturais é importante para a minimização do risco de cheia e a degradação da qualidade da água.

keywords

Peri-urban, land-use, soil properties, overland flow, flow connectivity, surface water quality.

abstract

Peri-urban areas represent one of the most important development forms. The aim of this study is to contribute for an improved knowledge about the impact of peri-urban areas on catchment hydrology and surface water quality. The research focus on a Portuguese peri-urban catchment (*Ribeira dos Covões*), under Mediterranean climate.

The study is based on a spatio-temporal multi-scale approach, involving the measurement of soil properties, runoff plot experiments as well as catchment and subcatchments monitoring.

Land-uses have distinct soil properties which provides different infiltration capacities and mechanisms for generating overland flow over the year. During the summer, the hydrophobic nature of woodland and abandoned agricultural-limestone fields exhibit low soil matrix infiltration capacity, being prone to induce infiltration-excess overland flow. However, wettable urban soils and low hydrophobic agricultural fields (overlaying sandstone) have greater matrix infiltration capacity, and can provide infiltration opportunities for uphill overland flow. On the other hand, throughout wet season, hydrophobicity switches off and matrix infiltration capacity increases under woodland soils. But increasing soil moisture limit the infiltration capacity of agricultural and urban land-uses, favouring saturation-excess overland flow, particularly in valley bottoms and hillslope shallow soils overlaying limestone.

Even under widespread hydrophobic conditions in driest settings, woodland areas can provide high infiltration through macropores. Nevertheless, dense eucalypt plantations are less suitable than open eucalypt stands and woodland areas, due to most severe hydrophobicity.

Climate pattern, and particularly rainfall, is the most important parameter affecting stream flow and surface water quality. Physical characteristics of the catchment, such as lithology are also important in determining soil permeability and the temporal stream flow regime.

During the summer, base flow represents a larger percentage of the stream discharge, but the limited flow provide minor pollutants dilution during rainfall events, mainly chemical oxygen demand and nutrients, which may threaten water quality standards. Over the wet season, increasing hydrological

connectivity of overland flow and pollutant sources provide greatest stream flow inputs. Enhanced pollutant loads, particularly of suspended sediments, heavy metals and nitrogen, can hinder surface water quality during wettest conditions.

Generally, increasing urban land-use extent, and particularly impervious surfaces, leaded to enhanced runoff coefficients and high mean concentrations of few pollutants, specifically chemical oxygen demand and nitric oxide. However, impacts on stream flow are largely dependent on the source position across the landscape. Overland flow and pollutant sources located upslope may have a minor impact on riverine ecosystems, due to greater infiltration and surface retention opportunities provided by downslope areas. Contrary, source areas with greater proximity to the stream network would have major impacts. The presence of urban drainage system can efficiently favour flow connectivity, enhancing the impacts on aquatic ecosystems.

Landscape managers and urban planners should employ a mosaic of different land-uses, in order to maximize infiltration and disrupt the flow connectivity between sources and stream network. The maintenance of a more natural hydrological regime would be important to minimize flood hazard and preserve water quality.

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A	Agricultural land-use
ADP	Antecedent dry period
API	Antecedent precipitation index
BFI	Baseflow index
Ca	Calcium
Cd	Cadmium
cfu	Colony forming units
COD	Chemical oxigen demand
Cr	Chromium
Cu	Cupper
DCIA	Directly connected impervious area
E	Nash-Sutcliffe model efficiency coefficient
DE	Dense eucalypt plantations
EIA	Effective impervious area
EC	Electrical conductivity
EMC	Event mean concentration
EO	Sparse eucalypt stands
EL	Event load
FB	Factory-based
FC	Faecal coliform
Fe	Iron
FTU	Formazin turbidity units
Hg	Mercury
$\mathbf{I_{15}}$	Maximum rainfall in 15-minutes interval
$\mathbf{I_{60}}$	Maximum rainfall in 60-minutes interval
IGP	Instituto Geográfico Português
Imed	Mean rainfall event
K	Potassium
Kuns	Unsaturated hydraulic conductivity
LULC	Land-use and land cover
MAV	Maximum admissible values
MED	Molarity of ethanol droplet
Mg	Magnesium
MPN	Most probable number
Mn	Manganese
MRV	Maximum recommended values
N	Nitrogen
$\mathbf{N_2O}$	Nitrous oxide
Na	Sodium

NH_3	Ammonia
NH_4	Ammonium
Ni	Nickel
Nk	Kjeldahl nitrogen (ammonia, organic and reduced forms of nitrogen)
NO_2+NO_3	nitric oxide
NO_3	Nitrate
NPS	Non-point source
O	Oak woodland
ON	Organic nitrogen
OP	Organic phosphorus
P	Phosphorus
Pb	Lead
r	Spearman's rank correlation coefficient
RMSE	Root mean square error
SAR	Sodium adsorption relation
SEL	Specific event loads
SE	Sparse eucalypt plantation
SS	Suspended sediments
TDS	Total dissolved solids as NaCl
TIA	Total impervious area
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
U	Urban land-use
VB	Vegetable-based
W	Woodland
WFD	European Water Framework Directive
WWTP	Wastewater treatment plant
Zn	Zinc

CHAPTER 1
INTRODUCTION

1.1. Research scope

1.1.1. Peri-urban areas

Urbanization has been a worldwide tendency over the last decades (e.g. Duh et al., 2008). In 2000 year, people living in urban areas represented 47% of the world's population, and 75% of European citizens (EEA, 2006). This tendency is expected to continue, with urban population reaching 56% of the world, and 80% of European population by 2020 (EEA, 2006).

The increase in urban surface area has been even greater than that of the urban population. In countries belonging to EU25, urban areas expanded by 78% between 1950s and 1990, while population increased only 33% (EEA, 2006). This trend continued until 2000, with more than 5% increase in urban areas, associated with a lower 2% growth of urban population. This greater increase of urban surface was mainly a result of expansion, increased number of households constructed farther away from the city centres (Jansson and Terluin, 2009).

These trends in urbanization have been driven by a mix of forces including both micro and macro socio-economic trends, such as improved transportation links and enhanced personal mobility, the price of land and individual housing preferences (EEA, 2006). People living in the areas surrounding the cities take advantage of more affordable accommodation than inner urban areas and better quality of life in certain ways (Oyeyinka, 2008).

The transition zones between completely urban and strictly rural landscape, called peri-urban areas, are responsible for the increased radius of urbanization spanning from inner city areas. The word peri-urban is most often used in Europe and Australia, where it refers to land made of a mixture of natural or agricultural lands and urbanised areas. In USA and UK, the word suburban is most commonly used, and it generally refers to residential areas with houses and gardens, but some urban areas are so large that some suburban areas are now distant from urban boundaries and no longer peri-urban.

Peri-urban areas are characterized by a wide range of population density (more than 40 inhabitants per km^2), larger than in rural areas, and comprises distinct land-uses, particularly associated with different urban features, including residential, commercial and leisure-related land-uses (Ravetz et al., 2013). These urban settlements may be linked to dispersed or constrained, scattered or contiguous developments, demonstrating distinct spatial patterns. Due to its complex pattern, peri-urban areas should not be seen as just a zone of transition between urban and rural landscape, but rather a new kind of multi-functional territory (Ravetz et al., 2013).

Peri-urban areas represent a significant part of city land, with almost the same size as urban areas across Europe (48,000 km^2 and 49,000 km^2, respectively) (Piorr et al., 2011). As Figure 1.1 shows, it is the dominant form of urbanization of the northeast European countries (e.g. Poland and Romania) and some southern ones, like Italy. In Portugal, despite peri-urban areas being not so widespread, they represent a significant part of the North-Centre and Algarve regions.

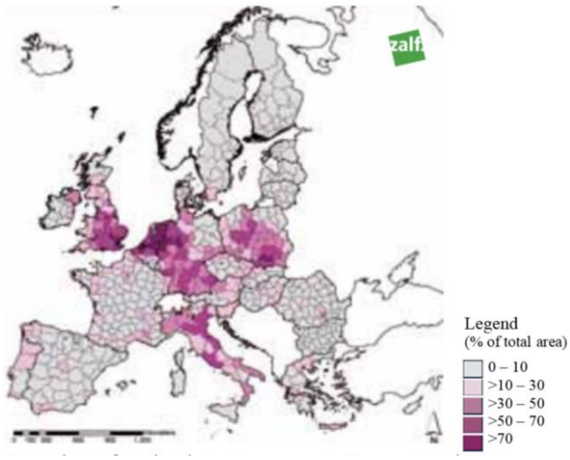


Figure 1.1 - Location of peri-urban areas across Europe, and percentage cover of the total area (Piorr et al., 2011).

Although most urban areas across the world are now growing relatively slowly at a rate of 0.5-0.6% per year (Piorr et al., 2011), but attaining 1.7% per year in developing countries (Ravetz, et al., 2013), built development in peri-urban areas is growing at four times this rate (Piorr et al., 2011). This trend is expected to continue in the future (Ravetz et al., 2013; Miller et al., 2014), even in regions where the population is decreasing. This is particularly the case in some European countries such as Portugal, Spain and in some parts of Italy (EEA, 2010).

Considering the current and potential growth of peri-urban areas, it is important to develop stormwater management strategies to mitigate the impacts of urbanization on both water quantity and quality at the catchment scale. The spatial planning of peri-urban areas represents one of the twenty-first century challenges (Ravetz et al., 2013).

1.1.2. Urbanization impacts on hydrochemistry

1.1.2.1. Hydrological processes

Urbanization, associated with the conversion of cropland, forestry and grassland into at least partly impervious surfaces lead to increasing hydraulic efficiency within the catchments. There have been many studies focusing on the hydrologic impacts of urban areas around the world, identifying changes in: 1) evapotranspiration, due to vegetation removal (Carlson and Arthur, 2000; Costa et al., 2003) and precipitation changes, allied to the “heat island” effects (Jauregui and Romales, 1996), 2) decreasing infiltration capacity following soil compaction and soil water proofing (Carlson and Arthur, 2000), 3) increasing overland flow and streamflow (Corbetts et al., 1997), and 4) shrinkage of groundwater recharge with a corresponding decline in baseflows (Klein, 1979; Smakhtin, 2001; Llorens and Domingo, 2007).

The impacts of urbanization on streamflow are also coupled with changes in hydrograph shape. Since water storage capacity and evapotranspiration decreases in urbanized catchments, more rainfall is available for streamflow and the hydrograph rises more abruptly (Sauer et al., 1983; Rhoads, 1995; Changnon and Demissie, 1996; Konrad, 2002), attaining higher peak flows as imperviousness increase (Espey et al., 1969; Changnon and Demissie, 1996; White and Greer, 2006). Greater peak flows are linked to decreasing return periods (Brath et al., 2006; Ying et al., 2009; Hawley and Bledsoe, 2011) and increasing flood hazard (Hollis, 1975; Swanson, 1998; Wijesekara et al., 2012; Konrad, 2002; Burns et al., 2005; Chang, 2007; Kjha et al., 2011). Urbanization impacts on hydrograph shape are also associated with steep falling limbs (Burns et al., 2005; Verbeiren et al., 2013).

The magnitude of the impacts of urbanization on the water cycle, and particularly on streamflow, are highly variable between research studies. Despite consistency as regards greater streamflow with increasing impervious surface area, the relationship is not linear. Arrigoni et al. (2010) realized that the most heavily modified catchment does not necessarily display the most altered flow regime. Using selected catchments in different parts of Germany, Tetzlaff et al. (2005) noticed that the magnitude of the flow acceleration was more influenced by the physical catchment characteristics, e.g. mean slope and mean elevation, than by urban land-use. Differences in the biophysical characteristics of the catchment, such as geology, lithology, climate and soil properties also affect the hydrological processes, and can mask the influence of land-use changes (e.g. Boyd et al., 1993; Konrad and Booth, 2005). Furthermore, recent studies have been reporting the influence of urbanization type and its spatial pattern accros the catchment on streamflow response (e.g. Leith and Whitfield, 2000; Pappas et al., 2008; Zhang and Shuster, 2014).

Despite several decades of scientific studies focussing on urbanization impacts on hydrological processes, peri-urban studies have been few. However, the different hydrological responses of distinct land-use patterns within peri-urban catchments provide a mix of overland flow sources and sinks, associated with fast and slow water fluxes over the landscape. The lack of few hydrological data from peri-urban catchments has been limiting the understanding of the impact of the landscape mosaic pattern on rainfall-runoff relationships and streamflow response.

Considering the current and potential growth of peri-urban areas, new hydrological data are required for improved assessement of the influence of different spatial land-use arrangements on flow connectivity. Hydrological connectivity influences water passage from one part of the landscape to another, and thereby determines catchment runoff response and flood hazards (Bracken and Croke, 2007; Borselli et al., 2008; Callow and Smettem, 2009; Lexartza-Artza and Wainwright, 2009).

During the last decade, the role of hydrological connectivity has become a key issue in catchment hydrology, but the spatio-temporal variation of hydrological processes is still not well understood (Bracken et al., 2013). In peri-urban areas, flow connectivity represents an additional challenge, considering the different hydrological responses of distinct land-uses. Forest areas have a high rainfall retention capacity due to interception and transpiration process (Legesse et al., 2003; Andréassian, 2004; Delgado et al., 2010), whereas agricultural fields are subject to annual harvesting cycles, which influence evapotranspiration and soil permeability (e.g. through compaction), and thus runoff generation (Martin and Shipitalo et al., 2013). Urban areas are organized in complex structures, consisting of built-up and green areas, separated by the street network. Different combinations and arrangements of land-uses and types of impervious and pervious surfaces within urban areas, affect the ultimate fate of rain during and after storms, influencing the amount of runoff produced and the time at which it is delivered to other parts of the catchment (Jacobson, 2011).

Hydrological connectivity is also affected by antecedent weather conditions, particularly associated with soil moisture status, which affect storage capacity (Bull et al., 2003; Easton et al., 2007). Soil moisture is recognized as a major runoff-controlling factor, particularly in regions under Mediterranean climate (Cerdà, 1997). However, soil moisture variation is not entirely understood, particularly in urbanizing catchments where its spatial and temporal variability are rarely reported (Easton et al., 2007).

Knowledge of runoff processes and flow connectivity across heterogeneous landscapes, and on their temporal variation under contrasting seasonal conditions, such as in a Mediterranean climate, is of utmost importance for catchment management. Understanding the impacts of land-use pattern on spatio-temporal variation of hydrological processes is required to improve urban planning and to support water management decisions, particularly within peri-urban catchments.

1.1.3. Surface water quality

Human interference in the natural environment, particularly through urbanization, also influences streamflow chemistry. Different land-uses such as woodland, agriculture and urban areas, residential, commercial and industrial uses, with different proportions of impervious and pervious surfaces (e.g. lawns and gardens) generate runoff with specific physical-chemical characteristics.

Land-use properties determine the ability to absorb, release and/or transport different concentrations and loads of chemical substances, such as nutrients, heavy metals, microorganisms, pesticides and hundreds of organic contaminants, such as hydrocarbons, hormones, antibiotics, surfactants, endocrine disruptors, human and veterinary pharmaceuticals (e.g. Goonetilleke et al., 2005; Pal et al., 2014). All these pollutants affect the physical, chemical, and biological health of a stream, with negative consequences for biological habitat, aesthetic value of natural watercourses, and utility of water for different purposes, such as human consumption and irrigation, linked to health hazards (Hammer, 1972; Arnold and Gibbons, 1996; Paul and Meyer, 2001; Brilly et al., 2006).

Many studies have focused on the impact of different land-uses, particularly agricultural activities, and point source discharges on water quality (Compton et al., 2000; Kulabako et al., 2007; Gooddy et al., 2014). Vegetated areas, such as forestry, cultivated fields and lawns are frequently associated with higher nutrient contributions to the streamflow (Steuer et al., 1997; Goonetilleke et al., 2005; Groffman et al., 2009), whereas impervious surfaces within urban areas and particularly industrial zones are prone to increase levels of nutrients in rivers and streams (Herngren et al., 2004; Pitt and Maestre, 2005; Zhang et al., 2007; Li et al., 2012). It is usually accepted that pollutant load increase directly with the percentage of total impervious area (TIA), and several authors have been considering this parameter has an indicator of the ecological and environmental conditions of an aquatic system (Schueler, 1994; Arnold and Gibbons, 1996; Paul and Meyer, 2001; Morse et al., 2003; Kuusisto-Hjort and Hjort, 2013). However, a wide range of water quality impacts resulting from land-use changes, particularly urbanization, has been reported.

Surface water quality is driven not only from land-use type but also from land-management, such as fertilizer and manure application (Gross et al., 1990; Easton and Petrovic, 2004; Khai et al., 2007; Antonious et al., 2008). The location of pollutant sources within the catchment and the connectivity with the stream network, driven by the spatial distribution of different land-uses and the presence or absence of urban drainage system, have been considered as an important parameter determining water quality impacts (Booth and Jackson, 1997; Brabec et al., 2002; Ouyang et al., 2009). In urban catchments, the connectivity issues can be far more important for water quality than percentage of impervious surface (Brabec et al., 2002; Wickham et al., 2002; Carey et al., 2011). Furthermore, catchment properties, such as lithology, influence not only the runoff processes and flow connectivity, but can also inprint specif physical-chemical properties on runoff, which affect water quality (Bricker and Jones, 1995; Richards et al., 1996).

The variation of surface water quality and pollutant loads is also a function of climatic factors including rainfall, which influence streamflow variability and thus pollutant loads (Goonetilleke et al., 2005; Thompson et al., 2012; Rodríguez-Blanco et al., 2013). Antecedent weather conditions also affects pollutant deposition at the catchment surface, resulting mainly from atmospheric deposition, particularly important due to anthropogenic emissions, such as vehicular traffic and industrial emissions (Bernhardt et al., 2008; Apeagyei et al., 2011). The length of antecedent dry period (ADP) influences the amount of pollutants available to be washed-off during rainfall events, with impacts on streamwater quality (Marsalek, 1976; Vaze and Chiew, 2002; Qin et al., 2013).

Understanding the spatio-temporal dynamic of runoff sources and its physical-chemical properties, as well as how connectivity governs pollutants transfer during and between rainfall events, is limited. Despite several studies focused on the relation between land-use and pollutant loadings, as well as the interactions between multiple land covers within a single catchment, outcomes to date have been inconclusive, particularly because of relatively scarce hydrologic and water quality data, and thus making it difficult to identify cause–effect relationships. However, knowledge on pollutant buildup and wash-off processes in distinct land-uses is a key research need.

Further investigation is required to better assess the impact of the landscape mosaic on surface water quality, particularly in peri-urban areas. This knowledge should guide decision-makers and policy actor on sustainable solutions for water quality management, in order to attain the "good ecological status" of rivers, as imposed by the European Water Framework Directive (WFD, 2000). The information of pollutant source areas is fundamental to develop and implement cost-efficient strategies to improve water quality, and to move beyond the dependency on customary structural measures and end-of-pipe solutions and prevent water quality problems at the catchment and urban planning scale.

1.2. Aim and objectives

The main aim of this research is to contribute to assess the impact of a mosaic of different land-uses on overland flow processes and its contribution to surface hydrology and streamwater quality in a Mediterranean climate and socioeconomic setting. The study focuses on a peri-urban catchment in Portugal, where this subject has been poorly investigated. The specific objectives are, for this peri-urban context:

1. Assess the spatio-temporal variability of soil hydrological properties in different land-uses of the mosaic;

2. Investigate how and why overland flow processes and its spatial pattern change over the year, as a result of the seasonal Mediterranean climate;

3. Assess the impact that different landscape patterns, marked by different extent and location of urban areas, have on flow connectivity and stream discharge, and also on streamwater quality;

4. Provide some guidelines to improve land management and urban planning on peri-urban catchments, in order to minimize flood hazards and water quality degradation.

1.3. Research design

The research is based on *Ribeira dos Covões* study site, a small peri-urban catchment undergoing rapid urbanization due to its proximity to Coimbra city centre, the largest city in the central part of Portugal. The main elements of the research design are shown in Figure 1.2. In order to fulfil the objectives regarding to the quantification of the hydrological processes, a combined approach of field data acquisition and analysis was adopted at different scales: pedon, plot and catchment. This inclusive methodology provides a better understanding of the rainfall-runoff processes and the impacts on catchment hydrology. Spatio-temporal variation of surface water quality was assessed using the same multi-scale approach, but focusing on the sub-catchment and catchment scales.

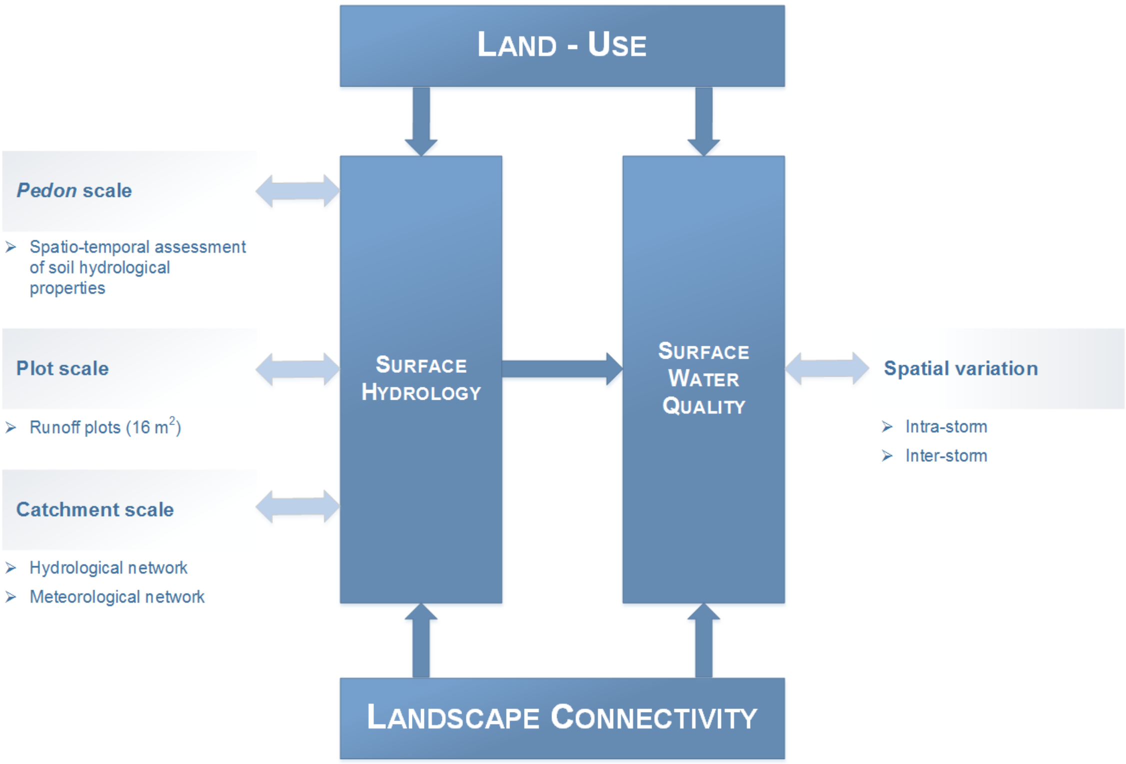


Figure 1.2 - Research design to assess the impacts of peri-urban areas.

At the Pedon scale, in order to assess the land-use impact on soil hydrological properties, a network of 31 sites was established focussing on six distinct landscape (land-use/lithology) units. The number of selected sites per landscape unit was a function of their representativeness within the catchment: 11 sites in woodland, 9 being on sandstone and 2 on limestone; 2) 11 sites in agricultural fields, including 5 on sandstone and 6 on limestone; and 3) 9 sites on unpaved urban soils, comprising 4 on sandstone and 5 on limestone. Over a one-year period, nine monitoring campaigns were carried out. These assessed the variability of surface soil matrix infiltration capacity, surface soil moisture content (0-50 mm) and hydrophobicity at different depths (0 mm, 20 mm and 50 mm) within the distinct landscape units. Spatial patterns of non-transient soil properties were also analysed at each site: bulk density, organic matter content, particle size and rock fragment content.

At the Plot scale, spatio-temporal variability of overland flow processes was explored through the installation and monitoring of runoff plots (8m×2m). However, the absence of landowners' authorization to install plots in agricultural and urban soils, restricted the study to woodland areas. Considering the representativeness of woodland areas within *Ribeira dos Covões* catchment, the study investigated the rainfall-runoff relationship in the three most representative woodland types: 1) dense eucalypt plantations; 2) sparse eucalypt stands; and 3) a relic of semi-natural oak woodland. Three replicated plots per woodland type were considered. Overland flow depth was measured at 1- to 2-weekly intervals, depending on rainfall events, during two hydrological years. To better understand spatio-temporal differences of overland flow, additional measurements of throughfall (manual gauges), soil moisture (0-100 mm) and hydrophobicity (0 mm, 20 mm and 50 mm depth) were performed at the same time as overland flow measurements.

The land-use impact on streamflow was assessed at the sub-catchment and catchment scales. Data at the catchment scale was derived from a continuos flow gauging station that had been established in 2008 at the catchment outlet. In order to assess the impact of different landscape patterns, characterized by different land-uses and urbanization styles, the hydrological and meteorological network was extended by eight additional raingauges and eight water-level recorders to provide continuous data records at the sub-catchment level. Discharge differences were evaluated through 1) annual and monthly flows, by runoff coefficient and baseflow index examination, and 2) analysis of individual rainfall events, in terms of flow depth, runoff coefficient, surface runoff coefficient, peak flow, response and recession time. A detailed characterization of the land-uses and the urban areas within each sub-catchment was performed, in order to enable the impact of flow connectivity to be explored. This strategy also enabled the roles of climatic variability on streamflow of different lithological units (sandstone vs limestone) to be explored.

The impact of land-use pattern on water quality was also assessed through several water samples collected in four sites of the stream network. Samples were taken at the catchment outlet and in three sub-catchments with distinct land-uses (urban areas ranging between 9-25% and 50%) at different times during eight rainfall events of differing magnitude and antecedent weather.

The integrated approach of this methodology was considered to provide a better understanding of the spatio-temporal variation of overland flow sources and sinks over the landscape and the influence on streamflow. This knowledge was used in the thesis to provide guidelines for urban planning and catchment management, in order to minimize flood hazards and maintain a good water quality status, through flow connectivity breaks between the potential sources and the stream network.

1.4. Thesis structure

Subsequent to this introductory chapter (Chapter 1), this manuscript is divided into six additional chapters. Chapter 2 was based on literature review and presents the state of the art regarding land-use impacts driven by urbanization on hydrology and surface water quality. Chapters 3-5 present and analyse the results of the programme aimed at quantification of surface hydrological processes in *Ribeira dos Covões.*

Chapter 3 is focused on the spatio-temporal variability of soil hydrological properties. Differences in soil moisture, hydrophobicity and soil matrix infiltration capacity were measured over one year, in different land-uses (woodland, agricultural and urban) overlaying sandstone and limestone lithologies. These results are analysed in terms of potential overland flow sources and sinks within the catchment, and how they may change over the year, as a result of contrasting seasonal patterns associated with Mediterranean climate.

Chapter 4 is dedicated to the field experiments carried out in woodland areas of *Ribeira dos Covões* over two years, analysing overland flow differences between dense eucalypt plantations, sparse eucalypt stands and oak woodland. Temporal variation of overland flow processes between dry and wet seasons are discussed based on soil moisture and hydrophobicity variation. The potential impact of different woodland patches as sources and sinks of overland flow in peri-urban catchments is also addressed.

The influence of land-use pattern on streamflow (sub-catchment and catchment scale) are investigated in Chapter 5. The influence of urban areas, characterized by distinct extent cover, proportion of soil sealing, distance to the stream network and dissimilar water management strategies, on stream discharge (e.g. runoff coefficients, flow depth, peak flow, response and recession times) are analysed and discussed. The influence of climate variability and lithology on catchment hydrological response is also analysed. Spatio-temporal differences in the flow regime are discussed in terms of flow connectivity.

Current problems of water drainage systems within the catchment are stressed, and the implications of the forecasted urbanization trend on flood hazard are pondered.

Chapter 6 focuses on the impact of rainfall pattern on water quality. Physical-chemical properties of distinct drainage areas within the peri-urban catchment are presented. The impact of different rainfall events on physical-chemical properties of surface water are assessed in relation to Portuguese standards for minimum environmental water quality. The results are analysed and discussed in terms of differences in the urbanization type.

The chapters focusing on field data analysis (Chapters 3, 4, 5 and 6) are structured in the format of individual scientific publications. Thus they each comprise a small introduction to the covered content, a study site description focusing the most relevant aspects regarding to that chapter, the methodology used to achieve the specific objectives, the associated results as well as their analyses and discussion, and the key conclusions. Because of this structure, the introductory sections involve partial repetition, although focussing on specific topics.

Chapter 7 summarises the main findings of the thesis. It then provides some suggestions to improve stormwater management in the study site, as well as guidelines to improve general land management and urban planning at the catchment scale, in order to minimize flood hazard and preserve surface water quality. The challenges and limitations of the research are also discussed.

A consolidated list of references for the entire thesis is provided. Thus, to avoid repetition, individual lists for Chapters 3-6 were not presented, despite their scientific paper structure in all the other aspects.

CHAPTER 2
URBAN AND PERI-URBAN LAND-USE CHANGE IMPACTS ON HYDROLOGICAL PROCESSES AND SURFACE WATER QUALITY: A REVIEW

2.1. Introduction

Population growth has been driven a global urbanization trend, associated with great environmental pressure, particularly as a result of land-use changes. The conversion of natural landscapes into agricultural fields and impervious surfaces can substantially affect hydrological processes at several scales and the equilibrium of aquatic ecosystems. The increasing tendency for urban sprawl from the urban cores, associated with a low-density development, is a major factor in the acceleration of the extent to which impervious surfaces come to dominate the landscape (Zhang and Shuster et al., 2014).

Over the last 50 years, land-use change impacts on water cycle have been widely monitored and documented, but the studies focusing the impact on water quality are more recent. Human activities and different land surface covers affect water yields, interception losses, evapotranspiration rates, flood peaks, sediment transport rates, and concentrations and loads of many water quality constituents.

Nevertheless, these consequences are not only affected by the spatial extent of land-use changes, but tend to be also site-specific, particularly due to the influence of climate on temporal variation of the hydrological processes (e.g. Cerdà, 1997; Cammeraat, 2002; Easton et al., 2007). Field observations and measurements are undoubtedly the base to understand human effects on the hydrological cycle and water quality issues. Recent improvements in data collection, data archiving, data distribution and computational capabilities to support such analyses represent important parameters to enhance knowledge about land-use impacts. However, it has proven to be quite challenging to draw conclusions from studies due to relatively short time series and great local spatial variation in parameters, such as geology, lithology and soil depth (Calvo-Cases et al., 2003; Güntner and Bronstert, 2004; Komatsu et al., 2011; Lorz et al., 2007; Hardie et al., 2012).

The consequences of land-use changes are of interest not only for the academic community, particularly hydrologists and ecologists, but are also of critical importance for land management and urban planners. The proper planning of landscape pattern and runoff management, associated with flood control measurements, as well as protective actions to ensure water quality standards and thus, public health and environmental protection, are critically dependent on the understanding of human impacts at the catchment scale. There is a clear trend towards approaches that attempt to restore pre-development flow-regimes and water quality simultaneously. There has been an increasing recognition that restoring a more natural water balance benefits not only the environment, but enhances the “liveability” of the urban landscape (Fletcher et al., 2013).

The main goal of this chapter is to present a synthesis of a wide-ranging literature on the effects of land-use change, particularly associated with urbanization on (1) hydrological processes and (2) surface water quality.

2.2. Hydrological consequences of land-use change focusing on urbanization/peri-urbanization

2.2.1. Methodologies to assess hydrological impacts at the catchment scale

The methods used by researchers to assess impacts of land-use change on the hydrological response of catchments, may be grouped into: 1) paired catchment monitoring, 2) time series analysis, and 3) hydrological modelling. The first approach is based on the comparison of adjacent catchments with different degrees of urban development and under similar climate settings, as well as similar geological characteristics. However, this methodology has been mostly applied in small catchments, given the difficulty to find two similar catchments with medium or large sizes. The use of one catchment has been also considered if it contains areas with different land-uses, but spatial differences in physical characteristics of the catchments are limiting to the conclusions. Increasingly, a "double comparison" approach has been adopted by including a "control" catchment in which there has been no land-use change in the study period, but which has had the same land-use history as the ones undergoing change.

The data exploration approach is based on statistic time-series analysis of hydrological data from areas undergone urbanization. Different studies focused on few years of streamflow data (e.g. Huang et al., 2008; Wijesekara et al., 2012), whereas other studies are based on a few decades of records (e.g. Mungai et al., 2004; Leopold et al., 2005). Several parameters have been considered by different authors to assess the impact of urbanization on streamflow regimes, including statistical tests and characterisation of high and low flows. Braud et al. (2013) reviewed the methods applied for streamflow analysis, and extracted five classes of indicators used to examine the impact of land-use/land cover change on discharge time series. These are 1) parameters related to hydrological regime, such as annual runoff, seasonal components, discharge quantiles and flow duration curves; 2) high flows characterization, focussing on annual maximum discharge and peak flows; 3) low flow indicators, such as minimum annual discharge, frequency of zero discharge, baseflow index (defined as the ratio between annual baseflow and total annual flow); 4) hydrograph analysis, including the study of event characteristics (runoff coefficient, rising and falling limbs of hydrographs) and the quantification of flow components into baseflow, interflow and quick flow; and 5) indicators based on statistical analysis of long time series, in order to compare differences between various periods as well as trend analysis.

Since controlled field-scale experiments are difficult to perform because of land-use and climate changes, numerical models have been widely implemented to predict the hydrological consequences of these alterations and to anticipate the impact of future global changes (e.g. DeFries and Eshleman, 2004; Delgado et al., 2010). These methods mostly rely on either simple or lumped, distributed or conceptual hydrological modelling

(Wijesekara et al., 2012). However, models are subjected to uncertainties in their structure, inputs, and parameter estimation so that the measure of their reliability is always questionable (Zhang and Shuster, 2014). For example, Bhaduri et al. (2001) compared modelling results from the L-THIA (Long-Term Hydrologic Impact Assessment) model with the SWMM (Stormwater Management Model) in two small catchments in Chicago. Results indicated that L-THIA predicts annual average runoff between 1.1 and 23.7% higher than SWMM.

Differences between modelling results reinforce the need for field data in order to improve model efficiency. In addition, the choice of model is always limited by available data, computing capabilities and thorough knowledge of the catchment hydrology (Chu et al., 2013). A review of different hydrological models used to assess the impacts of land-use changes was performed by DeFries and Eshleman (2004). Recently, the Peri-Urban Model for landscape Management (PUMMA) was specifically designed to study the hydrology of peri-urban catchments. This model combines rural and urban hydrological models, and is used for process understanding (Jankowfsky et al., 2012).

2.2.2. Urbanization impacts on catchment hydrology

The process of urbanization leads to changes on the water cycle. As an area becomes dominated by impervious surfaces, decreasing evapotranspiration and soil infiltration capacity lead to increasing surface runoff and enhanced hydraulic efficiency over the landscape, promoting a decreasing groundwater recharge. Nevertheless, the magnitude of such impacts varied greatly among study sites. Some examples are given below.

Based on modelling results, increasing urban surface from 20 to 100% in U.S.A catchments leads to a 50% increase in total runoff and a 50% reduction in actual evapotranspiration and percolation to groundwater (Albrecht, 1974). In contrast, in Canada, a 65% increase of built-up areas in southern Alberta, was calculated to provide decreases of only 1% and 2.3% in total evapotranspiration and water infiltration, respectively. These changes led to a 7.3% increase in stream runoff, but also to a 13.2% decrease in baseflow, resulting in a total flow decrease of 4% (Wijesekara et al., 2012).

In the Southern River catchment, Western Australia, 20% urbanization of a natural area fomented a significant reduction in evaporative losses from the soil profile, and a decrease from nearly 80% to less than 20% in infiltration, causing a decrease on water table after urbanization. In addition, increases in total annual discharge were associated with a predicted runoff coefficient rise from 1% to more than 40%. However, increased streamflow was mainly due to higher groundwater recharge and subsequent catchment baseflow, as a result of the roof and road runoff infiltration and establishment of subsurface drainage adopted in local construction practices (Barron et al., 2012).

Other studies also reported greater impacts of imperviousness on surface flow than on total streamflow (Choi et al., 2003; Li and Wang, 2009). A comparison between streamflow of a mixed land-use catchment and an urban catchment in the Portland Metropolitan Area of Oregon, USA, reported significant increases in runoff during storm events rather than increases in mean annual runoff (Chang, 2007). In Dardenne Creek catchment, Missouri, the urban area increase from 3.4% to 27.3% was accomplished by a modelling forecast of >70% increase in average direct runoff (Li and Wang, 2009).

In Leipzig, Germany, modelling analysis of available data demonstrated increased storm flow with the extent of impervious land, but storm flow increased less severely where the soil had a poor infiltration capacity before it was surfaced, depending on soil texture. Only when the impervious area reached 20% of the surface, did storm flow values start to double, since before that impervious threshold there were still sufficient un-built surfaces in which the precipitation could percolate and infiltrate. When the surface was largely unsurfaced, annual storm flow was of the order of 25-150 mm, but reached 200 mm when imperviousness amounted to 40–60%, and attained more than 300 mm when imperviousness exceeded 80% of the area (Haase, 2009).

Based on Gwynns Falls catchment near Baltimore, Brun and Band (2000) found a threshold of 20-25% impervious cover was necessary to identify changes in runoff coefficient. Also Hawley and Bledsoe (2011) found from the analysis of 43 gauging stations installed on urban streams within semi-arid southern California, that with more than 20% imperviousness, streamflow experienced five times as many days of mean daily flows higher than 3 $m^3\ s^{-1}$ and approximately three times as many days of the order of 30 $m^3\ s^{-1}$ relative to the undeveloped setting.

In Accotink Creek, Virginia, Jennings and Jarnagin (2002) identified statistically significant increases in mean daily streamflow response when impervious cover increased from 13% to 21%, associated with mean and extreme daily precipitation levels. Analysis of historical mean daily streamflow also revealed a decrease in the precipitation amount required to produce a given level of streamflow. However, Burns et al. (2005) reported a 300% increase in mean peak discharges for a catchment with only 11% impervious surface compared with a similarly sized catchment with no impervious surface.

Increasing frequency of high flow events resultant from urbanization was also reported in other studies, accompanied by a decreasing frequency of low-flow events. In the Big River catchment, in east-central Missouri, a three fold increase in urban area in 15 years resulted in a 140% increase of high flow events, as well as a decrease in frequency of low flow events by up to 100% (Chu et al., 2013).

In Atlanta Metropolitan Area, Georgia, USA, a comparative study of streamflow characteristics of non-urbanized, less-urbanized and highly urbanized catchments, exhibited 30–100% greater peak flows in the latter. In the highly urbanized catchment, shorter storm recession period (1–2 days less than in the other catchments) and baseflow recession constants (35-40% decrease), were attributed to the more efficient routing of stormwater and the paving of groundwater recharge areas (Rose and Peters, 2001).

In the Tanshui catchment, Taiwan, urban development from 4.8% to 12.5% led to shortened times to peak flow from 9 to 6h, and the recurrence intervals of 200, 100, 50, and 25 years before urbanization were reduced to about 88, 33, 16, and 8 years (Huang et al., 2008). However, in the Mid-Atlantic Region, Jarnagin (2007) reported a 20% development has a 'hard limit' (with 10% imperviousness) without significant changes in stream hydrology, particularly on stream flashiness.

Rogers and DeFee (2005) suggested that when urban development exceeds 25% of the catchment area, the potential for floods and droughts increases exponentially. Increased flood frequency was also demonstrated in the streamflow records of six urbanized basins in Puget Lowlands, Washington, subject to distinct degrees of urbanization (Moscrip and Montgomery, 1997). Generally, events of 10-year recurrence interval in pre-urbanization stage, were shortened to 1 to 4-year recurrence interval events in post-urbanization records.

Some authors also suggest that urbanization mainly affects the flow peaks of smaller events with higher frequency, and have only a minor impact on larger storm events. In the Apennines of Itally, a 5% urbanization of a meadow and pasture region over a 20 years period, showed a greater incidence of lower return period discharges, but only small increase in peak flows of 10 and 200 years return periods.

In Xitiaoxi catchment, China, modelling results revealed that for an urban area increase from 9% to 17% of the catchment, the expected peak flow increase was 3.9%, 2.7% and 2.3% associated with recurrence intervals of 10, 50 and 100 years. For the same recurrence intervals and for a scenario of urban area increase from 9% to 14%, the peak flow increases were 3.3%, 2.4% and 2.1%, respectively (Ying et al., 2009). In Qinhuai River catchment in Jiangsu Province, China, an increase in impervious surface from 2.3% to 13.9% led to daily peak discharge rise from 2.3% to 13.9%, but also indicated greater impacts associated with smaller than larger rainfall events (Du et al., 2012).

The long-term observation of urban growth and sprawling land consumption has proven that it is the cumulative impact of land-use change and surface sealing, rather than short-term consequences of construction that is likely to impair the urban water balance. However, research along 47 southeastern Wisconsin streams found that baseflow declined significantly when catchment imperviousness exceeded a threshold range of 8 to 12% (Wang et al., 2011). In Philadelphia catchments, baseflow declined steadily until catchment imperviousness reached 40% to 50% (Hammer, 1972).

Detailed reviews of the urban impacts on catchments hydrology are given by Shuster et al. (2005), Jacobson (2011) and Fletcher et al. (2013), but a synthesis of streamflow variation resultant from urbanization is shown on Figure 2.1.

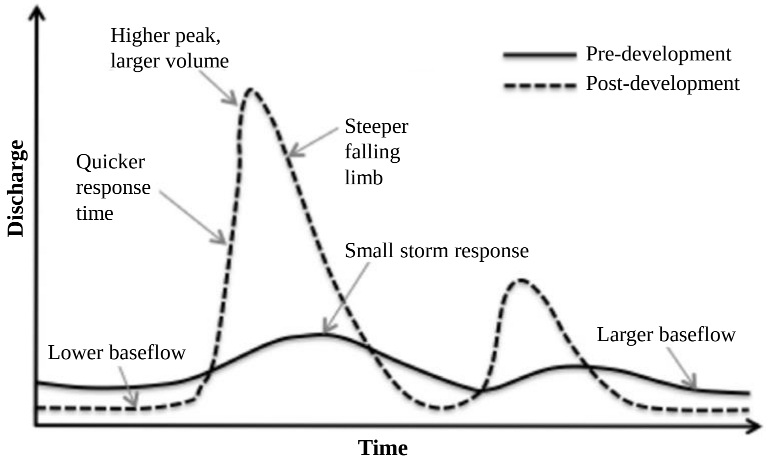


Figure 2.1 - Schematic illustration of the urbanization impacts on hydrograph shape (adapted from Fletcher et al., 2013).

2.2.3. Overland flow processes and flow connectivity over the landscape

Despite a large degree of consencus between hydrological studies focusing on urbanization impacts on the water cycle, particularly on streamflow changes, magnitudes of impact vary and differ concerning the existence of an urban cover threshold. These variations may be a consequence of differences in (1) the spatio-temporal pattern of runoff processes generated within the catchments, and (2) the flow connectivity between sources and the stream network.

In urban and peri-urban catchments, overland flow can occur on both pervious and impervious surfaces. Pervious surfaces can generate infiltration-excess overland flow (Hortonian flow) when precipitation intensity exceeds the soil infiltration capacity (Horton, 1933). It depends on soil properties, such as unsaturated hydraulic conductivity, which may be an important predictor of runoff timing and volume (Shuster et al., 2005). Urban soils are usually associated with lower infiltration capacity, due to physical degradation through compaction, linked to increased soil bulk density and decreased porosity (Dornauf and Burghardt, 2000; Yang and Zhang, 2011). Infiltration-excess mechanism is very important not only in pervious urban surfaces, but also in bare soils and cultivated areas, where significant soil crusting and/or surface sealing occurs during rain events (Steenhuis et al., 2005).

During wet periods, overland flow can be also generated in saturated areas of permeable soils. It is driven by rainfall amount and antecedent weather conditions (Dixon and Earls, 2012) and is dependent on landscape factors such as shallow soil depth (affects available water storage capacity), slope concavities and hollows (Walter et al., 2000; Steenhuis et al., 2005). This saturation mechanism is mainly important in humid and well vegetated regions (e.g. Dunne and Black, 1970).

Impervious surfaces, such as roads and roofs, are prone to generate overland flow, given their small storage capacity and smooth surface (Albrecht, 1974). Road surfaces in UK cities were found to infiltrate only 6 to 9% of the rainfall, depending on the nature of the surface, subsurface layers, level of traffic, etc. (Rabag et al., 2003). However, if overland flow from impervious surfaces flows onto pervious surfaces, it may infiltrate before reaching the catchment drainage network (Boyd et al., 1993). Thus, streamflow response will depend on the extent and distribution of impervious and pervious surfaces, as well as the connectivity between land surface and the drainage network, driven by the spatial form and location of different land-uses (Hawley and Bledsoe, 2011; Jacobson, 2011; Mejía and Moglen, 2009; Parikh et al., 2005).

Slopes can therefore behave as a mosaic of runoff and run-on areas, providing non-uniform infiltration. On each surface, interception and depression storage must be satisfied before overland flow commences. Initial losses are known to be small on impervious surfaces (Melanen and Laukkanen, 1981; Pratt et al., 1984; Jensen, 1990), but larger on pervious areas (Boyd et al., 1993). As a consequence, overland flow from pervious sites is more difficult to predict than runoff from impervious surfaces, because it depends on land-use, soil properties, geology, surface topography, as well as antecedent wetness. These factors influence the landscape structure and spatial organisation of a catchment which, in turn, determine the distribution of water flow paths, the patterns of water storage and residence time distributions (Soulsby et al., 2006).

When rainfall intensity exceeds infiltration capacity and/or the soil become saturated, the excess water remains on the surface and partly fills depressions. If rain persists, depressions become filled and overland flow occurs, connecting adjacent depressions. With additional rainwater, more and more depressions become connected and a network of flow paths is eventually formed and may reach the outflow boundary (Darboux et al., 2001). If rainfall has occurred prior to an event, soil moisture stores will be part full and the water retention capacity is lower (Boyd et al., 1993).

A simulation study performed by Liu et al. (2006) demonstrated than in Steinsel catchment, Luxembourg, the overland flow coefficient and runoff partitioning from different land-use areas vary from one storm event to another due to the differences in soil moisture and storm characteristics. Increasing overland flow with greater soil moisture was also reported in a small catchment located in a suburban area near Nantes, France, where base flow represented on average 14% of the total per-event streamflow, but increased to average 36% during rainfall events (Berthier et al., 2004). These studies also show that the pervious part of a catchment may contain source areas which generate most of the runoff, with little runoff coming from the remaining pervious areas.

The presence of vegetation and litter increases soil roughness (soil irregularities and cavities) and therefore depression storage capacity (hydraulic resistance), which may provide local water storage capacity and aid infiltration, by providing runoff obstructions and delaying or eliminating overland flow transfer downslope (Darboux et al., 2001; Calvo-Cases et al., 2003; Bracken and Croke, 2007; Borselli et al., 2008; Rodríguez-Caballero et al., 2012). The capacity of the vegetation to reduce runoff volume and velocity depends on: (a) the plant cover/biomass (Kirkby et al., 2002) and its characteristics (width and slope of the vegetation strip, vegetation height, density, stiffness and species composition); (b) the inflow (runoff velocity, discharge, and volume); and (c) the antecedent weather conditions (López-Vicente et al., 2013). Vegetation creates a mixture of run-off and run-on sites determined by soil wetness (Castillo et al., 2003), reason why it has been considered by many authors as a key factor interrupting hydrological connectivity (e.g. Bracken and Croke, 2007).

In urbanized areas, vegetation is cleared and the soil surface is often graded, depressions are filled and impervious surfaces are extended. This leads to decreased depression storage capacity and a concomitant decline in natural sinks for water infiltration. As a consequence, larger volume of water is available for overland flow, reaching higher velocities due to water resistance reduction at the surface. In addition, overland flow amount and velocity is also a function of the slope, since gentle slopes favour infiltration but also lead to easier saturation due to the influence of throughflow, whereas steep slopes lead to larger amounts of overland flow (Bronstert et al., 2002).

2.2.4. Influence of spatial land-use pattern

Considering the relevance of the extent and location of pervious and impervious surfaces to overland flow and runoff generation, the understanding and quantification of the hydrological impacts of urbanization require a detailed characterization of different land covers (Shuster et al., 2005; Mouri et al., 2011; Berezowski et al., 2012). Several methods have been used to analyse the spatial arrangement of land-uses and imperviousness within catchments, as can be found in the reviews by Jacobson (2011) and Weng (2012).

The distance between overland flow sources (pervious soils and/or impervious surfaces) and the drainage network (main channel or tributaries) represents an important parameter influencing streamflow response (e.g. Wang et al., 2000). Source areas located close to the drainage network can be significant contributors to runoff, while those located further away may provide no or only a minor impact on streamflow, due to the greater opportunities for surface flow retention and infiltration over the hillslope. Through the modelling of two small catchments (<1 ha), Zhang and Shuster (2014) demonstrated less hydrological connectivity between impervious elements and the outlet when pervious elements are located downslope.

The lack of flow connectivity between runoff sources and the stream network has been used to explain unexpected patterns between total impervious area (TIA) and streamflow parameters (Hawley and Bledsoe, 2011; Jacobson, 2011). In order to overcome these problems, some authors have been considering the Effective Impervious Area (EIA) parameter, which represents the impervious areas directly connected to the stream network (Roy and Shuster, 2009; Jacobson, 2011; Yang and Zhang, 2011).

A laboratory study by Pappas et al. (2008) showed higher stream runoff generation when impervious surfaces were located downslope comparing with similar upslope imperviousness. Overland flow from directly connected impervious surfaces will reach the slope outlet more rapidly than where impervious surfaces run-off onto areas having significant capacity for abstraction or storage. In contrast, if the runoff from upslope impervious surfaces are not directly connected with the outlet, it will only contribute for streamflow if downslope soil infiltration capacity or water storage capacity are exceeded by rainfall and generate run-on. Through rainfall events, as the downslope soil infiltration capacity and/or storage capacities decline, soil surface generates overland flow and can become similar to an impervious surface.

In the lower Fraser Valley of British Columbia, Canada, discharge data from streams draining areas with similar percentage urbanization increase but distinct types of urban development, displayed greater runoff coming from areas with large housing developments and extensive parking lots, than areas with small housing developments distributed throughout the catchment (Leith and Whitfield, 2000).

The mixed land-use character of peri-urban catchments can therefore provide increasing retention capacity of the overland flow, showing a lower hydrologic impact than classical urban catchments (Jankowfsky et al., 2012). However, seasonal variation of runoff sources can result from changes in pervious area contribution during wettest periods. In Chaudanne catchment, which is located in the peri-urban area of Lyon, France, under a temperate climate with Continental and Mediterranean influence, uncalibrated model results showed the importance of overland flow from impervious areas in summer events and flow contributions from rural zones during winter events (Jankowfsky et al., 2012).

Based on the analysis of the streamflow records from 26 urban basins located in 12 countries, Boyd et al. (1993) showed that small amounts of pervious runoff occurred for most storms, but increased for larger storms. These led to a greater scatter of data in catchments with pervious overland flow than those dominated by impervious overland flow. These authors also reported that larger basins tend to generate both pervious and impervious runoff.

Variable runoff contributions from pervious areas can be enhanced by the subsurface water connectivity. During a wet period, Burns et al. (2005) observed greater flows from an undeveloped catchment in Croton River basin, New York, USA, than an alike residential one (similar size, geomorphology and physiographic characteristics) as a result of greater subsurface storage and/or hydraulic conductivity of the soil at depth, leading to greater baseflow contribution. On the other hand, with increasing impervious cover and a concomitant decrease in subsurface runoff, the importance of antecedent soil water content to overland flow formation is restricted (Shuster et al., 2005).

Within urban areas, the road network has been considered an important source of overland flow and a main cause of decreased water concentration time. Eisenbies et al. (2007) estimated that road networks could increase the effective drainage density by 40-100%. Road cuts may also intercept subsurface water by breaking the natural movement of pipeflow, or by creating artificial areas of water resurgence through disruption of subsurface flow networks. In recent years, best management practices consider the location and form of road networks in order to redirect overland flow at topographic breaks and other permeable sites, thus minimizing connectivity with streams (Eisenbies et al., 2007; Hümann et al., 2011).

2.2.5. Impacts of water management activities

Besides the spatial distribution of pervious and impervious surfaces within a catchment, flow connectivity is also affected by water management activities (Reed et al. 2006; DeFries and Eshleman 2004). Problems of urban runoff are usually managed with engineered solutions linked to the channelization of water. In urban/peri-urban areas there are three basic types of drainage systems: 1) sanitary sewerage for domestic and industrial wastewater, 2) storm drains intended to rapidly and safely convey storm runoff, and 3) combined sewerage, which drains wastewater and storm runoff in one system.

The introduction of artificial drainage increases the direct input of precipitation into stream channels, by circumventing depression storage and groundwater recharge (Foster et al., 1999). In the urban area of Nassau County, total streamflow declined when local water users began to send wastewater to a regional sewer system and abandoned the use of on-site septic systems (Sulam, 1979). Konrad and Booth (2002) also attributed the flow decrease in Issaquah Creek to the combination of wastewater collection and ground-water pumping. Simmons and Reynolds (1982) reported decreases of 20% to 85% of groundwater flow in sewered urbanized catchments.

Storm runoff channelization leads to a faster rise and recession of streamflow, higher peak rates and increased storm flow volume from a given amount of precipitation (Konrad and Booth, 2005; Tetzlaff et al., 2005; Wheater and Evans, 2009). Streamflow records from two adjacent catchments in Swindon, United Kingdom, showed that the area served by a storm drainage system was a stronger determinant of streamflow response than either impervious area or development type (Miller et al., 2014). Here, the introduction of a large-scale storm drainage system in a 44% urban cover was accompanied by a 50% reduction in rainfall-runoff duration and a peak flow increase of over 400%. The study also revealed a significant increase in flashiness of storm runoff, above that attributed to impervious area alone.

The quicker runoff resulting from the storm drainage systems can, however, induce flood risk in downstream areas, particularly in small catchments (Boyd et al., 1993; Navratil et al., 2013). Nevertheless, in a peri-urban area of Lion, France, Braud et al. (2013) reported an increase in frequency of smaller floods as a result of the sewer overland flow devices, but a marginal impact on the largest floods, mainly governed by saturation of the rural parts of the catchments.

The maintenance of the artificial drainage systems can also influence the catchment hydrology. Generally, such drainage systems are not watertight and leakage from drinking water, storm drainage and wastewater pipes can provide an important source of groundwater recharge, thus sustaining baseflow during dry periods (Foster et al., 1999; Scholz and Yazdi, 2009; Jankowfsky et al., 2012).

Increases in baseflow have been also noted due to irrigation (Barron et al., 2012), car washing (Meyer, 2005) and water imports from outside the catchment (Walsh et al., 2005; Konrad and Booth, 2002). In a high density residential catchment of New York, Burns et al. (2005) reported an increase of 0.25 mm day^{-1} in low streamflow due to groundwater pumping for human consumption and irrigation.

In peri-urban areas, flow connectivity and streamflow response is often further complicated by the installation of reservoirs and stormwater retention systems. In a Mediterranean catchment near St Tropez, France, the installation of a reservoir with a storage capacity of 14% of the catchment area, decreased the runoff from the small upslope urban core (1.7% of the catchment area) by approximately 15% if the reservoir was filling. Nevertheless, if the reservoir was full, no impact on streamflow was recorded (Fox et al., 2012). Detention tanks are used to store water during high intensity rainfall and gradually release it when the drainage network is not overloaded (Cembrano et al., 2004).

In addition, surface runoff retention in specific infrastructures can favour infiltration and groundwater recharge. Thus, in Long Island, New York, the use of recharge basins for collection and disposal of urban storm runoff led to a 12% increase in annual groundwater recharge (Ku et al., 1992).

Nevertheless, construction of dams and subsequent regulation of river flow regime can either increase or decrease low-flow discharge levels, depending on the operational management of the reservoir. It is necessary to distinguish between small impoundments, such as farm dams, where there is little or no control over the level of storage, and larger dams where artificial releases can be made. Large artificial impoundments probably constitute the single most important direct impact on the low flow regimes of rivers (Smakhtin, 2001).

The complex interaction between all the above stated factors affecting flow connectivity over the landscape and the hydrological response of a catchment requires additional scientific information to understand better in which ways flow dynamics are changed by human impacts. Understanding the controls of runoff generation and transmission in relation, for instance, to rainfall events, and how they differ according to temporal or spatial constraints, will give key information regarding flow pathways and hillslope connectivity. Although some pathways might be dominant, they can change under different circumstances (Lexartza-Artza and Wainwright, 2009).

2.3. Surface water quality

2.3.1. Sources of pollutants within peri-urban areas

Concern with water quality degradation within peri-urban and urban areas has raised awareness regarding sources of pollution. In mixed land-use catchments, there can be numerous sources of contaminants, such as nutrients, organic compounds and heavy metals. Sources can include untreated solid waste disposal, leachate from landfills, wastewater contamination (e.g. sewerage systems leakage, inefficient wastewater treatment), industrial processes and spills, atmospheric deposition and stormwater runoff.

Percolation of rainwater through waste layers leads to various physical, chemical, and microbial processes that generate leachate which threaten water resources, particularly groundwater. Landfill leachate plumes have been recognized as important sources of dissolved organic carbon, nitrogen, as well as ferrous iron, chloride and bicarbonate (Christensen et al., 2001; Corniello et al., 2007; Lorah et al., 2009). In a peri-urban floodplain adjoining the city of Oxford, landfills contributed nearly 40% of the in-stream ammonium (NH_4). High concentrations of NH_4 and low concentrations of nitrate (NO_3) and dissolved oxygen in groundwater were also linked to landfill leachate in a peri-urban floodplain adjoining the city of Oxford, UK (Gooddy et al., 2014). In a peri-urban area of Uganda, solid waste dumping, together with animal rearing and grey water/stormwater disposal in unlined channels have been the main causes of groundwater contamination by nitrogen compounds (up to 370 mg Nk L^{-1} and 779 mg NO_3 L^{-1}), phosphorus (up to 13 mg L^{-1}), thermotolerant coliforms and *faecal streptococci* (median values of 126^3 cfu 100 mL^{-1} and 154^3 cfu 100 mL^{-1}, respectively) (Kulabako et al., 2007).

In peri-urban areas, **sewage** is generally either disposed and treated in septic systems, or piped into wastewater treatment plants (WWTPs), together or separated from the stormwater flow. Septic fields have been recognized as significant sources of NO_3, phosphate (PO_4), chemical and biochemical oxygen demands (COD and BOD), as well as coliforms. In Rhode Island, for example, leachate from residential septic fields led to NO_3 concentrations of 68 mg L^{-1} and mass losses of 47.5 kg ha^{-1} (Gold et al., 1990). Groundwater contamination derived from septic systems has been well documented (Robertson, 1995; Robertson and Harman, 1999; Wilhelm et al., 1994), but it eventually contributes to surface water pollutant inputs (Gold et al., 1990; Wernick et al., 1998; Castro et al., 2003).

On the other hand, centralized WWTPs ensure compliance with regulatory standards, but the characteristics of the effluent released can vary considerably depending on the level of wastewater treatment. For example, Andersen et al. (2004) compared streamwater quality at multiple sites in South Carolina and reported higher average nitrate and soluble reactive phosphorus concentrations in streamwater downstream than upstream of WWTPs (NO_3: 50.5 mg L^{-1} vs 1.6 mg L^{-1} and reactive phosphorus: 3.7 mg L^{-1} vs 0.3 mg L^{-1}).

Surface water quality may be particularly affected by WWTP discharge during dry seasons, since it may represent a major fraction of downstream flows and dilution rates are reduced (Andersen et al., 2004; Ekka et al., 2006). The impact of WWTPs discharge on surface water quality can therefore obscure the impact of the catchment land-use (Miltner et al., 2004). Furthermore, sewage and storm drainage system leaks during larger storm events have also been considered a relevant source of pollution (Le Pape et al., 2013).

The efficiency of wastewater treatment is also dependent on the characteristics of the input sewage. In combined drainage systems, sewage pollutants such as BOD, ammonia (NH_3), total phosphorus (TP) and faecal coliform bacteria are diluted, but added to stormwater runoff pollutants like heavy metals (e.g. Cd, Cr, Cu, Pb, Ni, Hg, and Zn). These stormwater pollutants can have a negative impact on the performance of biologic treatments in the WWTPs (Gromaire et al., 2001; Schoonover and Lockaby, 2006; Soonthornnonda and Christensen, 2007).

Erosion is prone to occur in bare soils, construction sites and road edges due to rainfall and storm runoff, depending on soil properties and topographic characteristics (e.g. Burton and Pitt, 2001). Line et al. (2002) reported sediment exports during the clearing and grading phase of a construction site nearly 10 times greater than in other land-uses, such as single-family residential areas, a golf course and dairy cow pasture. Line and White (2007) also reported sediment exports from a developing area about 95% greater than forested and agricultural areas.

Erosion has been considered a major factor perturbing the ecological status of the rivers, due to greater suspended sediment concentrations and stream channels clogging. The presence of sediments in streamflow increases the turbidity and leads to reduced amount of light penetration, with detrimental impacts on photosynthesis, which affect dissolved oxygen concentration and food availability to aquatic life (e.g. Atasoy et al, 2006).

Furthermore, fine sediments can also represent a threat for surface water quality due to their absorptive properties for several inorganic pollutants, such as phosphorus, heavy metals and polycyclic aromatic hydrocarbons (PAHs) (Goonetilleke et al., 2005; Le Pape et al., 2013; Yu et al., 2014). Nitrogen inputs resulting from sediments released in a construction site in North Carolina (TN: 36.3 kg ha^{-1} yr^{-1}; TP: 1.3 kg ha^{-1} yr^{-1}) were similar to total N exports from residential (23.9 kg ha^{-1} yr^{-1}) and golf course areas (31.2 kg ha^{-1} yr^{-1}) (Line et al., 2002).

Atmospheric chemistry can play an important role in influencing surface water quality, mainly via its influence on runoff process properties. Dry and/or wet deposition (through precipitation) can contribute significant amounts of nutrients (nitrogen and phosphorus) from 1) tree pollen, mostly from forestry but also lawns within residential areas (Hu, et al., 2001; Easton and Petrovic, 2004); 2) livestock emissions associated with agriculture (e.g. NH_3) (Spokes and Jickells, 2005); 3) wind-eroded particles (Smil, 2000); and 4) fossil fuel combustion, released from vehicle traffic and industrial activities (Bernhardt et al., 2008; Apeagyei et al., 2011).

Nutrient contributions from vegetated areas in San Bernardino Mountains, California, were investigated by Fenn and Poth (2004), who recorded nitrogen deposition rates of 146 kg ha^{-1} yr^{-1} (NH_4 + NO_3) from ponderosa pine trees (*Pinus ponderosa Laws*).

In Waquoit Bay, atmospheric deposition supplied 30% of estuary nitrogen loads, whereas fertilizer use and wastewater accounted for 15% and 48%, respectively. These contributions were provided by fractions of the catchment, specifically from urban (39%), natural vegetation (21%) and turfgrass areas (16%) (Valiela et al., 1997)

Traffic emissions also provide an important nitrogen source to the atmosphere, ranging from 10 to 155 mg NH_3 km^{-1} depending on vehicle type (Emmenegger et al., 2004). The relationship between automobile emissions and NH_3 concentrations in freeway runoff was demonstrated by Pitt and Maestre (2005).

Anthropogenic sources of air pollution can also act as sources of many metals in urban environments (Ellis et al., 1986; Yu et al., 2014). Based on moss bags and total deposition collectors installed in seven urban sites throughout London, Duggan and Burton (1983) calculated mean total deposition of 193.3, 433.3, 30.0 and 2.0 µg m^{-2} day^{-1} for Pb, Zn, Cu and Cd, respectively. In Milwaukee, USA, rainfall falling in residential areas exhibited a 10-fold higher mass rate of metals (Zn, Cu, Cd, Ni, Pb, Hg and Ag) than open land areas, due to vehicular traffic emissions (Soonthornnonda et al., 2008). In Shanghai, a significant amount of heavy metals identified in sediments from the lake was provided by dust from coal combustion (represented 50% of Pb concentration) and vehicular traffic (10–30% of total Pb and Hg content) (Li et al., 2012).

Overland flow has been considered by several authors as the major non-point source of pollutants at the catchment scale (e.g. Bannerman et al., 1993; Qian et al., 2002). Impervious surfaces have been considered as a concentrator and transporter of pollutants, mainly due to its efficient capacity to convert rainfall into overland flow. In many cases, overland flow from impervious areas is piped directly to streams, rather than filtered through soils.

Overland flow from impervious surfaces is typically associated with several pollutants, particularly heavy metals (Zhang et al., 2007; Yu et al., 2014), nutrients (Gilbert and Clausen, 2006; Ouyang et al., 2009), major ions (e.g., sulphate, nitrate, chloride, calcium, magnesium and potassium) (Rose, 2002), pesticides (Hatt et al., 2004) and faecal coliforms (Gregory and Frick, 2000; Mallin et al., 2000).

In USA, Schueler (2003) reported 2.0 mg L^{-1} of TN and 0.26 mg L^{-1} of TP as typical concentrations in urban stormwater runoff. In Seattle, Washington, under baseline conditions, streamflow from urban areas displayed average TN, TP and dissolved P concentrations higher than in forest streams (greater values by 44%, 95%, and 122%, respectively) (Brett et al., 2005). Urban impervious surfaces (18%) within a forest and agricultural catchment in Indianapolis, Indiana, also led to greater TN, TP and total Pb loads (24%, 22% and 43%), associated with higher annual runoff (34%) (Lim et al., 2006). In the peri-urban stream around Shanghai, East China, nitrogen and phosphorus concentrations were much higher than in agricultural streams (NH_4: 9.2 mg L^{-1} vs. 1.5 mg L^{-1}, TP: 1.4 mg L^{-1} vs 0.2 mg L^{-1}) (Qian et al., 2002). Shields et al. (2008) also reported higher nitrogen exports with increasing urbanization, with particularly high values in fully urbanized catchments than in low-density peri-urban, agricultural and forest catchments.

Other land-uses within mixed catchments can also influence surface water quality. In a rapidly developing mixed land-use catchment in southeastern China, urban areas were the dominant contributor of Pb and Cd loads, whereas farmland provided most of the Cu, Zn, Cd and Mn loads. Forest and green land did not supply metal loads (except Cr) into streamwater (Yu et al., 2014). Nevertheless, Göbel et al. (2007) identified Cu and Zn, as well as Ni, as typical metals associated with urban land-uses in German.

Mallin et al. (2000) found that % impervious surface was the single most important determining factor of faecal coliform (FC) contamination in coastal catchments of North Carolina, explaining 95% of the variability in average FC abundance. In western Georgia, a study performed within 18 mixed land-use catchments revealed nitrogen and FC concentrations within catchments having more than 24% impervious surface to be higher than non-urban catchments, both under baseflow (N: 1.64 mg L^{-1} vs. 0.61 mg L^{-1} and FC: 430 vs. 120 MPN100 mL^{-1}) and storm flow conditions (N: 1.93 mg L^{-1} vs. 0.36 mg L^{-1} and FC: 1600 vs. 167 MPN100 mL^{-1}) (Schoonover and Lockaby, 2006).

2.3.2. Contributions from different impervious surfaces

It is usually accepted that pollutant loads tend to increase directly with % TIA. Thus, several authors have been considering this parameter has an indicator of the ecological and environmental conditions of an aquatic system (Schueler, 1994; Arnold and Gibbons, 1996; Paul and Meyer, 2001; Morse et al., 2003; Kuusisto-Hjort and Hjort, 2013). Brabec et al. (2002) identified different thresholds of TIA for different water quality parameters. Thresholds ranged from 8% for oxygen to 30-50% for other chemical properties and 5-50% for physical variables. Other authors have also identified different impervious thresholds for specific water quality parameters. For example, Griffin et al. (1980) identified a 42% impervious cover for degradation due to nutrients, May et al. (1997) recognised a 45% for phosphorus and Horner et al. (1997) reported a 50% imperviousness for significant metals increase in streamwater quality, but only 40% in the case of zinc.

Aquatic ecosystems may be affected by a combination of pollutants rather than by individual water quality parameters. As a result, Schiff and Benoit (2007) considered that a threshold of 5-10% TIA can impair water quality due to urbanization effects. On the other hand, Exum et al. (2005) suggested that 5-10% TIA produces modest impacts related to urbanization, which can be addressed through planning and catchment management. These authors considered that urbanization of only 10-20% TIA can lead to significant aquatic degradation, whereas for catchments exceeding 20% TIA the likelihood of successful remediation efforts being able to improve water quality are minimal. Schueler (1994) reviewed eleven published studies and reported their evidence that stream quality declines at 10 to 15% imperviousness. Based on a review of different studies, Arnold and Gibbons (1996) also defined a 10% TIA threshold for minimum degradation start and a 30% threshold for unavoidable impacts. Based on the magnitude of the impacts of TIA, Arnold and Gibbons (1996) suggested a classification of the stream health "which can be roughly characterized as 'protected' (<10% impervious surface), 'impacted' (10%-30% impervious surface), and 'degraded' (>30% impervious surface)."

Although the establishment of an impervious cover threshold can be very useful for management purposes, results from different studies are not unanimous. Differences between the reported thresholds can be driven by site-specific characteristics of the catchment, such as the proportion of different types of impervious surfaces.

Impervious surfaces within urban areas are mostly represented by rooftops and roads, both characterized by distinct pollutant loads, with different potential impacts on catchments' water quality. A number of studies have reported the release of certain compounds from **rooftops** during rainfall events (Athanasiadis et al., 2007). Because of this, rooftop runoff can be an important source of pollutants for the aquatic ecosystems.

Gromaire et al. (2001) compared the runoff pollution in an urban district in Paris, France, derived from rooftops (54% of the area) with different types of covering material (Zn sheet, slate, interlocking tiles, flat tiles) and guttering (Zn, Cu, cast Fe), streets (22%) and impervious miscellaneous structures (24%). The results showed that rooftops contributed more than 80% of the Cd, Pb and Zn contamination during the wet season in the combined sewer system. The runoff from sawmill rooftops along Washington coast also exceeded the water quality guidelines for Cu, Pb and Zn in all the samples tested (Good, 1993). In Austin, Texas, the runoff from a rooftop of an Army fort contributed as much as 55% of the specific heavy metal concentrations measured in the total catchment loads (Van Metre and Mahler, 2003).

Other authors, however, reported a low impact from rooftop runoff. For example, Simmons et al. (2001) measured the concentration of heavy metals (Zn, Cu and Pb) in the runoff of 125 domestic rooftops in four rural areas of Auckland, New Zealand, but only a few sites exceeded the drinking water standards: 14%, 2% and 1% of the sites for Pb, Cu and Zn, respectively.

The type of roof material, the age and the conservation status of the roof are important parameters on runoff properties and pollutant loads (e.g. Chang et al., 2004; Adeniyi and Olabanji, 2005). Schriewer et al. (2008) studied the runoff properties from a 14 years old zinc roof and measured mean concentration of 4.9 mg Zn L^{-1}. According to a study by the German Federal Environmental Agency, roof runoff in Germany releases almost 85.2 tonnes of copper every year (UBA, 2005). A detailed review of rooftop runoff pollution is given by Lye (2009).

Some authors have considered **roads** has a major source of pollutants within urban catchments, particularly due to the heavy metal composition (e.g. Ellis et al., 1986; Bannerman et al., 1993; Herngren et al., 2004). Studies in Europe and USA catchments encompassing highways reported maximum heavy metal loads of 244, 499 and 288 µg m^{-2} day^{-1} for Pb, Zn and Cu, respectively (Mance, 1982; Randall et al., 1979). However, road runoff properties are highly variable. For a highway in metropolitan London, UK, with 500 vehicles day^{-1}, Ellis et al. (1986) measured a metal removal rate varying between 15.6 and 167 µg m^{-2} day^{-1} for Pb, 17.2-194 µg m^{-2} day^{-1} for Zn and 4.9-69.2 µg m^{-2} day^{-1} for Cu. Greatest variability of pollutants concentration was even reported by Crabtree et al. (2006), based on runoff discharges from several highways across UK: 2.1 - 304.0 μg L^{-1} of Cu, 5.0 - 1360 μg L^{-1} of Zn and < 0.01 - 5.40 μg L^{-1} of Cd. In Western Washington State, however, runoff properties from 35 highways varied less, displaying 3.1 - 18.1 μg L^{-1} of Cu, 13 - 134 μg L^{-1} of Zn and 0.9 - 2.8 μg L^{-1} of Cd (Herrera Environmental Consultants, 2007).

Spatial and temporal differences in road runoff composition can be due to several parameters, such as:

- Vehicular traffic

Besides the impact of gas exhaustion discussed on section 2.3.1., wear of vehicles components, such as tyres and brakes, as well as fluid losses, can be important sources of pollutants in road runoff, but also in the runoff from car parks and service stations (Ellis et al., 1986; Sullivan et al., 1978; Bannerman et al., 1993; Soares, 2014).

In several small peri-urban catchments around Madison, Wisconsin, the runoff from streets, driveways and parking lots supplied 21% and 28% of the dissolved and total phosphorus loads of the surface waters (Waschbusch et al., 1999).

A positive relationship between the amount of vehicular traffic and pollutant concentrations has been described in several studies. Steuer et al. (1997) reported nitrogen and phosphorus concentrations in the runoff from high traffic streets to be twice as high as in low-traffic streets (TN: 2.95 mg L^{-1} vs 1.17 mg L^{-1}; TP: 0.31 mg L^{-1} vs 0.14 mg L^{-1}). Pollution from traffic also varies with urban type. For example, in UK, a sub-catchment dominated by a highway showed three times more Fe and a 16-fold increase of Cu than a residential area (Ellis et al., 1986).

Similarly, Herngren et al. (2004) measured, through rainfall simulation experiments, greater runoff pollution in a road in a highly urbanized area (dominated by town houses) than on an access road in suburban residential area of Brisbane, Australia. Suspended sediment concentration was almost twice higher in the highly urbanized than suburban area. As regards to organic carbon compounds, dissolved fractions were twice as high in the most urbanized area, but three times higher for total organic compounds. Greater metals concentration in the highly urbanized area were also found, particularly as regards to Al (17 times higher in the dissolved fraction, but only 2 times higher for the total fraction) and Fe (8 times higher in the dissolved fraction and slightly higher in the total fraction). Polycyclic aromatic hydrocarbons also displayed 15 times greater dissolved fraction concentration and 40 times more total fraction in the road of the highly urbanized area.

- Pavement material, conservation status and management activities

Pavement material influences surface permeability and pollutant accumulation rates (Sartor and Boyd, 1972; Gilbert and Clausen, 2006). Furthermore, it affects the release of chemical compounds and thus, the sort of pollutants washed-off. This is also influenced by the conservation or degradation status of the road surface (Sartor and Boyd, 1972), as well as by cleaning activities. Street sweeping may have an adverse impact on pollutant wash-off because it releases the finer material of the pavement, which is not removed by the cleaning equipments (e.g. due to the reduced suction), making the fine sediments available for wash-off during the next storm (Vaze and Chiew, 2002).

Management activities during colder weather conditions, linked to sand and de-icing materials commonly applied to assure safe road driving, can also have a detrimental impact on water resources. Interlandi and Crockett (2003) measured increasing streamwater concentrations of chloride (37%) and sodium (25%) as a result of salts deposited on roadways of Philadelphia.

- Rainfall and runoff

Rainfall intensity determines the available energy to overcome the initial resistance provided by both the amplitude and scale of surface roughness (Athayde et al., 1982), whereas rainfall amount determines the runoff volume generated. Runoff volume influences both pollutant removal rates (Helsel, 1978) and the dilution factor (Deutsch and Hemain, 1984). In a highway surface of metropolitan area of London, UK, Ellis et al. (1986) found that storm duration and runoff volume together explain over 90% of the observed variance in Pb, Cd, Mn and sediment loads, as well as 79% of Zn concentration.

- Antecedent dry period

The extent of time without rainfall determines the amount of pollutant material deposited on road surface resulting from vehicular traffic, pavement degradation and atmospheric deposition (Sullivan et al., 1978; Owe et al., 1982; Zhang et al., 2007; Qin et al., 2013). According to Marsalek (1976), the antecedent dry period (ADP) explained 83-92% of the variance in heavy metal concentrations from road runoff. Based on the study of a road surface in a Melbourne urban area, Vaze and Chiew (2002) demonstrated that pollutant build-up (accumulation) over dry days occurs relatively quickly after a rainfall event, but slows down after several days as redistribution by wind occurs.

2.3.3. Land-use contributions for water quality

The complex land-use pattern of peri-urban areas provide distinct sources of pollutants. Generally, agricultural and vegetated areas are associated with nutrient sources (e.g.

Crawford and Lenat, 1989; Groffman et al., 2004; Zhang et al., 2007), whereas urban areas are mostly associated with heavy metal and organic pollutants to streamwater pollution (e.g. Pitt and Maestre 2005; Yu et al., 2012).

Diffuse pollution from agricultural fields, particularly associated with high concentrations of NO_3, have been widely reported due to fertilizer application (Oakes et al., 1981; Addiscott et al., 1991). Groffman et al. (2004) reported NO_3 losses from agricultural catchments to be 2-4 times higher than urban/peri-urban catchments in Baltimore. Crawford and Lenat (1989) also found greater nutrient concentrations in streams from agricultural catchments comparing with catchments dominated by forest and urban land-uses. On the other hand, highest temperatures and concentrations of heavy metals were found in the urban catchments (Crawford and Lenat, 1989).

Livestock manure and sludge application into agricultural fields can represent additional risks of nutrients and heavy metal contaminations of rivers and groundwater (Gupta and Charles, 1999; Antonious et al., 2008). In a peri-urban region of Vietnam, the application of livestock manure provided a surplus of 85 to 882 kg ha^{-1} $year^{-1}$ of nitrogen, 109 to 196 kg ha^{-1} $year^{-1}$ of phosphorus and 20–306 kg ha^{-1} $year^{-1}$ of potassium. According to Khai et al. (2007), sludge application in agricultural fields of Hanoi, Southeast Asia, leaded to high accumulation of heavy metals in the soil, ranging between 0.2 to 2.7 and 0.6 to 7.7 kg ha^{-1} $year^{-1}$ of Cu and Zn.

In the Yellow River catchment, Asia, farmland and forestry were found to be the main sources of nitrogen and phosphorus (Ouyang et al., 2009). In Gold Coast, Australia, greatest total organic carbon concentrations were also found in surface waters from catchments dominated by forestry than other land-uses. In forest areas, nutrients release are provided by the degradation and leachate from the leaf litter, supplied by the extensive tree canopy (Goonetilleke et al., 2005).

Zhang et al. (2007) studied the impact of two contrasting peri-urban areas in the Yangtze River of China, comparing a vegetable-based (VB) area, dominated by agricultural fields used for vegetables production, with a factory-based (FB) area, encompassing 400 small-scale factories producing a variety of materials including chemicals, fertilizers, pesticides and steel. The surface water in the VB area had significantly higher levels of NO_3, organic N and TN than those in the FB area. In contrast, heavy metal concentrations in the surface water from the FB area were higher than those in the VB area.

Despite agricultural and forest areas being considered important non-point sources of nutrients, the lower amount of runoff produced limits the loads of pollutants reaching the stream network (Ouyang et al., 2009).

The type of urban land-use influences pollutant contribution to the stream network. For example, based on the study of 200 municipalities of Alabama, USA, Pitt and Maestre (2005) demonstrated substantial differences in the chemical composition of the runoff from distinct urban land-uses (industrial, residential and commercial areas, freeways and open spaces). Industrial areas showed the greatest concentrations of nitrogen oxide (0.73 mg L^{-1} NO_2+NO_3), Cd (2.0 µg L^{-1}) and Cr (14.0 µg L^{-1}). Together with freeways, industrial areas showed the highest concentrations of Pb (both had 25 µg L^{-1}) and Zn (200 µg L^{-1} and 210 µg L^{-1}, respectively), as a result of gas emissions. Freeways showed greater concentrations of total suspended sediments (99 mg L^{-1}), COD (100 mg L^{-1}), NH_3 (1.07 mg L^{-1}), phosphorus (0.20 mg L^{-1}) and Cu (µg L^{-1}) than all the other land-uses. On the other hand, residential areas showed the highest faecal coliform concentration (8345 MPN 100 mL^{-1}), due to sewer contamination. Open spaces showed the lowest values of COD (42 mg L^{-1}), NH_3 (0.18 mg L^{-1}), Cd (0.38 µg L^{-1}), Cu (10 µg L^{-1}), Pb (10 µg L^{-1}) and Zn (40 µg L^{-1}), whereas freeways showed the lowest values of NO_2+NO_3 (0.28 mg L^{-1}).

The intensity of urbanization has been reported by some authors as a major parameter influencing water quality impacts (e.g. Mallin and Wheeler, 2000). A comparative study focusing on surface water quality from 28 urban and peri-urban catchments in USA, indicated decreasing loading rates of nutrients (TP, TN, NO_3+NO_2, and NH_3) from low house density to high density (USEPA, 1983). The difference between the urban areas of high and low density reached 90% of the nutrient loads. In the Grand Canal of China, surface water quality also showed increasing levels of nutrients (TN and TP) and dissolved metals (Cu, Zn, Cd, Cr and Mn) from towns (<150000 inhabitants) to large cities (up to 2200000 inhabitants) (Yu et al., 2012).

The form of urban settlements is another parameter reported on literature with impacts on surface water. Corbetts et al. (1997) measured higher sediment yelds in the runoff genererated from dispersed impervious surfaces than from clustered development areas, despite no significant different runoff volume. This was because of less protection to the soil surface. Goonetilleke et al. (2005) also reported greater pollutant loads from detached houses than multifamily dwelling units, possibly due to greater extent of road surface area but also landscaped gardens. Greater extent of gardens/open spaces and the associated application of fertilisers, explained the high nitrogen loads in runoff from duplex housing developments comparing with single detached-dwelling areas.

Increasing nutrient concentration in urban catchments have been attributed to green areas and their management activities, particularly fertilization. Steuer et al. (1997) reported that runoff concentrations from lawns contributed five to ten times more nutrients than other landscape surfaces, such as streets, into Lake Superior in Michigan. Besides fertilization, grass clipping can be another source of nutrients in urban green areas, particularly of nitrogen (Goonetilleke et al., 2005) but also COD (Schoonover and Lockaby, 2006).

Nutrient losses from urban green areas have been considered similar to forest areas. Gold et al. (1990) reported similar nitrogen losses in leachate from home lawns and forest areas.

Groffman et al. (2009) suggested similar carbon cycling rates between turfgrass and forest. However, the different growing stages of the vegetation can lead to seasonal variation in nutrient losses (May et al., 2001; Ouyang et al., 2009). For instance, Wherley et al. (2009) reported greater NO_3 uptake during the active growth period of summer (>90%), slightly decreasing during fall and spring transition months (80-90%) and being significantly reduced during winter dormancy (10-20%).

Although urban green areas can be important sources of nutrients, mostly due to inappropriate management practices (e.g. fertilization and irrigation) performed to maintain the desired aesthetic characteristics (Gross et al., 1990; Easton and Petrovic, 2004), these areas may have a positive impact on catchment water quality. Some researchers highlighted the capacity of lawns to retain nutrients within residential areas (Groffman et al., 2004). Furthermore, the low runoff generated on green pervious urban surfaces also limit the rate of nutrient losses.

Based on rainfall simulation experiments performed in different pervious surfaces, Ross and Dillaha (1993) measured limited runoff amount from grass and turf surfaces (5% and 3%), associated with small amounts of suspended sediment, but 3 times more soluble phosphorus in grass than turf cover. Nevertheless, runoff from grass and turf displayed similar soluble nitrate loads than runoff from bare soil, despite the greatest runoff coefficient of the latter (33%). Nevertheless, the runoff from the bare soil was linked with greater total suspended sediments (3-fold), soluble nitrate and phosphorus (11- and 13-folds) than a gravel driveway (51% runoff coefficient). Meadow and mulched landscape did not produce runoff.

Differences in runoff characteristics from various pervious surfaces are critical to land-use planning, because land-uses vary widely in their ability to absorb or shed rainfall and thus, transport sediment and pollutants. Some researchers have stressed the relevance to identify the areas prone to generate pollutants, called sensitive or critical areas, in order to improve catchment management (Thompson et al., 2012; Easton et al., 2007).

2.3.4. Influence of landscape connectivity

The multiple mosaic features determined by different land-uses over the peri-urban catchments are very complex in terms of potential sources and sinks of runoff pollutants, as discussed in the previous sections. The research studies above cited highlight that imperviousness may not be the only or even the most important catchment variable, since the pervious surfaces, such as vegetated areas, can represent an important source of nutrients.

Nevertheless, the impact of land-uses on surface water quality is dependent on the flow connectivity within a catchment, which is affected by the location of pollutant sources and the downslope land-use and land cover (LULC). Considering the greater runoff volume and pollutant loads from impervious surfaces, the placement of these infrastructures within a catchment influences the possible absorption by pervious surfaces and, thus, the amount and speed with which contaminants in flow enters the stream (under natural conditions, without runoff piped directly to the stream) (Carey et al., 2011). Overland flow infiltration or retention in surface depressions is the key to accomplish nutrients and pollutants removal and prevent environmental risks (Horner et al. 1997; Brabec et al. 2002; Easton et al., 2007; Thompson et al., 2012), by breaking flow connectivity and using soil as a filter.

Wickham et al. (2002) modelled alternative land-use change scenarios in the mid-Atlantic region of the USA to identify the most vulnerable areas to increased N and P exports. Areas with a forest and agricultural land-use with a ratio of 6:1 and projected urbanization rates of 20%, were vulnerable to increased N export; at similar urbanization rates, P vulnerability increased in areas with a 2:1 forest and agriculture ratio.

However, depending on the location and extent of forest areas, they can contribute considerably to water quality protection, especially due to the high infiltration capacity and thus, the ability to act as sinks of overland flow and pollutants (Groffman et al., 2002; Lorz et al., 2007).

Few studies have investigated the role of riparian vegetation as an effective solution for reducing non-point sources of nutrients. Hicks and Larson (1997) explored the relationship between imperviousness, forest cover and the width of riparian buffer on stream chemistry. The authors reported the degradation of water quality with increasing imperviousness and decreasing forest and riparian buffer cover. No discernible human impact on water quality was found on catchments with 4% impervious surface, >50% forest land-use and riparian buffer of 60 m in more than 80% of the stream network. A low level of impact was reported in catchments with 9% impervious surface, 30-50% forest stand and 50-80% of riparian buffer. A moderate level of impact was described in catchments with 10-15% impervious surface, 10-29% forest area, and 20-49% riparian buffer. A high level of impact was showed in catchments with 15% impervious surface, 10% forest stand, and <20% riparian buffer.

The role of riparian vegetation on surface water quality was also investigated by Steedman (1988), who found an inverse relation between the extent of riparian cover and impervious surfaces on sustainable biological integrity of the aquatic ecosystem. This author reported that in catchments without urban areas, 75% of the riparian forest could be removed without detrimental impacts on aquatic communities, but no riparian forest should be removed for a 55% urbanizated catchment. In turn, Horner et al. (1997) identified a threshold of 45% impervious surfaces for cease the effective protection of riverine systems provided by riparian buffers. Nonetheless, Roth et al. (1996) found that regional land-use was more important than local riparian vegetation for stream integrity.

In peri-urban and urban catchments, artificial drainage systems provide higher connectivity between pollutant sources and the stream network. Ouyang et al. (2009) highlighted the role of the artificial drainage system on phosphorus linkage between farmland areas and streamflow. In urban areas, Bannerman et al. (1993) demonstrated the water quality impacts of the overall connectivity between road runoff and the stream network, whereas only 2% of the roof runoff reached the stream.

In recent years, runoff channelling have been considered in order to evaluate pollutant pathways. The term directly connected impervious area (DCIA) covers the impervious surfaces that are hydrologically linked to the watercourses (Booth and Jackson, 1997). Some authors have been stressing the relevance of DCIA percentage rather than TIA percentage on pollutant loads reaching urban streams (Brabec et al., 2002).

Based on modelling results, Wilson and Weng (2010) demonstrated that the spatio-temporal variation in areas that contribute towards runoff, i.e. the spatial extent of hydrologically active areas within a catchment, are more important than the spatial extent of LULC for surface water quality.

2.3.5. Temporal variation of pollutant sources

Pollutant sources and transport mechanisms are directly linked to the hydrological processes, and thus, associated with temporal variation between overland flow processes and hydrological connectivity at catchment scale.

Schoonover and Lockaby (2006) considered the hydrological processes to explain the minor impact of a heavily grazed catchment (>25%) on streamwater quality. The free cattle access and the deposition of faecal material near the stream channel provided a low faecal coliform concentration in the stream. This was explained by the insufficient volume of surface runoff generated and/or energy to transport faecal coliform bacteria from the pastures to the streams.

Temporal variation of pollutant sources are influenced by the rainfall pattern, since it is the driver of the hydrological processes, as discussed in section 2.2.3.. In a hydrologically isolated grassland hillslope in Co. Down, Northern Ireland, overland flow was highly variable and dependent on rainfall intensity. There were some areas of the hillslope that either did not generate overland flow or generated overland flow that was not connected through flow pathways. The size of the area prone to generate overland flow ranged between 20% and 80% of the hillslope, and was found to control the streamflow variation and temporal changes on dissolved phosphorus inputs. However, it did not seem to explain the particulate phosphorus concentration, which may be due to rapid exhaustion of fine particles, and a switching from transport-limited to detachment-limited processes at early stages in each storm (Thompson et al., 2012).

Antecedent climatic conditions, particularly the length of time without rainfall, is an important parameter determining not only the flow connectivity over the catchment during rainfall events, but also the build-up and wash-off processes from different land-uses and, therefore, pollutants composition and loading (Goonetilleke et al., 2005). Generally, rainfall events with longer ADP have more pollutant build-up at the beginning of the rainfall, thus higher pollutant loads can be potentially flushed off during rainfall events, as referred in section 2.2.3.. Greater rainfall amount has the ability to flush off the higher amount of pollutants deposited over the catchment, leading to higher Event Mean Concentration (EMC) on streamflow. However, when the capacity of pollutant wash-off is greater than the pollutant build-up, additional rainfall causes lower EMC due to a dilution effect.

The influence of ADP on pollutant availability and transport over the hillslope has been considered to explain distinct EMCs resulting from similar rainfall events (Qin et al., 2013), as well as seasonal variation on runoff quality (Interlandi and Crockett, 2003; Lee et al., 2009; Zhang et al., 2007). In a mixed land-use catchment in Galicia, Spain, Rodríguez-Blanco et al. (2013) reported that 68% of phosphorus transport was influenced by storm events. In a small catchment in Macau, Huang et al. (2007) showed that mean concentration of COD ranged from 41 to 464 mg L^{-1} between five rainfall events. Qin et al. (2013) found maximum EMC for COD over five times higher than the minimum value in a typical urbanizing area of China.

In Mediterranean regions, summer droughts create a long period for pollutant build-up and, therefore, the initial storm of the wet season may have higher pollutant concentrations than later events (Lee et al., 2009). However, few researchers have determined the effect of the ADP in their studies of stormwater discharge, particularly in Mediterranean environments. This deficiency is one of the research gaps trackeled in this thesis.

2.4. Final considerations

Land-use changes, particularly associated with urbanization, have impacts on catchment hydrology, but the magnitudes of the changes are dependent on several local biophysical characteristics, which determine the flow connectivity over the landscape. Only in recent years has flow connectivity been recognised as a major parameter influencing the hydrological processes and the catchment response (e.g. Shuster et al., 2005; Bracken et al., 2013).

Flow connectivity is driven by the spatial distribution of runoff sources, particularly impervious surfaces, as well as temporal variation associated with climate and weather. Generally, urban areas are considered one of the most important runoff sources within development catchments, but under wet conditions, increasing soil moisture favours the flow connectivity within the landscape, thus the runoff contributions from other land-uses may become increasingly important for streamflow variation.

Despite several studies focusing on the impact of land-use changes and advances in hydrological processes understanding, the runoff processes from mixed land-use patterns and their impact at the catchment scale are not fully understood. Mosaics of different land-uses provide a combination of fast and slow responses, runoff sources and water fluxes over the landscape. Mosaic landscapes are typical of peri-urban areas, but the relative lack of available hydrological data, limits understanding of hydrological processes within these areas. Despite the spatial variation of runoff processes, understanding the temporal fluctuation of soil moisture, as well as the relation between rainfall and overland flow processes, particularly in seasonal climates such as the Mediterranean, remains a major challenge on hydrology.

Surface water quality is undoubtedly coupled to the hydrological regime. Different land-uses are associated with different pollutants, with green areas usually recognized as potential sources of nutrients, whereas urban land-uses can be important sources of heavy metals, organic and microbial pollution. Flow connectivity between pollutant sources and the stream network has been considered a key issue for surface water quality. However, the relationship between land-use sources and the mechanisms of transmission and dispersion of pollutants over the catchment is still not fully understood.

Improved knowledge about the spatio-temporal pattern of runoff processes and its impact on surface hydrology and water quality is important to improve catchment management and urban planning in order to minimize flood hazard and pollution risks. Furthermore, this information should guide decision-makers to establish and implement strategies to solve current problems within the catchments. Management strategies to minimize runoff and pollutant loads, require understanding of the sources and their temporal variation resulting from rainfall characteristics and antecedent weather conditions. These will allow the implementation of cost-efficient measures to prevent runoff and pollution problems, as well as raise awareness on local population.

CHAPTER 3

SPATIO-TEMPORAL VARIABILITY OF HYDROLOGIC SOIL PROPERTIES AND THE IMPLICATIONS FOR OVERLAND FLOW AND LAND MANAGEMENT

ABSTRACT

Planning of semi-urban developments is often hindered by a lack of knowledge on how changes in land-use affect catchment hydrological response. The temporal and spatial patterns of overland flow source areas and their connectivity in the landscape, particularly in a seasonal climate, remain comparatively poorly understood. This study investigates seasonal variations in factors influencing runoff response to rainfall in a peri-urban catchment in Portugal, characterized by a mosaic of landscape units and a sub-humid Mediterranean climate. Variations in surface soil moisture, hydrophobicity and infiltration capacity were measured in six different landscape units (defined by land-use on either sandstone or limestone), during nine monitoring campaigns at key times over a one-year period.

Spatio-temporal patterns in overland flow mechanisms were found. Infiltration-excess overland flow was generated in rainfalls during the dry summer season in woodland on both sandstone and limestone and on agricultural soils on limestone due probably in large part to soil hydrophobicity. In wet periods, saturation overland flow occurred on urban and agricultural soils located in valley bottoms and on shallow soils upslope. Topography, water table rise and soil depth determined the location and extent of saturated areas. Overland flow generated in upslope source areas potentially can infiltrate in other landscape units downslope where infiltration capacity exceeds rainfall intensity. Hydrophilic urban and agricultural-sandstone soils were characterized by increased infiltration capacity during dry periods, while forest soils provided potential sinks for overland flow when hydrophilic in the winter wet season. Identifying the spatial and temporal variability of overland flow sources and sinks is an important step in understanding and modelling flow connectivity and catchment hydrologic response. Such information is important for land managers in order to improve urban planning to minimize flood risk.

Keywords: soil moisture, soil hydrophobicity, infiltration capacity, Mediterranean, spatial and temporal variability, landscape units, overland flow, flow connectivity.

3.1. Introduction

Land-use changes associated with urbanization strongly affect hydrological processes. Research into the hydrological effects of urbanization has focused on its impact on runoff processes, but conclusions have proved difficult to extrapolate because of the complex interplay of such parameters as climatic setting (Boyd et al., 1993; Costa et al., 2003), geologically-controlled topography (Wilson et al., 2005), soil properties (López-Vicente et al., 2009; Hardie et al., 2011), vegetation and land-use (Mallick et al., 2009), including land-use change history, the percentage of impervious surface and its spatial arrangement (e.g. Konrad and Booth, 2005). Variation in the combined effect of these factors is arguably the main reason for observed differences in impact of urban land-use change on hydrology.

Soil moisture, linked to storage capacity, is recognized as a major runoff-controlling factor, particularly in a Mediterranean climate (Cerdà, 1997). Its seasonal variability can mean that greater rainfall intensity is required for overland flow initiation in summer than in winter (Cammeraat, 2002). When saturation overland flow mechanisms are involved, the influence of soil moisture is more varied and not entirely understood, particularly in urbanizing catchments where its spatial and temporal variation is rarely reported (Easton et al., 2007).

Although there have been many studies of soil hydrophobicity and its impacts on infiltration and overland flow processes in a range of seasonal and sub-humid environments (e.g. Glenn and Finley, 2010; Carrick et al., 2011; Orfánus et al., 2014), in areas of Mediterranean climate they have mainly focussed on forested terrain (e.g. Doerr et al., 1996, 1998, 2000; Varela et al., 2005; Keizer et al., 2008; Neris et al., 2013; Nyman et al., 2014). Furthermore, relatively little is known about ‘switching’ between hydrophobic and hydrophilic conditions in dry and wet periods, and the net effects on catchment hydrological response in areas affected seasonally by soil hydrophobicity (Leighton-Boyce et al., 2005). In hydrological modelling of urbanizing areas, the phenomenon has not even been considered.

The seasonal and spatial variability of soil moisture and hydrophobicity on heterogeneous landscapes affects overland flow sources and sinks, and is critical in understanding flow transfer between different landscape units (Kirkby et al., 2002; Bull et al., 2003). Relatively little research into such hydrological effects has been carried out in Mediterranean environments, so the impact of marked seasonal changes on runoff processes is not well understood. This is even truer of peri-urban areas, which represent the transition zone between urban and rural environments on the outskirts of cities and which often comprise a mosaic of land-use types. Here, better understanding of the interplay between these factors would help in the prediction of the flow response and estimation of the overland flow amount reaching any point in a catchment (Borselli et al., 2008).

This chapter focuses on temporal and spatial variations in key soil hydrological properties (soil moisture, hydrophobicity and infiltration capacity) in different land-uses in a small, peri-urban, partly limestone, partly sandstone catchment in central Portugal. The catchment has changed rapidly from agricultural land and forest to a discontinuous urban fabric, with urban patches interrupting both woodland and semi-abandoned agricultural terrain. The urban areas comprise a complex mosaic of tarmac, gardens and walls, in addition to buildings and derelict ground. The distinctive mosaic pattern of the catchment is typical of Portuguese urbanization. Specific aims of the paper are to: 1) assess spatial and temporal variability of hydrological soil properties in different land-uses/lithology landscape units in the catchment; 2) identify seasonal changes in overland flow sources; 3) evaluate the impact of landscape units (characterized by different land-uses and lithologies) on flow connectivity and streamflow response; and 4) explore implications of urbanizing mosaics for landscape management and urban planning, especially with respect to streamflow regimes and flood risk.

3.2. Study area

The study site is the S-N elongated *Ribeira dos Covões* catchment (40°13’N, 8°27’W; 6.2 km^2) in the suburbs of Coimbra, the largest city of central Portugal. The climate (as recorded at Bencanta, 0.5 km north of the catchment boundary) is sub-humid Mediterranean, with a mean annual temperature of 15ºC, a mean annual rainfall of 892 mm (INMG, 1941-2000), hot and dry summers (8% of rainfall in the months June-August) and wet winters (Figure 3.1). The main watercourse is perennial, supplied by several springs, and there are several smaller ephemeral tributaries (Figure 3.2). The geology (Figure 3.2a) comprises Jurassic dolomitic and marly limestone in the east (49% of the catchment area), and Cretaceous and Tertiary sandstones, conglomerates and mudstones in the west (47% of the area), with some Pliocene-Quaternary sandy-conglomerate (colluvium) and alluvial deposits (4% of the area) in the main valleys. Soils are generally deep (>3m) Cambisols and Podzols (Tavares et al., 2012). Only on steeper slopes in the northwest is soil depth less than 0.4 m. Altitude ranges from 29 m to 201 m. The average slope is 9º, but a few slopes reach up to 46º.

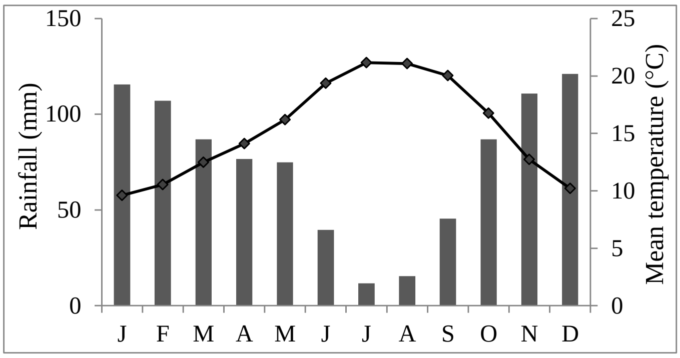


Figure 3.1 - Average monthly rainfall and temperature at Coimbra (Bencanta weather station), calculated from data regarding to the period 1941-2000 (INMG, 1941-2000).

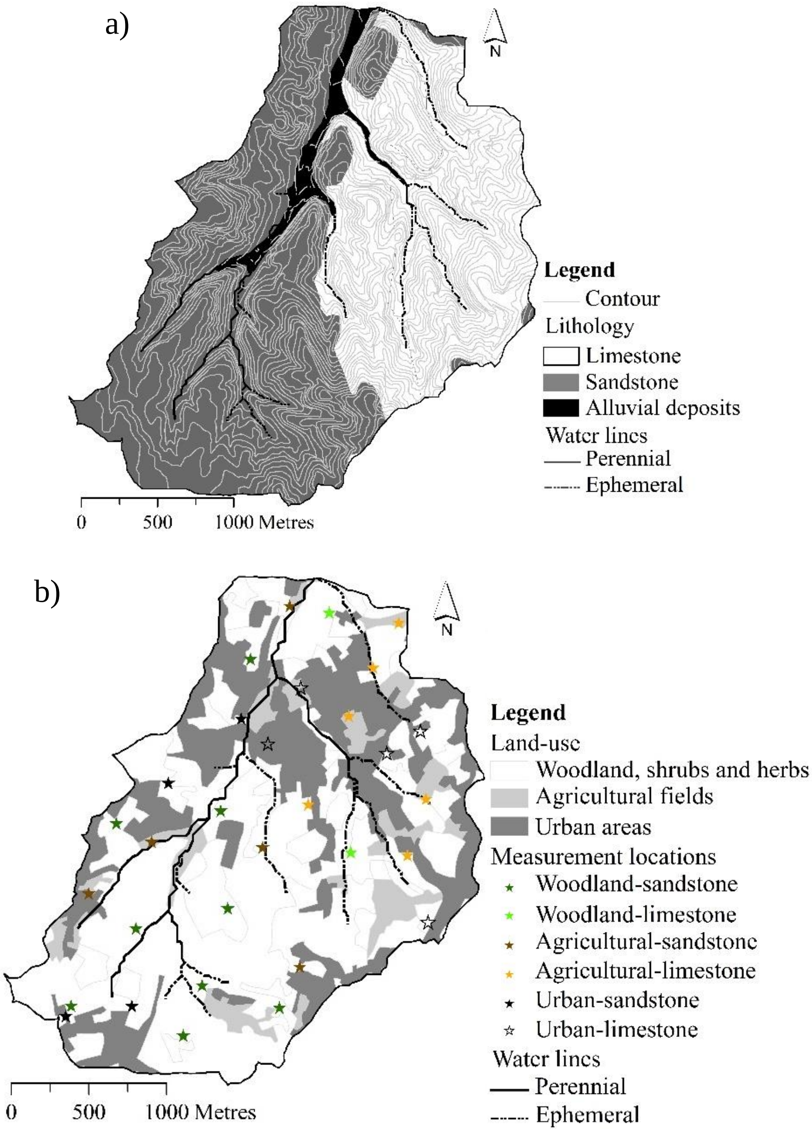


Figure 3.2 - *Ribeira dos Covões* catchment: (a) topography, lithology and streams; (b) land-use in 2009 and location of the study sites.

The catchment, totally rural until 1972, underwent discontinuous urbanization in 1973 - 1993, followed by urban consolidation after 1993 (Tavares et al., 2012). The agricultural area, mainly olives and arable land, declined from 48% in 1958 to 4% of the catchment in 2009. Woodland increased from 46% to 66% over the same period, changing also in nature from *Quercus suber* and mixed woodland to large commercial plantations of pine (*Pinus pinaster*) and eucalypt (*Eucalyptus globulus*) (Tavares et al., 2012). Urban land-use increased from 6% in 1958 to 30% in 2009 (Figure 3.2b), of which 14% comprised impervious surfaces and 16% urban soil. The result was a mosaic of older urban cores, with detached houses and gardens, contrasting with newer apartment blocks. There are also a few small industrial premises, recreational areas and an enterprise park begun in 2009. Urban storm runoff (from roofs, streets and concrete paved areas) is either piped to tributaries or flows directly towards the stream network. Where urban buildings and derelict urban land are surrounded by fields, however, stormwater is not controlled.

3.3. Methodology

3.3.1. Research design

A network of 31 representative sites was established in the catchment to assess hydrological properties of the six different land-use/lithology combinations or "landscape units" (Figure 3.2b). There were: 1) 11 sites in woodland, 9 being on sandstone (dominated by eucalypt, pine and mixed deciduous forest) and 2 on limestone (in small areas of oak and mixed deciduous woodland); 2) 11 sites on agricultural fields, including 5 on sandstone (dominated by light grazing pasture, small olive groves and minor cultivated patches) and 6 on limestone (in olive groves and abandoned fields undergoing natural succession); and 3) 9 sites on uncultivated urban soil, 4 on sandstone (bare soil sites associated with construction and open spaces with ground vegetation between houses) and 5 on limestone (derelict spaces between houses and between houses and roads).

At each site, soil moisture content, hydrophobicity and soil matrix infiltration capacity were monitored 9 times between September 2010 and June 2011, to cover a representative range of antecedent weather and seasonal conditions, including prolonged periods of wet weather and long dry spells. Temperature and rainfall data during the study period were provided by the national meteorological weather station 12G/02UG, located at Bencanta, 0.5 km north of the study catchment.

Replicate measurements of soil hydrological properties, spaced approximately 1m apart, were carried out at each site. In total, 558 measurements of each parameter were obtained. Three soil samples (c. 100 g each) were collected on the nine occasions at each site to assess surface soil moisture (0-50 mm depth). Additional soil samples were taken at all sites on 23rd November 2010 to determine dry bulk density, rock fragment content, organic matter and particle size distribution. The excavation method (150×150 m and 100 mm depth) was used for bulk density and rock fragment analyses (three samples per location) (Dane and Topp, 2002). Composite samples were also collected at depths of 0-50 m and 50-100 mm for organic matter and particle size distribution analyses. Each composite sample comprised 17 sub-samples collected at 150 mm intervals along a 2.4 m transect at each site.

3.3.2. Field methods and procedure

Soil matrix infiltration capacity was measured using a Minidisk Tension Infiltrometer (Decagon Devices; 45 mm diameter and pressure head of -30 mm). Before measurements, ground vegetation was trimmed and surface litter carefully removed. Following preliminary trials, measurements were taken over 30 minutes by which time steady-state conditions were assumed to have been reached. Unsaturated hydraulic conductivity was calculated using published guidelines (Zhang, 1997; Li et al. 2005; Decagon, 2007). Infiltration capacity, however, was calculated from the final 10 minutes of data (i.e. when the values were judged to have stabilized). Taking all measurements as recommended by Decagon (2007) would have given spurious values due both to initially high infiltration in hydrophilic soils and to delayed infiltration when soils were hydrophobic.

Near each infiltrometer location, soil hydrophobicity was assessed at depths of 0, 20 and 50 mm using the Molarity of an Ethanol Droplet (MED) technique (Doerr, 1998). Fifteen drops of distilled water and then progressively higher concentrations of ethanol were applied until the lowest concentration was identified at which at least 8 out of 15 drops were absorbed within 5 seconds. Ethanol concentrations of 0, 3, 5, 8.5, 13, 18, 24 and 36 percent by volume were used. The soil was considered wettable (hydrophilic) when distilled water drops infiltrated within 5 seconds. The classes of levels of hydrophobicity used were: low for 3 and 5% ethanol, moderate for 8.5 and 13%, severe for 18 and 24%, and extreme for 36% (Doerr, 1998).

3.3.3. Laboratory methods

Soil physical properties (bulk density, rock fragment, organic matter content and particle size) were analysed using standard methods (Dane and Topp, 2002). Bulk density was obtained from undisturbed samples dried at 105°C. Disturbed soil samples were oven-dried at 38°C until a constant weight was reached, and the <2 mm fraction extracted. The >2 mm rock fragment content was calculated as a percentage of the total dry soil sample weight. The organic matter content was analyzed by oxidation at 600ºC and detected by close infra-red, using SC-144DR equipment (Strohlein Instruments). Porosity was calculated from the dry bulk density and the organic matter content according to methods recommended by Dane and Topp (2002), assuming a soil mineral particle density of 2.65 g cm^{-3} and organic matter bulk density of 0.90 g cm^{-3}. The particle size distribution of the minerogenic component of the soil samples was determined where organic matter content was > 2% either by: 1) oxidation using hydrogen peroxide (6%), for samples with organic matter contents of 2-4%; or 2) heating to 550ºC for samples with higher values. The samples were then dispersed using Na-hexametaphosphate and the ultrasonic method (Dane and Topp, 2002). Particle size distribution was subsequently determined using a combination of sieving, gravity sedimentation and pipette analysis. Soil texture classes were based on the ISSS international classification (Soil Survey Division Staff, 1993).

Soil moisture content was assessed on each measurement occasion by the thermogravimetric method following oven-drying at 105ºC. Soil saturation was than estimated by dividing the volumetric water content (estimated from gravimetric water content and bulk density) by porosity.

3.3.4. Data analysis

The statistical significance of soil property differences between the land-use/lithology landscape units was investigated first using the non-parametric Kruskal–Wallis H test (SPSS 17.0). Where significant differences between units were identified, the Least Significant Difference (LSD) Post-Hoc test was applied to identify distinct units or groups of units. The same tests and procedure were applied to differences in soil hydrological properties between measuring dates. A 95% level of significance ($p<0.05$) was used. In addition, Pearson-r correlation coefficients were calculated to assess linear relationships between: 1) soil properties (organic matter content, bulk density and particle size) and soil moisture, soil hydrophobicity and infiltration capacity ($n=64$); and 2) antecedent weather and soil hydrological properties on each monitoring occasion. Principal Component Analysis was used to quantify the infiltration variance explained by the correlated variables. Although the data were not normally distributed, it was considered useful to apply this technique for explorative purposes to improve understanding of the controls on overland flow. Spatial patterns of hydrological soil properties were analysed using geostatistical methods, based on Thiessen Polygons, carried out using ArcGIS 9.3 software.

3.4. Results and analysis

3.4.1. Soil properties

Soil organic matter was generally higher and more consistent for surface (0-50 mm) than subsurface soil (50-100 mm) (Figures 3.3a and 3.3b). For both soil depths, organic matter content increased from urban (1-3%) to agricultural (3-9%) and woodland soils (averaging 7% and 14% on sandstone and limestone, respectively). In the woodland and agricultural-limestone landscape units, organic matter was highly variable, but greater than in agricultural-sandstone and urban soils ($p<0.05$).

Bulk density increased from woodland (0.7 g cm^{-3}) to agricultural (1.0 g cm^{-3}) and to urban soils (1.2 g cm^{-3}) (Figure 3.3c). In woodland and urban soils, bulk density was similar on both lithologies ($p>0.05$), but it was higher for agricultural-sandstone than agricultural-limestone soils (median values of 1.1 g cm^{-3} and 0.9 g cm^{-3}) ($p<0.05$). Values for the latter were similar to woodland, whereas agricultural-sandstone values were similar to urban soils ($p>0.05$). Bulk density decreased as soil organic matter increased ($r=-0.341$, $p<0.001$).

Soil porosity ranged from 40 to 65% (Figure 3.3d) with generally lower values for urban soils, despite no significant difference ($p>0.05$). Greater heterogeneity was found in agricultural soils, with higher values on limestone than sandstone ($p<0.05$). Rock fragment content ranged from 14 to 57% and was similar amongst landscape units ($p>0.05$). Particle size varied between individual sites (Figure 3.3e and 3.3f), but not between landscape unit averages ($p>0.05$), with sandy-loam and loamy-sand textures dominating. Particle size distribution affected bulk density, which increased with larger coarse sand ($r=0.189$, $p<0.001$) and clay fractions ($r=0.115$, $p<0.001$), and diminished with larger fine sand ($r=-0.287$, $p<0.001$) and silt fractions ($r=-0.190$, $p<0.001$).

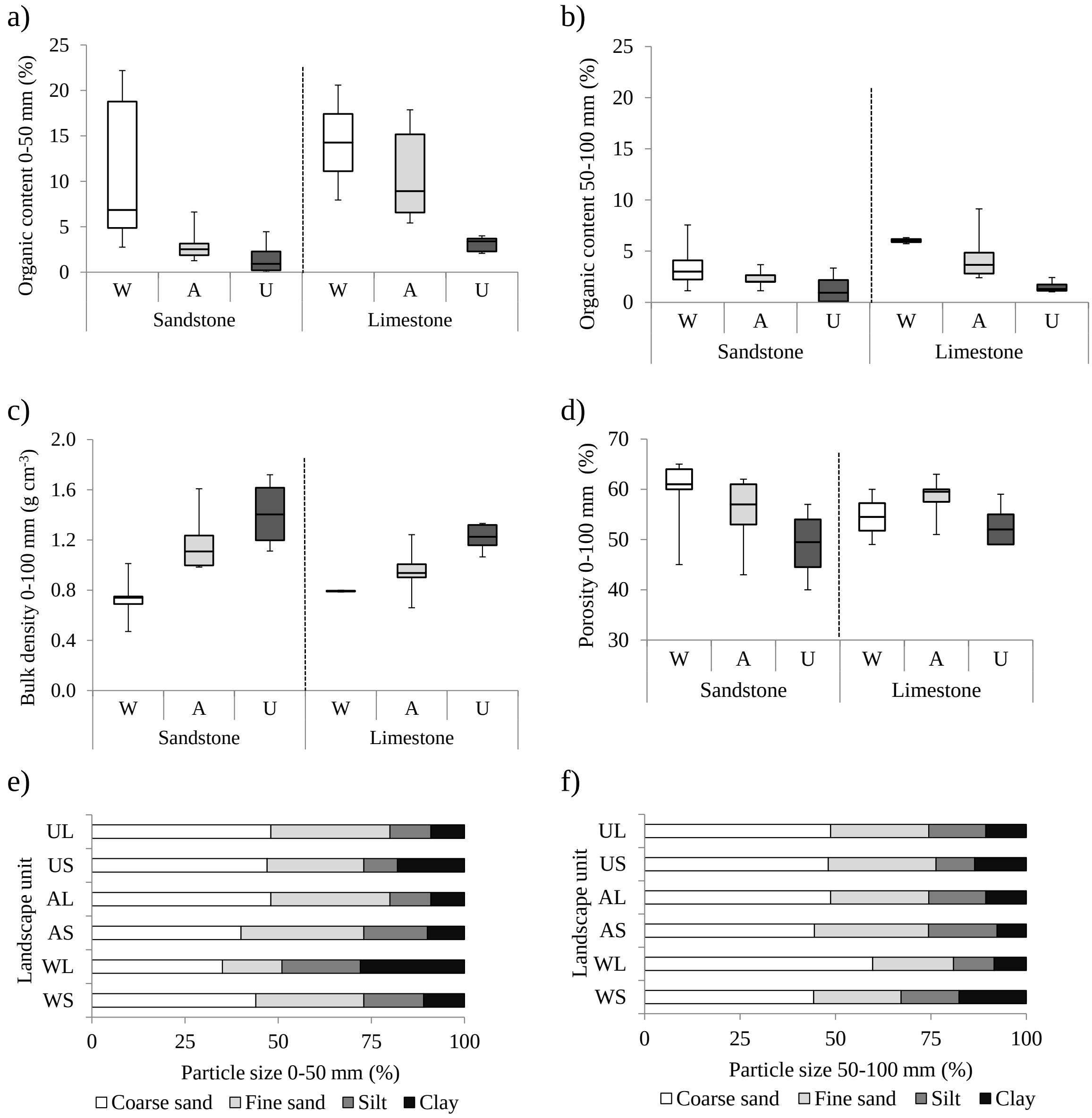


Figure 3.3 - Soil properties in different landscape units: a) organic matter content at the surface (0-50 mm) and b) subsurface (50-100 mm), c) bulk density (0-100 mm) and d) porosity (0-100 mm).

3.4.2. Antecedent weather conditions

Rainfall and temperature patterns during the monitoring period are shown in Figure 3.4 and antecedent conditions for each measurement date are summarized in Table 3.1. Antecedent 30-day rainfall ranged from 5.0 mm (30/09/2010) to 141.8 mm (23/11/2010). Antecedent 5-day rainfall ranged from rainless (prior to 30/09/2010 and 13/06/2011) or trace (0.2 mm prior to 15/10/2010 and 24/01/2011) to 26.0 mm (prior to 03/01/2011) and 75.4 mm (prior to 02/11/2010).

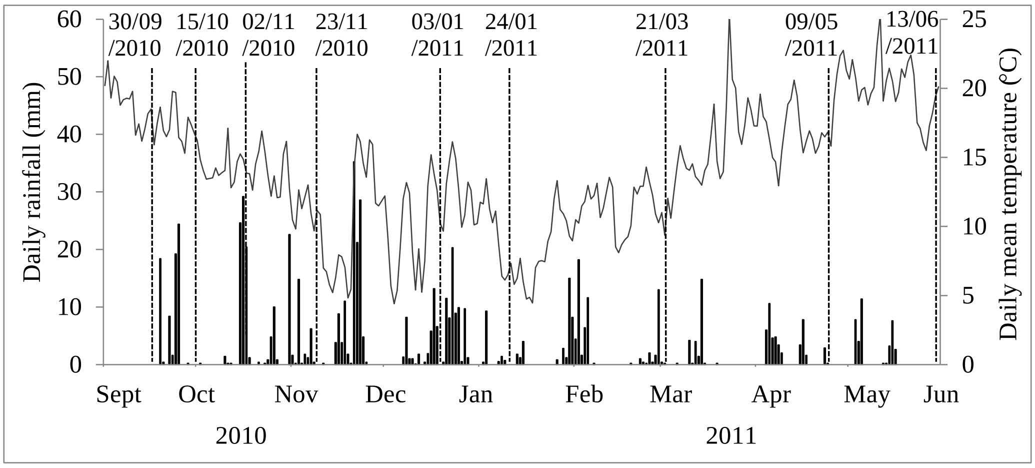


Figure 3.4 - Daily rainfall and mean daily temperature during the monitoring period September 2010 – May 2011 with dates of field measurements.

Table 3.1 - Rainfall amount between measurement dates and in previous days, and mean temperature in prior 5 days.

Measurement date	Total rainfall (mm)	Antecedent rainfall (mm)				Mean temperature (ºC)
		2 days	5 days	10 days	30 days	
30/09/2010	-	0.0	0.0	0.0	5.0	18.9
15/10/2010	72.6	0.0	0.2	53.8	72.6	16.7
02/11/2010	77.2	1.2	75.4	77.2	131.6	14.1
23/11/2010	66.0	0.4	9.6	49.0	141.8	11.4
03/01/2011	161.5	0.5	26	30.2	131.5	12.3
24/01/2011	82.8	0.7	2.6	12.3	112.5	6.9
21/03/2011	97.0	0.2	0.2	15.8	19.8	13.1
09/05/2011	72.3	0.2	3.1	12.5	47.2	16.3
13/06/2011	37.0	0.0	0	0.0	37.0	18.1

3.4.3. Soil hydrophobicity

Soil hydrophobicity varied greatly in severity and frequency both between landscape units and with season and antecedent weather (Figures 3.5 and 3.6). Surface (0 mm) and subsurface (20 mm and 50 mm) soil (results not shown) exhibited similar spatial and temporal trends. Hydrophobicity increased with temperature ($r=0.337$, $p<0.001$) and decreased with antecedent 2- and 30-day rainfall ($r=-0.298$ and -0.373 respectively, $p<0.001$). The area affected by hydrophobicity was larger in summer (50% of all measurement sites) and hydrophobicity was more severe in summer than in winter. It disappeared in late November and January, except at woodland-sandstone sites (<20% of all sites).

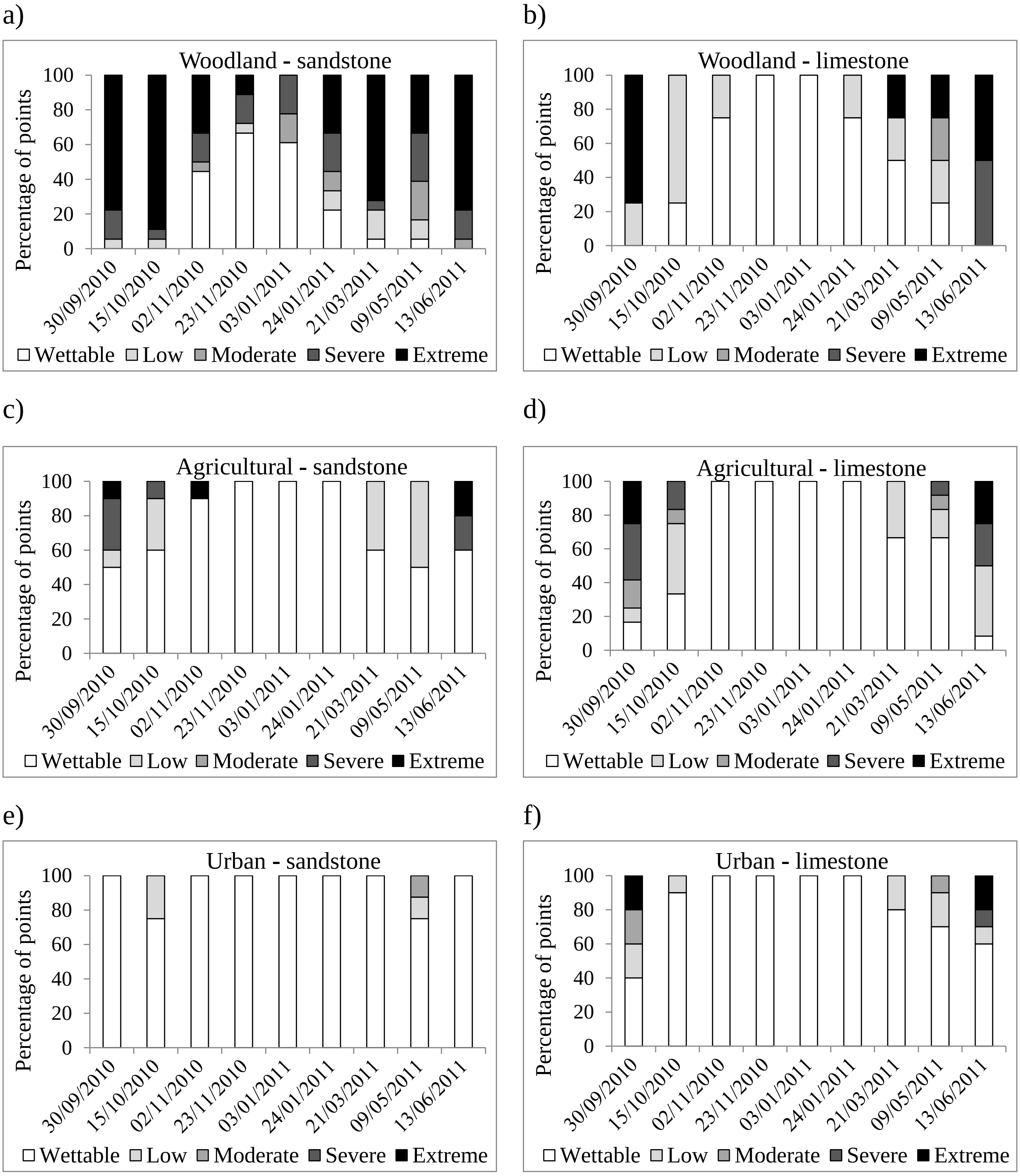


Figure 3.5- Temporal variability of surface hydrophobicity for individual landscape units: a) woodland-sandstone, b) woodland-limestone, c) agricultural-sandstone, d) agricultural-limestone, e) urban-sandstone, f) urban-limestone.

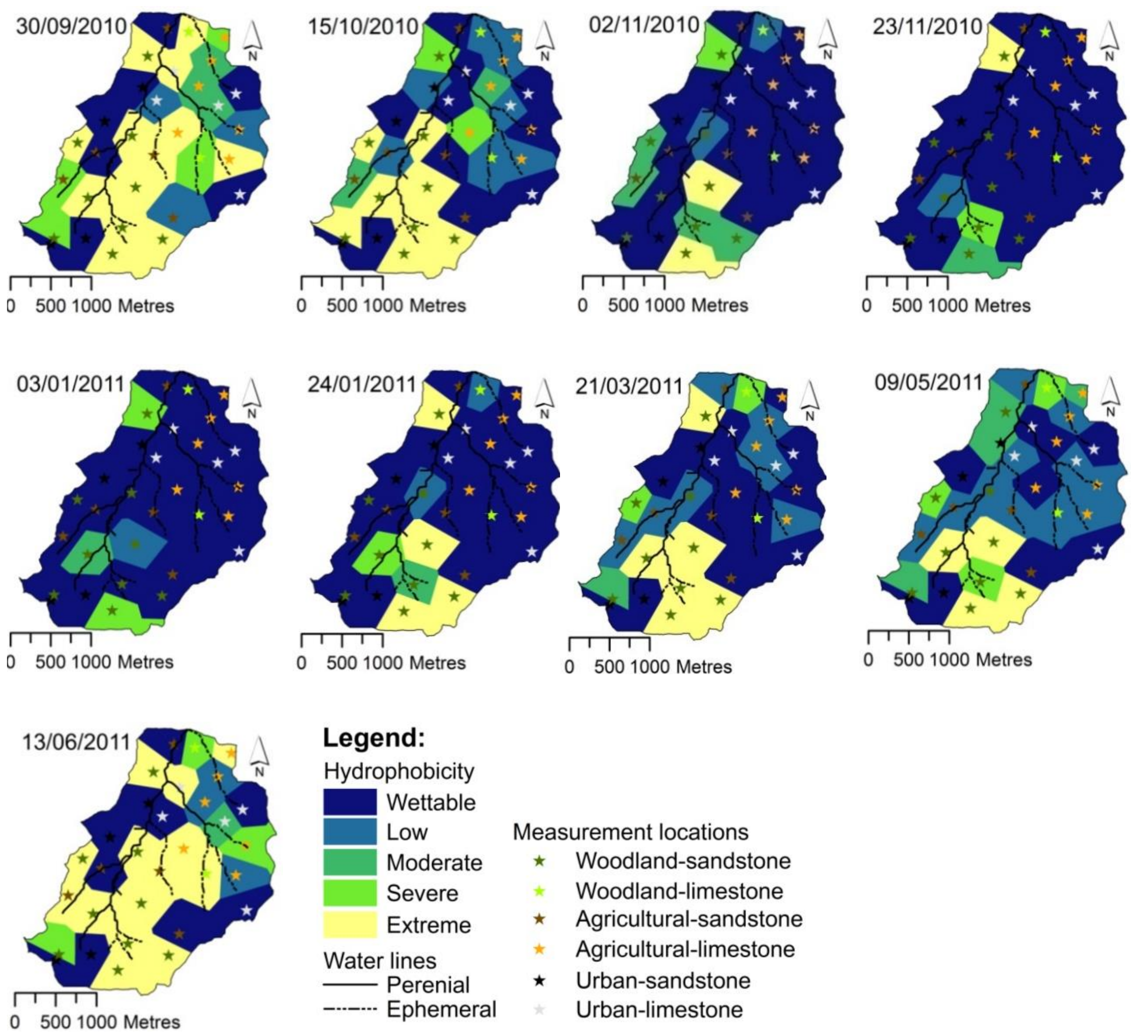


Figure 3.6- Spatial variation of median soil hydrophobicity at the measurement dates, based on the Thiessen polygon method.

Hydrophobicity was of greater severity and spatial extent in woodland, where after dry spells it required several rainfall events to lessen its impact, particularly on sandstone (Figures 3.5a and 3.5b). At agricultural sites especially on limestone (Figures 3.5c and 3.5d), hydrophobicity was also present in dry periods but was less severe than on woodland and rapidly decreased in frequency following rainstorms and disappeared in wetter periods. Urban soil was mostly hydrophilic (Figures 3.5e and 3.5f), with hydrophobicity only affecting a minority of sites even in the driest periods. Re-establishment of hydrophobic conditions in dry weather also varied with land-use, being rapid in woodland, particularly on sandstone where it re-appeared by 24 January 2011, but far slower on agricultural and urban soils, where it was absent until March 2011. Significant differences between woodland and urban soils were found ($p<0.05$).

A positive correlation was identified between hydrophobicity severity and organic matter content (r=0.308 for surface and 0.345 for subsurface soil, p<0.001). Hydrophobicity was correlated with particle size, increasing with surface fine sand (r=0.197, p<0.001) and decreasing with subsurface clay fraction (r=-0.226, p<0.001). This was reflected also in a negative correlation with bulk density (r=-0.240, p<0.001). Hydrophobicity was also found to be inversely correlated with soil moisture (r=-0.363, p<0.001, n=558). Nevertheless, hydrophilic conditions were recorded at least at some locations in all agricultural and urban landscape units over the range of soil moisture contents recorded (see section 3.4.4), whereas in woodland soil was invariably hydrophobic at contents below 20%. There seemed to be no particular moisture threshold, although at 75% of the measurement sites, at least low hydrophobicity was characteristic below 45% soil moisture. Hydrophobicity, however, was recorded at a few woodland sites with 70% soil moisture.

3.4.4. Soil moisture

Surface soil moisture varied with antecedent weather (Figures 2.7 and 2.8), increasing after rainfall (although correlations were weak: r=0.375, 0.168, 0.258 and 0.541 with -2, 5-, 10- and 30 day antecedent rainfall, respectively, p<0.001), and declining with higher temperature (r=-0.593 with values in previous 5 days, p<0.001). During summer and after long rain-free periods (30/09/2010 and 13/06/2011), soil became dry (<20% moisture) across the catchment.

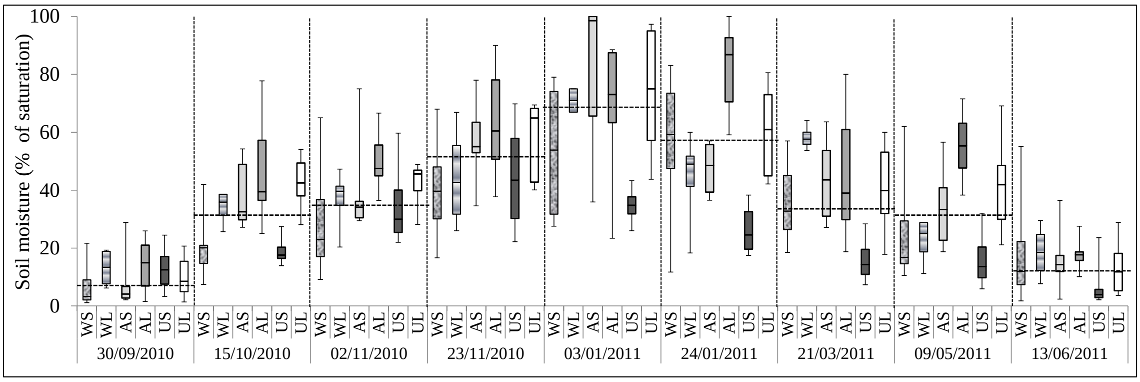


Figure 3.7 - Box-plots of soil moisture content for the different landscape units for the study period (W: woodland, A: agricultural, U: urban, S: sandstone, L: limestone). Horizontal dashed lines represent median soil moistures across the catchment, for the 9 measurement dates.

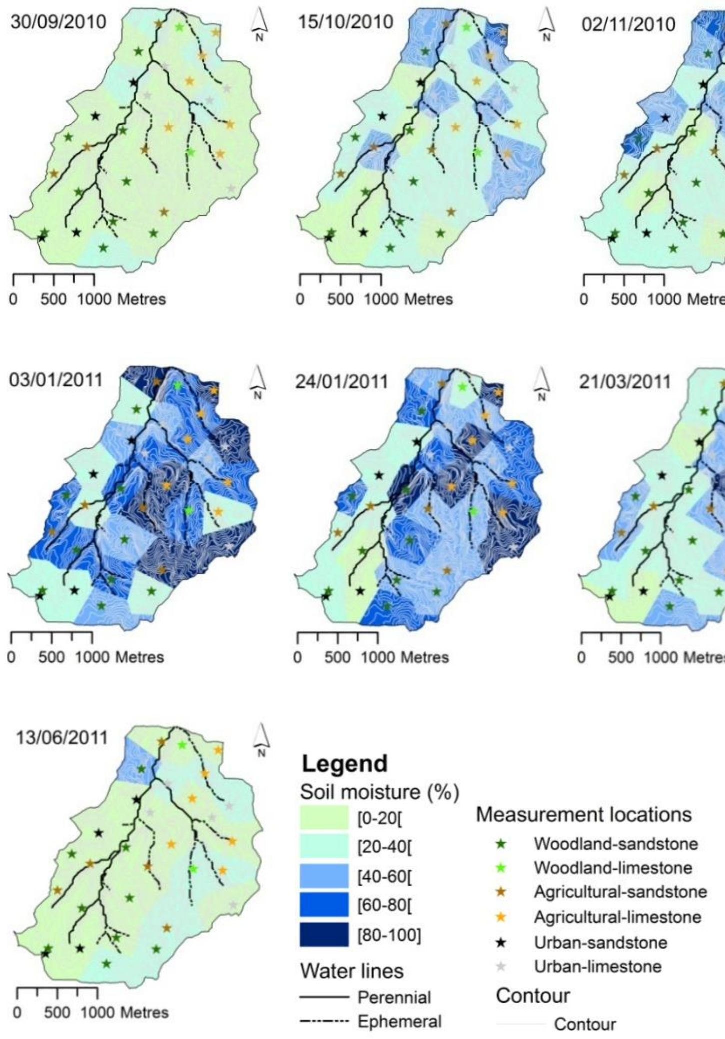


Figure 3.8 - Spatial distribution in median soil moisture content for each the measurement date, using the Thiessen polygon method.

Land-uses responded differently to rainfall, but limestone areas generally had higher soil moisture than sandstone areas. This was very pronounced on 2nd November 2010 (Figure 3.7). Soil moisture was generally lower in urban sandstone soils throughout the year, but also on woodland sandstone in winter and in dry-wet and wet-dry transition periods. Indeed, the lowest post-summer (30/09/2010) median soil moisture content was recorded in woodland sandstone areas, where it persisted until late autumn (23/11/2010). Conversely, agricultural and urban limestone soils generally exhibited higher moisture contents, especially in the wettest periods, when soil saturation occurred at a few valley-floor sites near streams (Figure 3.8). Nevertheless, the locations and sizes of wettest areas in *Ribeira dos Covões* changed through time, and high soil moisture values were recorded occasionally at a minority of woodland sandstone sites in winter. In general, soil moisture content increased with greater silt ($r=0.220$, $p<0.001$) and clay ($r= 0.163$, $p<0.001$) fractions.

3.4.5. Infiltration capacity

Soil matrix infiltration capacity in the *Ribeira dos Cov*ões catchment was generally low, despite occasional higher values (Figures 3.9 and 3.10). In general, sandstone soils recorded greater permeability than limestone soils. Land-use also affected infiltration capacity but differences varied with season and weather (Figure 3.9). Generally, woodland recorded higher values in wet than dry periods ($p<0.05$), with median values increasing from 0.1 - 0.2 mm h^{-1} on 13/06/2011 and 30/09/2010 to 2.8 mm h^{-1} on 03/01/2010. Nevertheless, after the summer, higher infiltration capacity in woodland occurred earlier on limestone than sandstone. Urban soils showed the opposite trend ($p<0.05$), with median infiltration capacity diminishing from 2.6 mm h^{-1} on 13/06/2011 and 3.1 mm h^{-1} on 30/09/2010 to 1.4 mm h^{-1} on 03/01/2010, with slightly higher values on sandstone than on limestone. In agricultural areas, the fall in median infiltration capacity (from 2.5 mm h^{-1} on 30/09/2010 to 0.8 mm h^{-1} on 03/01/2010) was not statistically significant.

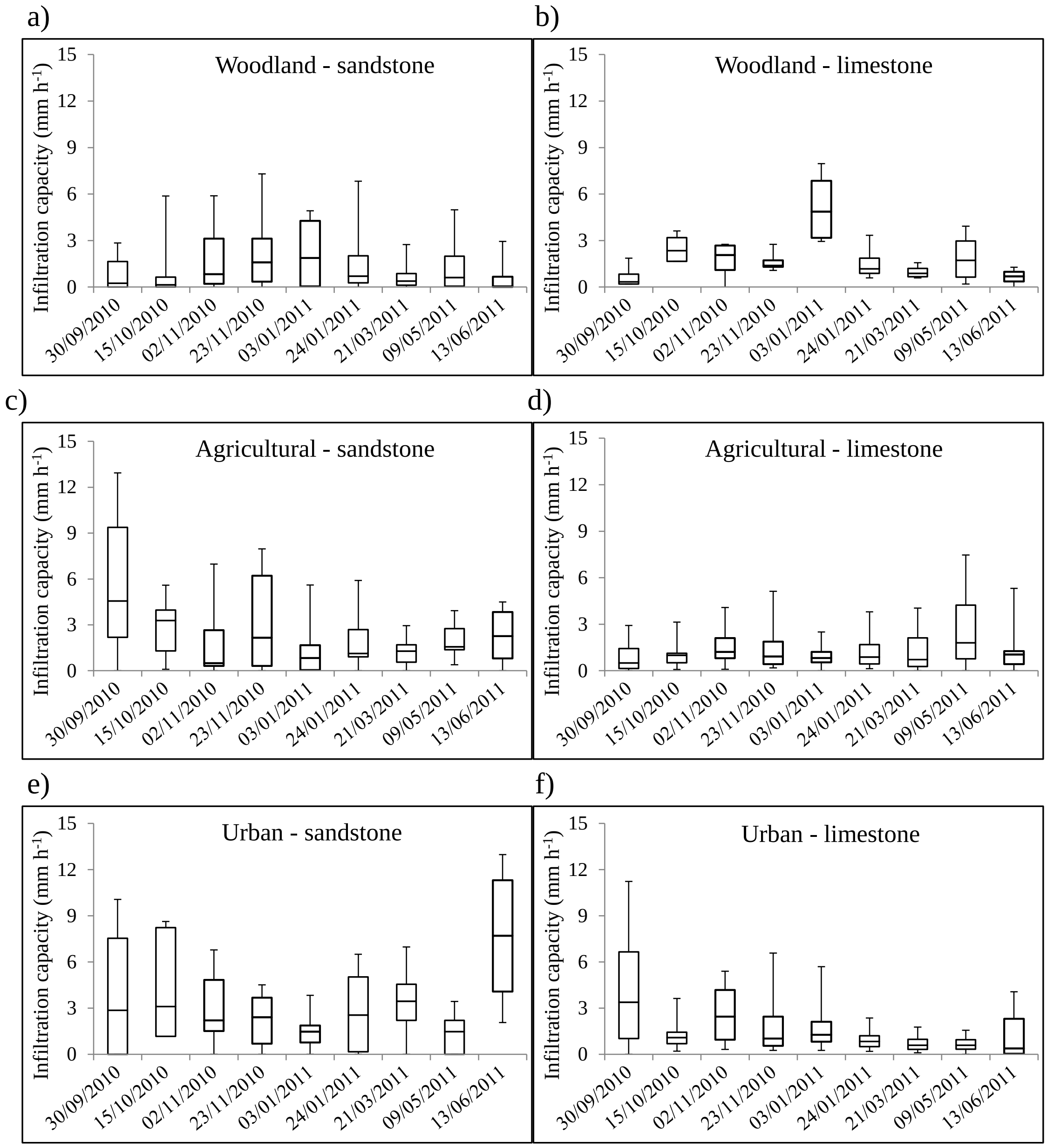


Figure 3.9 - Box plots of temporal variability of matrix soil infiltration capacity for each landscape unit. Dashed lines represent median temporal variability through the whole study period: a) woodland-sandstone, b) woodland-limestone, c) agricultural-sandstone, d) agricultural-limestone, e) urban-sandstone, f) urban-limestone.

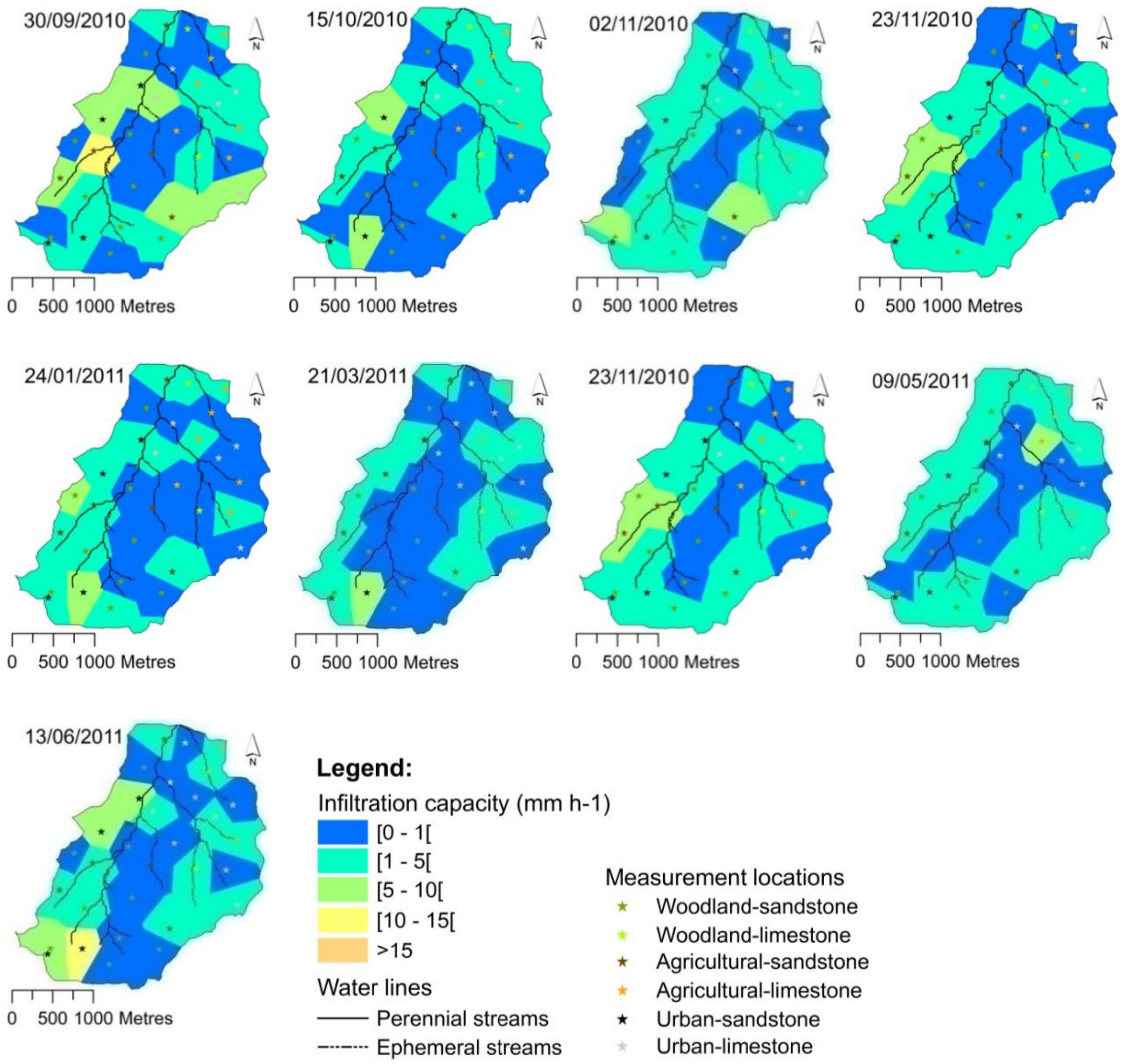


Figure 3.10 - Spatial variation in median matrix soil infiltration capacity at each measurement date, considering Thiessen Polygon method for data distribution.

Infiltration capacity increased with sand content ($r=0.228$ and $r=0.201$ for surface and subsurface soil respectively, $p<0.001$), but decreased with clay fraction ($r=-0.140$ for subsurface soil, $p<0.001$) and organic matter ($r=-0.149$, $p<0.001$). Statistically significant correlations were also found between infiltration capacity and hydrophobicity ($r=-0.314$ and -0.111 at 0 mm and 20 mm depth respectively, $p<0.001$), as well as soil moisture ($r=-0.117$, $p<0.001$).

Generally, infiltration capacity was significantly correlated with hydrophobicity and soil moisture, but the lower correlation coefficients may be because infiltration capacity was only calculated during the last 10 minutes, and hydrophobicity and soil moisture were measured separately on adjacent soil. Nevertheless, Principal Component Analysis (PCA) showed that despite the complex interaction between hydrophobicity and soil moisture, these variables together explain 63% of total infiltration capacity variance (Table 3.2). When particle size characteristics (surface and subsurface coarse sand and silt fractions, and subsurface clay) and organic matter content (surface and subsurface) are considered, the three component variables together explain 76% of infiltration variance (Table 3.3). However, the results of PCA must be interpreted as only indicative, since the variables do not follow the normal distribution that is strictly required by the approach.

Table 3.2 – Principal Component Analysis results considering only hydrophobicity at different depths and soil moisture variables.

Factors	FC 1
Hydrophobicity (0 mm)	0.780
Hydrophobicity (20 mm)	0.894
Hydrophobicity (50 mm)	0.893
Soil moisture (0-50 mm)	-0.595
Cumulative variance explained (%)	64.0

Table 3.3 – Principal Component Analysis results including hydrophobicity, soil moisture and soil properties at different depths.

Factors	FC 1	FC 2	FC 3
Hydrophobicity (0 mm)	-0.108	0.772	-0.230
Hydrophobicity (20 mm)	-0.297	0.809	-0.214
Hydrophobicity (50 mm)	-0.298	0.777	-0.314
Soil moisture (0-50 mm)	0.378	-0.342	0.518
Organic matter content (0-50 mm)	0.044	0.622	0.627
Organic matter content (50-100 mm)	0.247	0.580	0.652
Coarse sand (0-50 mm)	-0.831	-0.163	-0.075
Coarse sand (50-100 mm)	-0.907	-0.150	0.169
Silt (0-50 mm)	0.870	0.183	0.006
Silt (50-100 mm)	0.906	0.170	-0.173
Clay (50-100 mm)	0.714	-0.100	-0.454
Cumulative variance explained (%)	36.3	61.9	76.0

3.5. Discussion

3.5.1. Characteristics of the landscape units and their influence on overland flow

3.5.1.1. Woodland

Woodland environments showed the highest soil organic matter content over the catchment. The high variability of this soil property within woodland areas may be due to differences in tree species and management practices, affecting the litter layer thickness. The lower organic matter of eucalypt than other woodlands may reflect (a) periodic understorey clearance to help prevent wildfires and (b) low understorey vegetation caused by reduced water availability (DeBano, 2000). The generally low values of soil bulk density in woodland units may be the outcome of higher organic matter in woodland soils than in soils of the other landscape units and the denser root systems associated with a tree cover. Reduced bulk density is also characteristic of soils with greater organic matter, since it helps the formation of soil aggregates and structure (Celik et al., 2010).

The greatest soil hydrophobicity of woodland units can be linked to the species involved and their organic matter produced. Seasonal changes in hydrophobicity, with high values in summer and considerable disappearance in winter, was more pronounced in woodland than other landscape units and is in accordance with previous studies (e.g. Dekker and Ritsema, 1994; Doerr et al., 2000; Martínez-Zavala and Jordán-López, 2009). Within woodland, however, hydrophobicity was more extensive, severe and persistent in sites overlying sandstone than limestone (Figures 3.5a and 3.5b). Thus, in woodland-sandstone areas a larger number of rainfall events were required for the soil to become hydrophilic, and even during the wettest periods, hydrophobicity persisted in a few soil sites. This is probably because sandstone areas were mainly dominated by eucalypt and pine plantations, whereas on limestone, oak is more dominant. The type of resins, waxes and aromatic oils produced by eucalypt (Doerr et al., 1998; Jordán et al., 2008) is thought to have caused hydrophobicity to be more extensive and resistant than in the other woodland stands, with hydrophobicity in eucalypt stands able to persist following rainfall of as much as 200 mm in 2 months (Ferreira, 1996; Doerr and Thomas, 2000). In contrast, in woodland-limestone areas, hydrophobicity was less severe and easier to switch to hydrophilic conditions because oak, which is not usually associated with hydrophobic soil (Zavala et al., 2009), is the dominant vegetation.

Generally, woodland areas were also characterized by a quicker re-establishment of hydrophobic conditions after rainfall events, comparing with the other landscape units, particularly under eucalypt plantations. The rate of re-establishment would depend on the biological productivity of the ecosystem (Doerr and Thomas, 2000; Hardie et al., 2012), the type of hydrocarbon substances produced and microbial activity (Keizer et al., 2008).

Santos et al. (2013) report greater dynamism and more frequent hydrophobic conditions in eucalypt than in pine.

Nevertheless, differences in hydrophibicity between sandstone and limestone, may also be linked to differences in particle size, given the statistically significant (albeit weak) positive correlation found between hydrophobicity and sand-fraction. This correlation has also been recorded elsewhere (e.g. DeBano, 1991; McKissock et al., 2000), although a few studies have reported hydrophobicity in finer-textured soils (e.g. Doerr and Thomas, 2000).

The higher evapotranspiration associated with a forest cover (e.g. Holden, 2008) may explain the low soil moisture contents recorded during dry periods in woodland, compared with in the other land-uses (Figure 3.7), although shading by ground vegetation and litter can reduce soil moisture loss in warm, sunny conditions. The more intense hydrophobic conditions in eucalypt and pine woodland, by hindering infiltration (Dekker and Ritsema, 1994; Doerr and Thomas, 2000), might also help to explain the lower soil moisture results recorded in woodland-sandstone compared with limestone at times of transition from dry to wet conditions (15/10/2010 and 02/11/2011).

Despite the inverse correlation found between hydrophobicity and soil moisture content in the woodland units, no soil moisture threshold seems to determine the switching pattern between hydrophobic and hydrophilic soil properties. This accords with the inconsistent results recorded elsewhere. Thus in field experiments in Portugal, Leighton-Boyce et al. (2005) reported no threshold for up to 50% soil moisture content, whereas Doerr and Thomas (2000) found one at 28%. Reports of thresholds outside Portugal vary from 21% for medium-textured soils in SE Spain (Soto et al., 1994), to 38% for Dutch clayey peats (Dekker and Ritsema, 1994) and 50% for some organic-rich Swedish soils (Berglund and Persson, 1996).

The seasonal changes in hydrophobicity of woodland areas would explain seasonal contrast in infiltration capacity. Thus, under driest conditions, when hydrophobicity is widespread on woodland soil, measured infiltration capacity was minimal, whereas in wettest conditions, the limited spatial extent of hydrophobicity allowed infiltration capacity of woodland sites to attain the highest values within *Ribeira dos Covões*. Nevertheless, the low inverse correlation coefficient found between infiltration capacity and hydrophobicity, despite being statistically significant, may have arisen because infiltration may sometimes have been delayed by repellency, but on other occasions have commenced with switching to hydrophilic conditions by the end of the final 10 minutes of the 30 minutes measurement period.

Organic matter arguably plays a dual role in explaining seasonal contrast in infiltration capacity in woodland units. Thus, although it is associated with hydrophobic conditions and low infiltration capacities in dry and transitional weather, in wet periods in winter, when hydrophobicity has largely disappeared, the same high levels of organic matter promote structured soils of high matrix infiltration capacity, representing the more typical situation of forest soils (e.g. Costa, 1999; Mouri et al., 2011).

The variations in hydrophobicity, soil moisture and infiltration capacity linked to geological and land-use controls and seasonal climatic influences, discussed above, result in spatio-temporal patterns of overland flow that differ seasonally and between woodland-sandstone and woodland-limestone areas. In storms following summer dry periods (e.g. following 30/09/2010 and 13/06/2010), drought-induced hydrophobicity in eucalypt and pine areas and resultant very low matrix infiltration capacity makes the woodland-sandstone areas particularly susceptible to infiltration-excess overland flow generation. The less hydrophobic nature of the predominantly oak vegetation of woodland-limestone areas means that they are less prone to infiltration-excess overland flow. Prolonged or repeated rainfall events lead to partial switching of woodland soils to a hydrophilic state, and reductions in spatial extent and severity of hydrophobicity. Hydrophobicity in eucalypt stands is more resistant to break down, requiring longer and/or a greater number of rainfall events. Because of this, infiltration capacity generally remained low in woodland sandstone areas (Figure 3.9a) and, therefore, prone to generate overland flow during transitions from dry to wet conditions, as recorded on 15th October 2010. In prolonged wet weather of the winter wet season, hydrophobicity largely disappeared even in woodland-sandstone areas, where no infiltration-excess overland flow occurred. Even under the wettest winter conditions, woodland areas showed relatively low soil moisture and high infiltration capacities, thus saturation overland flow was rare.

The potential for infiltration-excess overland flow in woodland landscape units in dry summer conditions was confirmed by rainfall simulation experiments, when a 43 mm h^{-1} simulated rainfall produced runoff coefficients of 20-83% in a small plot (0.25 m^2), under extremely hydrophobic woodland soils (slope: 5-36º) (Ferreira et al., 2012b).

Under natural rainfall in larger runoff plots (16 m^2) in woodland, however, under extremely hydrophobic conditions, overland flow did not exceed 3% even for a 23 mm rainfall event (Ferreira et al., 2012a), mainly because of infiltration bypassing the hydrophobic soil matrix via macropores that can be provided by root-holes, invertebrate activity and high concentrations of stones (e.g. Urbanek and Shakesby, 2009; Hardie et al., 2011), Such bypass (preferential) flow is viewed as an important mechanism not only in extremely hydrophobic soils (Doerr and Thomas, 2000), but also in dry loamy soils with high clay and silt contents (Yang and Zhang, 2011; Bracken and Croke, 2007). Cracks in clay soils were observed in dry conditions during fieldwork in the catchment study.

3.5.1.2. Urban

In contrast to woodland areas, urban landscape units in the *Ribeira dos Covões* catchment are characterized by lowest soil organic matter content. This is probably linked to the reduced and patchy vegetation cover and, in some locations, either loss or deposition of surface soil. The higher bulk density may be largely due to compaction by people and vehicles (Silva et al., 1997), as a result of vehicle access and parking in the discontinuous urban fabric. Soil bulk densities measured (1.07-1.72 g cm^{-3}) were similar to those reported in Nanjing, China, where lowest values were recorded in greenbelt areas and maximum ones in parking zones (1.19-1.62 g cm^{-3}) (Yang and Zhang, 2011).

In the *Ribeira dos Covões* catchment, the dominance of bare surfaces and sparse grass and shrub vegetation is the main cause of the recorded widespread hydrophilic conditions throughout the year. Only at particularly well vegetated sites was hydrophobicity recorded during the driest periods. Bare soil sites, mainly found on sandstone, being more susceptible to evaporation (Nunes et al., 2011), may have led to the low soil moisture content recorded particular in dry-wet transitional periods, such as in the southwest of the catchment on 02/11/2010 and 21/03/2011 (Figure 3.8).

The generally hydrophilic conditions found in urban soil would help to explain the high soil matrix infiltration capacity values recorded particularly after prolonged dry weathers (Figure 3.9), despite the high bulk density, which elsewhere has been noted to be associated with lower infiltration capacities (e.g. Dornauf and Burghardt, 2000; Yang and Zhang, 2011). The very low and in some cases zero values of soil matrix infiltration capacity recorded during wet periods may be linked to a decline in the suction force and then saturation of the soil. The inverse correlation recorded between soil moisture and infiltration capacity was also found in Tasmania, Australia, where the application of dye tracer showed infiltration to an average depth of 1.03 m (with a wetting front velocity of 1160 mm h^{-1}) in low antecedent soil moisture conditions, compared with a depth of 0.35 m (and a wetting front velocity of 120 mm h^{-1}) with wet antecedent conditions (Hardie et al., 2012).

In urban landscape units, overland flow is readily generated on paved and tarmac impervious surfaces, but for urban soils it varies in importance both seasonally and between urban-sandstone and urban-limestone areas. In dry summer conditions, the generally hydrophilic soils of greater infiltration capacity (Figures 3.9 and 3.10) lead to little or no overland flow and make these areas overland flow sinks. In contrast, after larger winter storm events, soil saturation or near-saturation was identified at urban-limestone sites (Figures 3.7 and 3.8), associated with a near-surface water table (on the valley floor) and shallow soils of low water storage capacity (on hillslopes). In both situations saturation overland flow was at least locally being generated. In contrast, in urban soils on sandstone, soil moisture levels recorded in winter were much lower than on limestone (Figure 3.7) and infiltration capacities (Figure 3.9) varied from low (on bare soil) to relatively high (on uncompacted, vegetated sites); the result was patchy Hortonian overland flow, mostly on the bare soil areas, with some of the vegetated patches acting as overland flow sinks.

The potential for overland flow generation in urban soils was demonstrated by runoff coefficients of 59-99% recorded on hydrophilic urban soils (slope: 6-30º) in 43 mm h^{-1} rainfall simulations on small plots (0.25 m^2) at the field sites, though it was unclear whether the overland flow was infiltration-excess or saturation in nature (Ferreira et al., 2012b).

3.5.1.3. Agriculture

In agricultural landscape units, different land-use/land management types lead to major differences on surface cover and soil properties. The agricultural types on sandstone (mainly pasture, small gardens and olive plantations) may explain the low organic matter content and high bulk density results of that landscape unit compared with the agricultural-limestone unit, where abandoned fields undergoing natural vegetation succession are dominant. This greater vegetation cover with higher soil organic matter content for agricultural-limestone would also explain the unit's enhanced spatial extent and severity than on sandstone. Nevertheless, hydrophobicity at agricultural-limestone sites was less severe than in woodland, and fewer rainfall events were required to accomplish switching from hydrophobic to hydrophilic conditions and hydrophobicity re-establishment in wet to dry transitions was also slower than for woodland (Figure 3.5). In a previous study of a partly urbanized Mediterranean catchment, Fernández and Ceballos (2003) only recorded lower hydrophobicity persistence when conditions were changing from dry to wet.

The generally greater soil moisture values of agricultural compared with other landscape units, despite the absence of irrigation, may be explained by the lower vegetation cover of the agricultural-limestone sites and the low hydrophobicity, particularly when compared with woodland. In addition, high surface roughness associated with tillage in agricultural-sandstone fields may enhance surface water retention and lead to higher soil moisture (Álvarez-Mozos et al., 2009), especially when compared with untilled urban soils.

Soil moisture, however, was slightly higher at agricultural-limestone than agricultural-sandstone sites, despite most of the former being abandoned. This may be a consequence of the marly nature of the limestone, which leads to greater fractions of fine material. However, the small soil moisture difference may reflect the fact that most sandstone agricultural sites are on valley floors (Figure 8), whereas limestone sites are mainly on upper slopes, where the soil is shallow (generally <0.4 mm depth), though in the wettest periods some saturation was observed here.

Differences in particle size distribution and land management practices, particularly wheeling, may explain higher soil porosity on abandoned limestone than on ploughed sandstone fields. Nevertheless, coarser particle size distribution and minor hydrophobicity may explain greater soil matrix infiltration capacity on sandstone compared with limestone agricultural areas in dry periods.

However, rising soil moisture content through the wet season, could restrict soil matrix infiltration capacity over agricultural areas, mostly noticed on sandstone fields. In agricultural-limestone sites, matrix infiltration capacity was relatively constant over the year. In this landscape unit, the slight infiltration capacity increase during early autumn, possibly due to soil hydrophobicity shrinkage, gives place to a decreasing capacity in later autumn and winter seasons, as a result of soil moisture increase. Throughout spring, with soil moisture decrease, infiltration capacity tend to increase, but possibly with hydrophobicity re-emergence, infiltration capacity was limited again. The development of hydrophobic conditions in the agricultural soils was clearly slower than woodland (Figure 3.5).

Overland flow generation, in response to the contrasts in soil moisture, hydrophobicity and infiltration capacity and their seasonal dynamics discussed above, differed between the agricultural-sandstone and agricultural-limestone landscape units. In agricultural-sandstone areas, high infiltration capacities associated with hydrophilic soils throughout the year and with sandy particle size meant that overland flow was absent in summer and in winter was only generated in big events or following very wet weather. In contrast, the greater vegetation of the abandoned fields on limestone led to hydrophobic soils in summer and a degree of proneness to infiltration-excess overland flow. Despite partial switching in transition periods and total switching to hydrophilic conditions in winter wet periods, the relatively low infiltration capacities and high soil moisture resulting from the marly limestone lithology meant that the agricultural limestone areas were more prone in winter to saturation overland flow than the sandstone areas. Unlike on urban and woodland soil sites, no infiltration-excess overland flow was recorded in 43 mm h^{-1} rainfall simulation experiments on hydrophilic agricultural land (slope 15-50º) in the study area (Ferreira et al., 2012b).

3.5.1.4. Synthesis: the influences of lithology, topography and land-use factors on overland flow and temporal variation in its distribution within the *Ribeira dos Covões* catchment

Lithology seems to play an important role in controlling spatio-temporal dynamics of overland flow in the *Ribeira dos Covões* catchment via its influence on particle size distribution, soil moisture and infiltration capacity variability over the catchment. Generally, the greater sand fractions and deeper soils of the sandstone areas promote greater infiltration capacity and water storage capacity, as well as lower soil moisture, leading to reduced proneness to both Hortonian and saturation overland flow. In contrast, the higher silt-clay content and shallower nature of soils on the marly limestone result in greater soil moisture, lower infiltration and water storage capacities and hence greater proneness to saturation overland flow than on sandstone. These are in line with reports elsewhere of the influence of shallow soils (Easton et al., 2007, Hardie et al., 2011) and variations in particle size (Rahardjo et al., 2008; Yang and Zhang, 2011) on overland flow.

Secondly local topographic characteristics also seem to be an important driver. Saturation was observed at urban soil sites near streams (Figure 3.8) caused either by (1) lateral subsurface flows from upslope (Aryal et al., 2005) or (2) groundwater table rise, as recorded at a woodland-sandstone site near to an active spring on 24th January 2011 (Figure 3.8). In a small cultivated Mediterranean catchment, Latron and Gallart (2007), also explained the saturation pattern with extent and height of the water table. The locations and extents of the wettest areas in the *Ribeira dos Covões* catchment varied temporally, a feature also reported elsewhere within agricultural hillslope (Walter et al., 2000) and mixed agricultural and forested areas (Easton et al., 2007).

Land-use and land management constitutes the third and perhaps most important influence on differences in overland flow between and within landscape units. This influence is exerted through the effects of different percentage ground covers, management practices and other human activities on degrees of soil compaction, soil moisture levels and soil permeability and via the effects of different plant species on hydrophobicity severity, switching dynamics and seasonality. Overland flow is consequently of greatest significance in urban landscape units, particularly in winter, when urban soils are often either saturated or bare and compacted, whereas in summer overland flow from impervious or bare areas is reduced by hydrophilic soil patches. Overland flow in the woodland units is in general greatly reduced by vegetation effects on infiltration, but is seasonally enhanced in storms following summer dry periods in eucalypt and pine woodland-sandstone areas because of their severe soil hydrophobicity, but absent in woodland-limestone areas because of the oak woodland land-use. The agricultural-sandstone landscape unit produces very little overland flow because of high infiltration capacities resulting from a combination of land-use and land management practices that do not result in compaction, but mostly because of the sandy soils. In converse fashion, the abandoned field land-use of agricultural-limestone areas probably has the effect of reducing overland flow responses from what they would otherwise be with active cultivation, but which for lithology-related reasons can be significant particularly in winter wet weather.

Differences in temporal variability of soil hydrological properties between landscape units led to spatial fluctuation in overland flow sources and sinks. In wet winter conditions, overland flow is greatest from the urban landscape units and also significant from the agricultural-limestone unit, but comparatively little from the hydrophilic and permeable agricultural-sandstone and woodland units except in the wettest weather. During transitions from wettest to dry conditions, the spatial pattern of response to rainstorms is reversed, with decreasing susceptibility to saturation overland flow as soil moisture declined (mainly associated with agricultural- and urban-limestone areas) and increasing vulnerability to infiltration-excess overland flow, enhanced by hydrophobicity re-establishment (particularly in woodland but also on agricultural-limestone). In summer, overland flow is comparatively low but still greatest in urban-limestone areas and to a lesser extent is also significant in the woodland and agricultural-limestone units because of their hydrophobic condition, but urban-sandstone and agricultural-sandstone areas produce comparatively little overland flow, because of locally or more widespread hydrophilic and permeable surface soils providing overland flow sinks. Finally, in the dry to wet transition of autumn, patterns of overland flow are broadly similar to the wet-to-dry transition, with hydrophobicity (and overland flow responses) becoming most rapidly re-established in eucalypt parts of the woodland-sandstone landscape unit.

Spatial variability of soil properties *within* the same landscape unit, such as particle size and hydrophobicity, provides heterogeneous infiltration capacities, where this particularly applies to the partly bare urban-sandstone unit and woodland and agricultural-limestone units in transitional periods (Figure 3.9). Soil spots with matrix infiltration capacity lower than rainfall intensity will lead to infiltration-excess overland flow, which may be infiltrated in surrounding soil spots with greater infiltration capacity. Not all the landscape units provided spots with sufficient permeability throughout the year. Urban and agricultural landscape units showed more sites of high permeability after dry periods, while even in wettest conditions, woodland provided sites of high infiltration capacity. Nevertheless, even the most permeable soil patches could not cope with the maximum rainfall intensity of 15.6 mm h^{-1} recorded in the rainstorm of 2nd November 2011. Thus infiltration-excess overland flow would be expected to occur widely during particularly intense storms in all landscape units.

3.5.2. Implications for catchment runoff delivery and land management

The changing nature of overland flow sources and sinks within the catchment can be expected to affect flow connectivity over the hillslope and influence storm runoff delivery to the stream network. Under hydrophobic conditions, infiltration-excess overland flow generated in relatively extensive woodland on steep slopes and on shallow upstream agricultural-limestone soils, may reach the stream network directly or be delivered to the urban cores situated downslope (Figure 3.2b).

Vegetation is widely considered as a key factor interrupting hydrological connectivity (e.g. Bracken and Croke, 2007; Appels et al., 2011). Greater vegetation interception provided by woodland and agricultural-limestone areas, compared with the other land-uses, tends to reduce overland flow, though the effect will be marginal in large storm events, when percentage interception is small. The more important effect of interception is in helping (together with transpiration) to reduce antecedent soil moisture levels prior to rainfall events. In central Portugal, Valente et al. (1997) reported relatively high interception losses of 17% in Pinus pinaster forest and 11% in eucalypt stands and attributed them to the greater canopy storage and, aerodynamic roughness (and hence higher evaporation rates) of forest covers. In addition, greater litter density and frequency of root holes compared with the other landscape units may lead to enhanced water interception, retention and infiltration, particularly in smaller storm events after dry spells. Surface roughness also enhances water retention and reduces overland flow rates, and promotes discontinuities between overland flow source areas (Rodríguez-Caballero et al., 2012). These infiltration/retention processes operating at larger scales, as well as preferential flow via root-holes and cracks, considerably reduce the risk that overland flow from low permeable soil sites might reach downslope contiguous urban areas and/or the stream network. Although urban soils may provide overland flow sinks, the impermeable tarmac and paved surfaces allow little infiltration, restricting the capacity of these areas to deal with rainfall and overland flow from upslope landscape units. Observations in *Ribeira dos Covões* over three years suggest that only small amounts of overland flow were generated in woodland and agricultural limestone areas, mainly after dry conditions. Nevertheless, preferential flow via macropores can reach streams relatively quickly and thus contribute to the flood peak, as reported in other areas of the world (Uchida et al., 1999; van Schaik et al., 2008; Yu et al., 2014).

Although not recorded during this study, clear-felling in woodland would cause increased overland flow and water connectivity by providing bare, compacted areas and reducing interception, transpiration and surface roughness. Thus the size and location of clear-felled areas require planning to ensure that most overland flow is intercepted by downslope woodland area sinks in order to reduce flood hazard. Clear-felling should also be timed to avoid storms of early autumn rainy seasons, in view of the greater extent and location of hydrophobic areas at that time (Figure 3.6). In addition, if forest managers select tree species that release less hydrophobic substances, overland flow may be correspondingly reduced (e.g. Ferreira et al., 2012a).

Under wet winter conditions, saturation overland flow becomes more likely in urban and agricultural land-uses, but saturated areas may be more influenced by topography and soil depth than by land-use (Figure 3.8). Overland flow generated in these landscape units would be delivered mostly to the stream network, but also to downslope woodland and urban cores in the case of upslope saturated shallow soils (Figures 3.2b and 3.8). Previous studies reported higher runoff coefficients in shallow soils affecting hillslope runoff connectivity (Kirkby et al., 2002; Easton et al., 2007; Hopp and McDonnell, 2009). In agricultural areas, however, overland flow paths would depend on land management. Land drains, ditches, wheel ruts and roads may enhance flow connectivity, particularly if they are aligned downslope, whereas terracing and stone boundary walls can form traps for water, enhancing infiltration and disrupting flow pathways. Overland flow transfer from agricultural and urban areas to downslope woodland soils when hydrophilic may be dissipated by enhanced infiltration and surface retention. Furthermore, although much of the overland flow from impermeable urban surfaces located in upslope positions (Figure 3.2b) is collected by the urban drainage system and delivered directly into the stream, some reaches nearby soil.

Because of the generally low infiltration capacity or saturated condition of downslope urban soil areas, saturation overland flow reaching such areas may be problematic, although this can be offset by spatial differences in modified and unmodified soil properties providing a mosaic of different infiltration capacities. Even if urban soils surrounding impermeable surfaces (e.g. roofs and roads) cannot act as sinks, obstructions (such as buildings and walls) may delay overland flow transfer. This will depend on urbanization style, since extended impermeable surfaces will enhance landscape connectivity, whereas detached houses surrounded by gardens and walls can provide sinks and flow discontinuity.

The susceptibility of urban core areas located in topographic lows (Figure 3.2b) to saturation overland flow and stream flooding may represent a real flood hazard for the inhabitants, particularly considering the scale of recent urban consolidation in the *Ribeira dos Covões* catchment. This risk may be enhanced by 1) additional overland flow resulting from greater connectivity with upslope areas subject to soil moisture increase and water table rise, and 2) the rapid transfer of most overland flow from upslope impermeable surfaces directly into the stream via the urban drainage system. These may be particularly important in larger storm events, considering the generally low soil permeability across the catchment. According to interviews with older citizens, flooding events were already experienced about 80, 50 and 10 years ago, when the urban area was considerably less extensive than now.

Analyses of storm hydrographs of the outlet stream (results not shown) suggest that the actual landscape mosaic of *Ribeira dos Covões* catchment, comprising extensive woodland areas and large urban areas near the catchment outlet, together with numerous smaller urban areas mainly along ridges and dispersed agricultural fields (Figure 3.2b), may be sufficient to promote discontinuities to the infiltration-excess overland flow generated by soil hydrophobicity. Thus, in dry settings, rainstorms of 2.8 mm (average) and 14.4 mm (large), recorded on 6th August and 1st September 2011, promoted runoff coefficients for the *Ribeira dos Covões* stream of only 5% and 2% respectively and peak streamflows of only 0.041 mm h^{-1} and 0.036 mm h^{-1}, compared with maximum 5-minute rainfall intensities of 2.4 mm h^{-1} and 9.6 mm h^{-1} respectively. Thus, hydrophobicity over the catchment does not translate into catchment-scale overland flow, presumably due to infiltration into sinks downslope. In wet conditions, however, enhanced soil moisture levels seem to increase flow connectivity over the catchment. Thus rainstorms of 2.8 mm and 15.0 mm registered on 11th February and 28th March 2011, led to 10% and 9% storm runoff coefficients and peak flows of 0.079 and 0.370 mm h^{-1}, compared with maximum rainfall intensities of 9.6 mm h^{-1} in both cases. Although lag times from peak rainfall to peak streamflow are short, ranging between 25 and 35 minutes, and probably a direct result of urban surface runoff and the urban drainage system, the overriding feature is the small size of the storm runoff coefficients both during dry and wet times of the year, which shows how little of the rain falling on the peri-urban mosaic actually reaches the stream network. This may reflect in part the ridge location of much of the urban expansion to date and in part a rather high proportion of infiltration into urban soil within the urban units and adjacent landscape units.

The short lag times between rainfall and streamflow peaks in urban areas, however, mean that future urban consolidation and the construction of new urban cores, already proposed, must be planned carefully in order to minimize urban flood hazard. From the hydrological point of view, instead of extending the existing urban cores, it would be better to establish new dispersed urban cores far from the stream network. The maintenance of a patchy mosaic of dispersed landscape units would reduce overland flow and river flood peak responses.

3.6. Conclusions

The peri-urban *Ribeira dos Covões* catchment is covered by soils of relatively low matrix infiltration capacity, but of greater permeability on sandstone than limestone, due to the marly nature of the latter. The different landscape units, associated with different land-uses and lithologies, display varying responses of soil hydrological properties to season and to antecedent rainfall with complex consequences for spatial patterns of overland flow and its flow connectivity. The main findings are:

1. In dry conditions, severe hydrophobicity in eucalypt and pine (but not oak) woodland and limestone-agricultural areas (abandoned fields) considerably reduces soil matrix infiltration capacity. In contrast, agricultural-sandstone soils (mainly covered by olives, pasture and gardens) and urban soils remain mostly hydrophilic, and have relatively high infiltration capacities. Under wet conditions, hydrophobicity in woodland and agricultural-limestone areas breaks down and infiltration capacity increases, reaching 6 mm h^{-1}. In contrast, on urban and agricultural sites, a rise in soil moisture leads to a decline in infiltration capacity, with soil saturation in areas of shallow soils and high water tables on hillslopes, in topographic lows and in valley bottoms.

2. Temporal variability of soil hydrological properties indicates that, in dry conditions, hydrophobicity-related infiltration-excess overland flow may be generated in woodland and agricultural-limestone areas, while in wet conditions saturation is likely in some locations on urban and agricultural soils. Nevertheless, soil property heterogeneity and the distinct temporal pattern of infiltration capacity indicate that much overland flow must be infiltrating before reaching the stream network in patches of unsaturated soil of relatively high permeability, either within the same landscape unit or on adjacent landscape units.

3. Despite the generally low soil matrix infiltration capacity across the catchment, macropores, vegetation, litter and surface roughness play important roles in surface water retention and facilitating infiltration. Nevertheless, these processes are influenced by the different landscape units, which provide overland flow sinks with differing temporal regimes. Because of this, a patchy mosaic comprising fragmented and dispersed land-uses, and the tendency for much of recent urbanization to have occurred along ridges, have to date led to relatively low flow connectivity over hillslopes, thereby attenuating river discharge peaks.

Understanding how the spatial and temporal variability in overland flow generation and infiltration affect flow connectivity in a catchment with varied land-use, geology and soils is vital for predicting flood hazards. Landscape managers and urban planners should employ a mosaic of different land-uses, where impermeable surfaces are joined hydrologically to infiltration-promoting “green” areas, in order to prevent or reduce downstream flooding. There need to be informed decisions about the precise spatial arrangement of different land-uses.

CHAPTER 4

DIFFERENCES IN OVERLAND FLOW DYNAMICS IN DIFFERENT TYPES OF WOODLAND AREAS WITHIN A PERI-URBAN CATCHMENT

ABSTRACT

Forest hydrology has been widely investigated, but the impacts of different woodland types on hydrological processes particularly in peri-urban catchments are poorly understood. This chapter investigates overland flow generation processes in three different types of hardwood stand in a small (6.2 km^2) catchment in central Portugal that has undergone strong urban development over the past 50 years. Two eucalypt plantations of differing tree density and a semi-natural oak stand were each instrumented with three 16 m^2 runoff plots and 15 throughfall gauges, which were monitored at c. 1- to 2-week intervals over two hydrological years. In addition, surface moisture content (0-50mm) and hydrophobicity (0-20mm, 20-50mm and 50-100mm) were measured after individual rainfall events. Although all three woodland types produced relatively little overland flow (< 3% of the incident rainfall overall), the dense eucalypt stand produced twice as much overland flow as the sparse eucalypt and oak woodland types, despite similar throughfall amounts. This contrast in overland flow can be attributed to infiltration-excess processes operating during dry antecedent weather conditions when severe hydrophobicity was widespread in the dense eucalypt plantation as opposed to being moderate and low in the sparse eucalypt plantation and the oak stand, respectively. In contrast, under wet conditions more overland flow (though still small) tended to be produced in the oak woodland than in the two eucalypt plantations; this was probably linked to saturation-excess overland flow being generated more readily at the oak site as a result of its shallower soil. Differences in water retention in surface depressions affected overland flow generation and downslope flow transport. Implications of the seasonal differentials in overland flow generation between the three distinct woodland types for the hydrological response of peri-urban catchments are addressed.

Keywords: Eucalypt plantations, oak woodland, saturation-excess overland flow, infiltration-excess overland flow, hydrophobicity, soil moisture content

4.1. Introduction

Forest and woodland represent the dominant land-use in Europe, covering 37% of the earth surface (FAO, 2001) and 35% of mainland Portugal (IFN6, 2013). In recent decades, globally forest cover has increased as a result of greater demand for timber and environmental concerns (e.g. Robinson et al., 2003). This increasing tendency is expected to continue in the future, in response to European policy, linked to the Common Agricultural Policy and Water Framework Directive. However, forest cover has decreased in peri-urban catchments, where urbanization has led to progressive deforestation and forest fragmentation (Nowak, 2006).

Forest hydrology has been widely documented, particularly with respect to some hydrological processes. Forest and woodland promote rainfall interception, evapotranspiration and infiltration, affecting baseflow recharge and storm runoff (e.g. Hewlett, 1969; Scherer and Pike, 2003; Eisenbies et al., 2007). Several studies report the hydrological impacts of afforestation (Wattenbach et al., 2007; Iroumé and Palacios, 2013; Salazar et al., 2013), thinning (Dung et al., 2012; Webb and Kathuria, 2012; Hawthorne et al., 2013) and wildfire (Doerr et al., 1996; Moody et al., 2013; Nyman et al., 2014), being unanimous as regards to overland flow increase. This increase may represent an additional problem when generated upslope urban areas.

Vegetation affects rainfall partitioning and its redistribution, influencing the amount and spatial distribution of water reaching the ground surface (throughfall) and deeper layers of the soil (stemflow) (Martinez-Meza and Whitford, 1996). Different tree species are linked to different canopy architecture, stem properties and root system, which affect the fate of water. For example, horizontal leaves direct water to branches, increasing the stemflow, while vertical leaves tend to increase throughfall (Ferreira, 1996). Crown characteristics affect water flow along branches towards the trunks (André et al., 2011). Nevertheless, throughfall and stemflow typically account for 70–90% of the net-precipitation, with stemflow representing a minor fraction of 5-10% (Herwitz and Levia, 1997; Crockford and Richardson, 2000), which reach 15% in the oak forest in northeast China (Wei et al., 2005). Generally, evergreen have lower throughfall than deciduous species (Barbier et al., 2009; Llorens and Domingo, 2007), as well as conifers when compared with broadleaves (Freedman and Prager, 1986; Keim et al., 2006). Stemflow decreased with bark roughness from smoother to rougher bark (Johnson and Lehmann, 2006; Livesley et al., 2014). Besides interception, transpiration is also dependent on tree species, attributed to distinct stomata, leaf water potential and hydraulic conductance (Ewers et al., 2002).

In addition, vegetation type have been associated with the release of different hydrophobic compounds, such as different resins and waxes (DeBano, 2000; Lozano et al., 2013; Zavala et al., 2009), leading to soil hydrophobicity which restricts infiltration capacity and may enhances overland flow, particularly in seasonally dry environments (Dekker and Ritsema, 1994). Hydrophobicity is mainly associated with dry settings

(Doerr and Thomas, 2000; Santos et al., 2013) and may influence seasonal pattern of overland flow, particularly under Mediterranean climate, marked by a long dry summer season (Doerr et al., 2000; Jordán et al., 2013). Nevertheless, under eucalypt plantations, hydrophobicity may persist after several rainfall events (Ferreira, 1996; Ferreira et al., 2000). In a previously rip-ploughed eucalypt plantation area of north-central Portugal, hydrophobicity was found to explain 74% of overland flow variation (Ferreira et al., 2000).

Many studies have demonstrated differences in degrees of hydrophobicity between different vegetation types (e.g. DeBano, 2000; Zavala et al., 2009; Lozano et al., 2013). Eucalypt stands are renowned for inducing high levels of hydrophobicity (Ferreira et al., 2000; Santos et al., 2013). In Portugal, some studies have reported greater overland flow under eucalypt than pine plantations caused by enhanced soil hydrophobicity (Ferreira et al., 2000; Keizer et al., 2005), but little is known about the slope hydrology of oak stands, particularly in wet Mediterranean climates. This is important as differences in overland flow between distinct forest stands can contribute to variations in total streamflow and the stormflow component with forest land-use change (Fritsch, 1993; Grip et al., 2005). However, in the literature, streamflow differences in areas subject to forest cover changes are mostly attributed to evapotranspiration adjustments. For example, Otero et al. (1994) reported reduced streamflow with conversion of native forest to fast-growing plantations of *Pinus radiata*. In the southern Appalachians, the conversion of a deciduous hardwood catchment to a *Pinus strobus L*. stand (eastern white pine) led to a 20% reduction of streamflow, attributed to the greater vegetative surface area of *Pinus strobus* (Swank and Douglass, 1974).

Although it is widely accepted that forests regulate water yield and their soils are usually highly permeable (Eisenbies et al., 2007; Bathurst et al., 2011), the role of forest areas in flood protection has been hotly debated. Some have argued that interception and higher soil moisture deficits under forest should reduce floods by removing a proportion of the storm rainfall (e.g. Bathurst et al., 2011), whereas others have argued that such water retention by forest is minimal in the extreme rainfall events that are responsible for floods (Eisenbies et al., 2007; Hümann et al, 2011; Komatsu et al., 2011). Thus, it is argued that forest cover might not significantly reduce peak flows during extreme events, particularly in small catchments, but that it could be effective in reducing the peakflow responses of more frequent, less intense rainfall events (Bathurst et al., 2011).

Impacts of different forest and woodland stands on overland flow may be particularly important in the hydrology of small peri-urban catchments. Such catchments tend to be characterized by a mosaic of different land-uses, which provide varying sources and sinks of overland flow (Ferreira et al., 2011). Any overland flow generated on forest areas may reach downslope urban areas and represent an additional contribution to the urban flood hazard, whereas in other cases forest patches can act as sinks for upslope-generated overland flow from urban surfaces. Knowledge of overland flow responses from different forest and woodland types is arguably particularly important for land-use planning and water resources management of catchments undergoing partial urban development.

This chapter investigates differences in overland flow generation, and its influencing factors, in distinct eucalypt and oak woodland types in a peri-urban catchment in central Portugal, using a plot-scale monitoring approach over a two-year period. The focus is on the roles played by differing temporal regimes in hydrophobicity and soil moisture of the woodland types studied. The implications of the results for catchment streamflow response in peri-urban catchments in such environments are also explored.

4.2. Study Area

The study was carried out in the peri-urban *Ribeira dos Covões* (8º27´W, 40º13´N) catchment, located 3km NW of Coimbra, the largest city in central Portugal. This catchment (6.2 km^2) is aligned S-N and ranges in altitude from 34 to 205 m a.s.l. The area has a sub-humid Mediterranean climate, with a mean annual temperature of 15°C and an average annual rainfall of 892 mm over the period 1941-2000 recorded at Coimbra-Bencanta (national meteorological weather station 12G/02UG), sited 0.5 km north of the study catchment. A distinct dry and hot season occurs from June to August (8% of annual rainfall), whereas the rainiest period is between November and March (61% of rainfall). Relatively small rainfall events are dominant over the year, with 83% of daily rainfalls between 2001 and 2013 at Coimbra-Bencanta being ≤10 mm. Maximum daily rainfalls over the same 2001-13 period ranged between 20 mm and 102 mm. The catchment is underlain by sandstone (57%) and limestone (43%). Soils developed on sandstone are classified as Fluvisols and Podzols, following WRB (2006) classification, and are generally deep (>3 m), while Leptic Cambisols found on limestone slopes are typically shallow (<0.4 m) (Pato, 2007).

The catchment has undergone profound land-use changes over the last five decades, mainly associated with rapid urbanization and increased eucalypt planting for timber production. Between 1958 and 2007, the urban and woodland areas expanded from 6 to 32% and from 44 to 64%, respectively, at the expense of a marked decrease in agricultural land from 48 to 4%. Since 2007, however, deforestation has occurred because of a main road construction and the building of an enterprise park, which now occupies 5% of the former wooded area. Thus by 2012, the urban area had increased to 40%, while the woodland area had decreased to 53%.This trend towards a reduced tree cover and increased urbanization is expected to continue.

Currently, wooded areas consists mainly of eucalypt plantations and few mixed stands of eucalypt and pine (84%), with minor fractions of scrub and herbaceous vegetation (15%) and relic oak woodland (1%) (Figure 4.1). The major eucalypt plantation species is *Eucalypt globulus Labill*.. Over the last years, increased eucalypt plantation in detriment of pine stands was due to harvesting interval of typically 10-12 as opposed to 50-60 years for pine (Robinson et al., 2003), as well as their relatively high commercial value for the pulp industry. Generally, eucalypt plantations are placed over sandstone, but some abandoned logged areas lead to sparse eucalypt stands which are densely covered by scrubs. These scrub areas, observed on sandstone, are dominated by heather (*Erica scoparia* L. and *E. umbellata* L.), broom (*Pterospartum tridentatum* L.) and gorse (*Ulex europaeus* L.), with eucalypt and pine encroachment. On limestone, vegetated areas are mainly covered by herbaceous associations, represented by grasses (mainly *Salvia verbenaca*, *Geranium purpureum* Vill, *Vicia* sp.), together with spanish broom (*Spartium juncium* L.), cypress (*Cupressus sempervirens* L.), pine (*P. pinea L.*) and olive (*Olea europaea* L.) encroachment. A relic of semi-natural oak is also observed in limestone area, consisting of a mixture of *Quercus robur L.*, *Q. faginea broteroi* and *Q. suber L.* trees (mean high of 4 m and 25%-50% cover), with strawberry (*Arbutus unedo* L.) and laurel (*Laurus nobilis* L.) bushes forming the ground cover (average height: 800 mm and 5%-25% cover). Invasive plants such as wattle (*Acacia longifolia* A.) and mimosa (*Acacia dealbata* L.) can be found in small numbers everywhere (Pato, 2007).

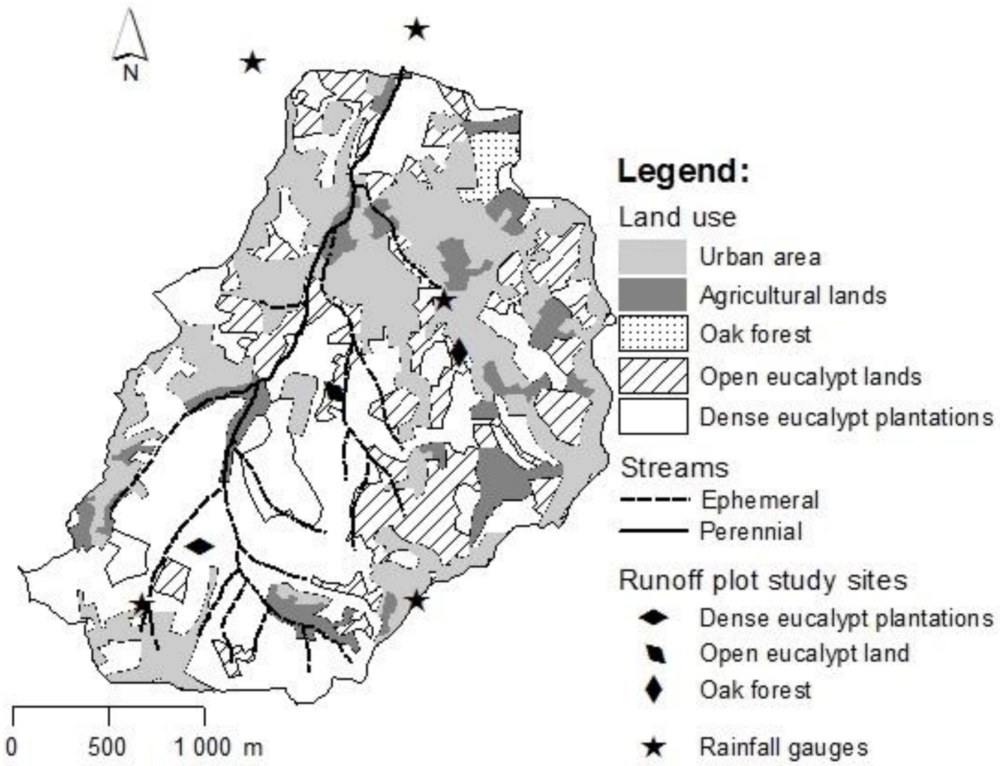


Figure 4.1- *Ribeira dos Covões* catchment land-use and location of the study sites instrumented with runoff plots.

4.3. Methodology

4.3.1. Research design and experimental setup

Runoff plots were established in the three principal types of woodland within *Ribeira dos Covões* (Figure 4.1): (1) dense eucalypt plantation, which may include occasional pine and acacia trees (plots DE1, DE2 and DE3); (2) sparse eucalypt areas, with an extensive cover of scrub (SE1, SE2 and SE3); and (3) oak woodland (O1, O2 and O3) (Figure 4.2). Similar topographic and soil properties between sites were search for the plot location (e.g. slope angle, aspect, parent material and soil type). However, the spatial distribution of woodland types within the catchment and site accessibility led to topographic and lithological (and hence soil) differences between the three study sites. For instance, dense and sparse eucalypt areas were largely located on sandstone, whereas oak was only overlaying on limestone.

a) b) c)

Figure 4.2 - Studied woodlands in the *Ribeira dos Covões* catchment: a) dense eucalypt plantation, b) sparse eucalypt, dominated by scrub, and c) oak woodland.

Each of the study sites was instrumented with three runoff plots placed 20 – 500 m apart, depending on local constraints (e.g. avoiding close proximity to tracks and locations with extensive stone lag). The plots were 2 m wide by 8 m long, bounded by metal strips of 150 mm high inserted into the soil to a depth of 50-100 mm. A modified Gerlach trough (Gerlach, 1967) was installed at the outlet of each plot to collect the overland flow and to retain the >0.5 mm fraction of the eroded material with the aid of a mesh. Overland flow was then routed via a garden hose, first to an automatic tipping-bucket device with a capacity of 0.5-L per tip (connected to a data logger), using an in-house design, and then to a 50-L tank. Plot installation was completed on 10th January 2011, but data collection started one month later, in order for the plots to recover from any disturbance caused during installation.

Each plot was further equipped with five throughfall gauges as well as with five automatic soil moisture probes to give an approximate idea of differences between woodland types. The throughfall gauges comprised funnels (Ø 200 mm) connected to a storage bottle, installed within half-buried PVC pipes (Ø 200 mm; height: 300 mm). The five gauges were placed randomly 0.5-2 m outside the plot boundaries beneath the tree and/or scrub vegetation. The soil moisture probes (Decagon EC-5, connected to Hobbo data logger) were divided amongst three soil depths (2 sensors at 0-20 mm, 2 sensors at 50-100 mm, and 1 sensor at 150-200 mm) and installed at 2-5 m distance from the plot boundaries. Volumetric soil moisture content was recorded at 5-min intervals. Laboratory calibration per woodland site was performed before installation in the field, using columns of sieved soil (<2 mm) from the sites where the sensor was going to be installed, on repacked soil material at the average dry bulk density of the sites. A linear curve was found to provide the best calibration for the sensor data in the three woodland sites. However, theft of devices considerably restricted soil moisture data acquisition.

Overland flow and throughfall were measured at mostly 1- to 2- weekly intervals, depending on previous rainfall, during the two years of study (9th February 2011 – 14th April 2013), in a total of 61 measurement occasions. Throughfall measurements in the oak woodland started later than the plot measurements on 23rd March 2011. A visual general description of the vegetation cover was performed at the beginning of the study period.

In the second week of March 2012, part of the dense eucalypt site was clear-felled, affecting two of the three existing plots (DE1 and DE2). Plot DE2 had to be abandoned since it was destroyed by logging activities. Owing to vandalism (theft in particular), the other two plots at the dense eucalypt site could only be monitored for total runoff. Furthermore, due to theft of equipment on several occasions after clear-felling, throughfall measurement at the dense eucalypt plot locations was also abandoned.

Rainfall was recorded continuously using five tipping-bucket rain-gauges (Davis Instruments) in open areas within and near the catchment. No significant inter-gauge spatial rainfall variation was identified, so that the weighted average of the five raingauges was used.

4.3.2. Soil data collection

During monitoring, at the same time as overland flow measurements, soil hydrophobicity was assessed at 0-20 mm, 20-50 mm and 50-100 mm depths along two 1-m transects at either side of each plot using the ‘Molarity of an Ethanol Drop test’ (Doerr, 1998). Sets of fifteen droplets of increasing ethanol concentration were applied along each transect until infiltration of at least eight droplets of the same concentration occurred within 5 seconds. The results for each transect were classified according to the following five repellency ratings and associated ethanol concentrations: wettable (0%); low (1, 3 and

5%); moderate (8.5 and 13%); severe (18 and 24 %); and extreme (36 and >36 %) hydrophobicity.

In addition, on each fieldwork visit, one composite sample per plot (0-50 mm soil depth), obtained by mixing 10 samples collected randomly on undisturbed land around each plot. Gravimetric was converted into volumetric water content using the mean soil bulk density of each site, calculated from 11 random samples of 143 cm^3 volume collected near to each plot, using soil ring samplers of 50 mm diameter. These laboratory measurements were considered highly important to assure soil moisture data over the study period, since malfunctioning and theft of soil moisture probes severely restricted the field data aquisition. Because of this, the soil moisture data used in the results and discussion sections relates to the soil samples and laboratory assessment, thus no soil moisture data from probes are shown.

Throughout the first year of study, soil matrix infiltration capacity was measured on 12 occasions, covering different weather conditions. The measurements were performed with a mini-disk tension infiltrometer (Decagon Devices), carrying out one experiment alongside each transect. Overall, 216 measurements were performed. Unsaturated hydraulic conductivity (K_{uns}) was calculated from soil matrix infiltration capacity, based on Decagon's instruction manual (Decagon, 2007).

The physical properties of surface soil (0-50 mm) were sampled in January 2011. Around each runoff plot, six core samples of 137.4 cm^3 were collected to determine dry bulk density following Dane and Topp (2002). In addition, 10 sub-samples were collected manually with a scoop and mixed to create one composite sample of c. 1.5 kg per plot. These samples were then oven dried at 38°C until a constant weight was reached and sieved to obtain the <2 mm fraction. This fine-earth fraction was analyzed with respect to organic matter content using infra-red detection after oxidation at 600°C (SC-144DR equipment, Strohlein Instruments) (LECO, 1997) and particle size distribution, using the standard pipette method (Dane and Topp, 2002).

4.3.3. Data analysis

In view of the non-normal distribution of the overland flow, throughfall, soil moisture and hydrophobicity data, non-parametric statistical tests were used to assess differences in median values between the three forest types and between plots of the same forest type. The Kruskal–Wallis test was employed to test the significance ($p<0.05$) of the differences with woodland type in overland flow, throughfall, hydrophobicity and soil moisture, and their seasonal variations. The Spearman correlation coefficient (r) was used to assess whether significant associations ($p<0.05$ and $p<0.01$) existed between rainfall characteristics (1- to 2-weekly totals, maximum 30-min rainfall intensities (I_{30}) and antecedent rainfall over the previous 30 days) and soil hydrological properties (hydrophobicity and soil moisture), as well as overland flow. All statistical analyses were carried out using IBM SPSS Statistics 22 software.

4.4. Results and analysis

4.4.1. Biophysical properties of the study sites

Vegetation differences between sites are linked to the woodland types and can be observed in Table 3.1. The greater tree density is clearly found in the dense eucalypt stands and contrast with the dominant cover of scrubs in sparse eucalypt areas. Despite the lower trees density in oak compared with dense eucalypt, oak canopy covers all the woodland area. Under dense eucalypt stands, the clear-felling performed in the first week of February 2012, removed the canopy cover, but biomass waste (leaves and smaller branches) was left on site. Eucalypt regrowth started in late April, following some rain but became more rapid by autumn. At the beginning of January 2013, a few trees surrounding the O2 plot were cut and the tree canopy cover decreased by about 20% near the upper boundary. Despite not being measured, the canopy cover decreased in autumn/winter for these deciduous trees, with a corresponding increase in the litter layer.

Table 4.1 – Biophysical characteristics of the three study sites in *Ribeira dos Covões* catchment. S: sandy, SL: sandy loam, L: loamy, LS: loamy sand.

	Woodland type	**Dense eucalypt**			**Open eucalypt**			**Oak**		
	Plot reference	**ED1**	**ED2**	**ED3**	**EO1**	**EO2**	**EO3**	**O1**	**O2**	**O3**
Vegetation and litter cover	Trees (number ha^{-1})	800	1300	900		150		500 (canopy fully covers the area)		
	Stage of trees development (years)	Mature (~15)	Young (~5)	Young (~8)		Mature (~10)			Adult (~80)	
	Vegetation (cover, height)	15%, 0.15 m	0%	95%, 0.5 m	100%, 0.8 m	100%, 1.5 m	100%, 1 m	40%, 0.8 m	55%, 0.8 m	75%, 1 m
	Litter layer (cm)	2	5	<1	<1	2	1	1	2	1
Topography	Elevation (m)	138	132	137	105	105	105	90	92	91
	Slope aspect	W	NW	NW	NE	NE	NE	W	W	W
	Slope (°)	18	16	26	26	28	26	13	16	22
Soil properties	Lithology		Sandstone			Sandstone			Limestone	
	Soil depth (m)		>2m			>2m			~0.4m	
	Texture	SL	S	SL	LS	LS	SL	L	L	L
	Particle size distribution (%)									
	Sand	80	95	75	44	59	65	53	49	45
	Silt	7	3	10	18	15	17	27	31	38
	Clay	13	2	15	39	26	18	20	20	17
	Organic matter (%)	8	7	9	5	4	3	7	7	6
	Bulk density (g cm^{-3})	0.74±0.38	0.69±0.23	0.64±0.11	1.28±0.24	1.13±0.29	1.24±0.40	0.80±0.29	0.65±0.11	0.75±0.16

The location of woodland types across the catchment and problems with accessibility led to differences in the site characteristics and soil properties between runoff plots (Table 3.1). Dense eucalypt plots were mainly on W- and NW-facing moderate slopes, sparse eucalypt on NE-facing steeper slopes, whereas oak locates on W-facing gentle slopes. Oak woodland, was on loamy soil laid on limestone, contrasting with dense and sparse eucalypt stands, mostly sandy loam and loamy sand soils, respectively, overlying sandstone. Soil depth in oak forest site (~0.4 m) was lower than in hardwood and scrub (>2m). Soil organic matter was significantly lower in sparse eucalypt sites (4%) than in the dense eucalypt plantation (8%) or in the oak woodland (6%). In contrast, the soil of the sparse eucalypt site had a significantly higher bulk density (1.22 g cm^{-3}) than that of the dense eucalypt site (0.69 g cm^{-3}) and of the oak site (0.73 g cm^{-3}).

Unsaturated hydraulic conductivity ranged from very slow (≤1 mm h^{-1}) to slow (>1 mm and ≤5 mm h^{-1}) over the year, according to Kohnke's (1968) classification (Figure 4.3). Values were in general higher in dense eucalypt (0.9 mm h^{-1}) than in sparse eucalypt and oak (0.6 mm h^{-1} for both woodland types) ($p<0.05$). Over the year, K_{uns} in eucalypt sites (dense and open) was greater in winter and spring seasons than in summer and autumn (dense: 1.4 vs 0.6 mm h^{-1}; open: 0.7 vs 0.3 mm h^{-1}; $p<0.05$), whereas in oak woodland no significant difference was observed ($p>0.05$). K_{uns} increased with increasing soil organic matter content ($r=0.60$, $p<0.01$) and decreased with increasing bulk density ($r=-0.34$, $p<0.01$). It was also affected by particle size, increasing with a greater sand fraction ($r=0.74$, $p<0.01$) and decreasing with increasing silt and clay fractions ($r=-0.72$ and -0.47, $p<0.01$).

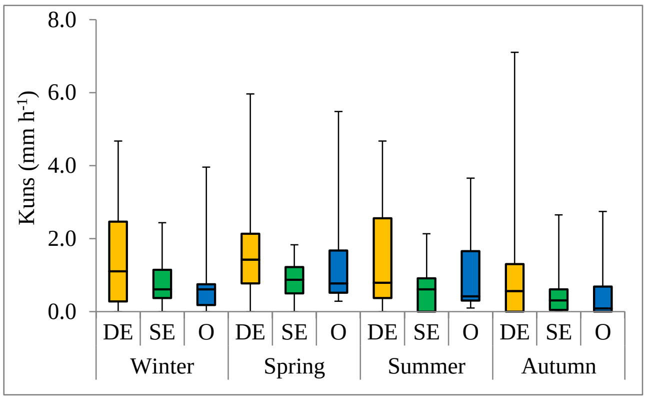


Figure 4.3 – Temporal variation of unsaturated hydraulic conductivity between woodland sites.

4.4.2. Rainfall

Overall, the 2-year period was relatively dry, with rainfall in 2011 and 2012 (607 and 565 mm) being 32 and 36% below the long-term (1941-2000) average of 892 mm. Nevertheless, the study period included three months that were wetter than their long-term averages (1941-2000): November 2011 (163 vs. 111 mm), January 2013 (166 vs. 116 mm) and March 2013 (228 vs. 87 mm). The differences in rainfall patterns between the studied years were also noticeable from the number of rainy days: 91 during the four months of monitoring in 2013 vs. 99 over the 11 months of measurements in 2011. In 2012, there were 157 rainy days, similar to the reference period (128±14 rain days per year) (Figure 4.4).

a)

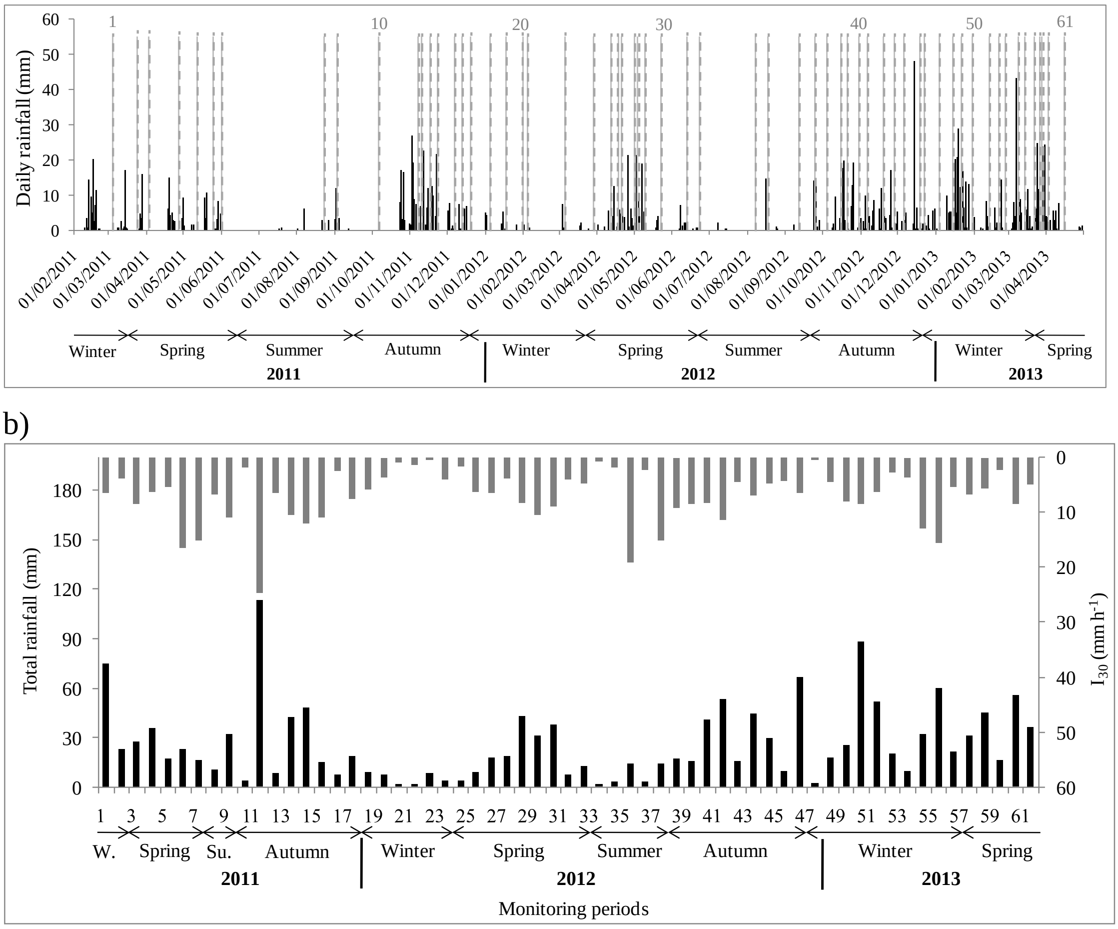


Figure 4.4 - Measurements periods of runoff plots, performed between 9th February 2011 and 14th April 2013: (a) over the time; b) total rainfall amount and average maximum 30-min rainfall intensity (I_{30}).

Seasonal patterns in rainfall were pronounced during the study period and followed the typical Mediterranean intra-annual variation, with distinctively lower rainfall in summer (4% of total rainfall) comparing with the other seasons (autumn: 35%, winter: 32% and spring: 28%) ($p<0.05$). Nevertheless, extremely dry conditions were observed in winter 2011/12 (21st December 2011 – 20th March 2012), pointing out the significant inter-annual variation between this and 2010 (from 9th February to 20th March 2011) and 2012/13 (21st December 2012 – 14th April 2013) winters ($p<0.05$). Spring 2013 (only until 14th April) was also rainiest than spring 2012 (120 mm and 182 mm, $p<0.05$). No inter-annual variability was observed among summers (42 mm vs 35 mm in 2011 and 2012) and autumns seasons (257 mm vs 297 mm in 2011 and 2012) ($p>0.05$).

Over the study period, most of the rainfall intensity was lower than 1 mm h^{-1} (67%), and intensities between 1 and 5 mm day^{-1} characterised 29% of the rainfall days. Values greater than 5 mm day^{-1} did not exceed 4% of the daily rainfall. No significant intra-annual variability was observed in between rainy days, or in maximum 30-min rainfall intensities ($p>0.05$).

The 61 measurement periods differed markedly in total rainfall amount (1.8-113 mm), number of rainfall days (2-12) and maximum 30-min rainfall intensity (I_{30}: 0.6-24.8 mm h^{-1}) (Figure 4.4), but none represented extreme rainfall events, since all beneath 2-years Intensity-Duration-Frequency curves of Coimbra (Brandão et al., 2001). Total rainfall amounts and I_{30}'s were significantly correlated (r =0.66, p<0.01) but there were several instances of minor rainfall amounts due to short-term high-intensity events.

4.4.3. Temporal pattern of hydrological variables

4.4.3.1. Throughfall

Overall throughfall for the period 2nd April 2011 to 5th March 2012 (periods 3-23), when measurements were carried out at all three woodland sites, was higher in dense eucalypt (99% of rainfall) than in sparse eucalypt (85%) and oak stands (67%) (Figure 4.5). For the 2-year period 2nd April 2011 to 14th April 2013 (periods 3-61), however, overall throughfall represented 97% and 72% of rainfall in sparse eucalypt and oak stands respectively. In both periods, no significant difference was identified in percentage throughfall between woodland types (p>0.05). No significant difference in throughfall between the gauges installed in each runoff plot was identified, except in O1 (overall study period average and standard deviation of 21±22 mm) and sparse eucalypt plots (SE1: 23±23 mm, SE2: 27±21 mm and SE3: 23±23 mm) (p<0.05).

Throughfall represented variable fractions of the rainfall over the year, with generally lower values under oak (85±33%) than eucalypt woodland (96±50% and 96±34% in both dense and sparse eucalypt). Nevertheless, there were monitored periods where the throughfall amounted to higher values than the rainfall in all the study sites, particularly in dense eucalypt areas and, for fewer measurements, under oak woodland. Median differences between rainfall and throughfall reached 6-7 mm in dense eucalypt (6.7, 6.0 and 6.8 mm in DE1, DE2 and DE3, respectively), 4-5 mm in sparse eucalypt (4.5, 4.3 and 5.1 mm in SE1, SE2 and SE3, respectively) and 4-6 mm in oak woodland (3.7, 5.6 and 4.1 mm in SE1, SE2 and SE3, respectively). Nevertheless, maximum water retention reached 30-38 mm at the dense eucalypt, 30-40 mm at the sparse eucalypt and 18-20 mm at the oak woodland for the period 11, during autumn (maximum rainfall and I_{30} for the whole study period, Figure 4.3).

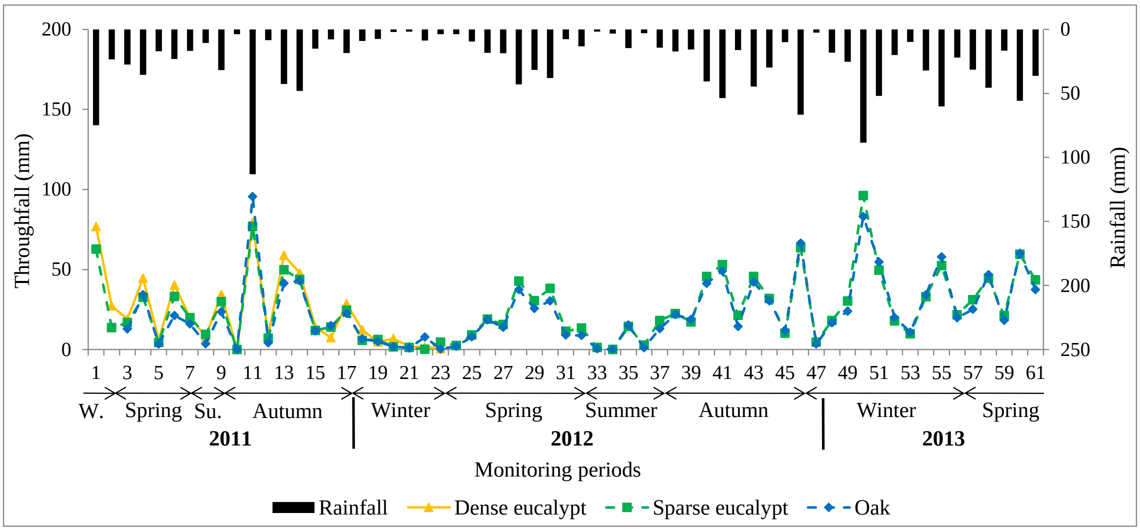


Figure 4.5 - Weighted average rainfall amount and median throughfall per woodland type, for the 61 measurement periods from 9th February 2011 to 14th April 2013. Throughfall results only until 5th March 2012 in dense eucalypt plantation due to collectors' theft.

Throughfall increased significantly with rainfall amount and maximum intensity (r=0.83 and 0.57, respectively; $p<0.01$). Generally throughfall percentages were lower in dry than wet periods, with median values of 90%, 74% and 46% in summer, and 93%, 92% and 86% in winter, for dense eucalypt, sparse eucalypt and oak stands, respectively. However, there was not a significant seasonal pattern of throughfall ($p>0.05$). Despite throughfall increased with rainfall, in smaller storm events the percentage of rainfall intercepted was also greater, particularly during drier periods. No throughfall was measured in any of the plots for rainfalls of 3.3 mm and 3.7 mm measured during summer (periods 10 and 34). However, for a rainfall event of 3.7 mm measured in late winter (period 23), throughfall represented 14% and 7% of the rainfall in dense eucalypt and oak woodland (under sparse eucalypt throughfall was higher than rainfall).

4.4.3.2. Hydrophobicity

In all the soil layers, hydrophobicity was most severe and frequent in the dense eucalypt plantations, intermediate in the sparse eucalypt stand and lowest in the oak woodland ($p<0.05$) (Figure 4.6). In the oak stand, hydrophobicity was absent on most measurement dates (69% at both 0-20 mm and 20-50 mm and 48% at 50-100 mm) and was largely of low or moderate severity when present. Hydrophobicity was mainly transient in nature, being recorded in all the sampling sites only on 14%, 13% and 17% of monitoring occasions, at 0-20 mm, 20-50 mm and 50-100 mm depth respectively. In the sparse eucalypt site, hydrophobicity showed the greatest spatial and temporal variations with hydrophilic conditions dominant on 49%, 34% and 39% of the measurement dates, at 0-20 mm, 20-50 mm and 50-100 mm, respectively, but with moderate to severe classes being more representative when hydrophobicity was recorded. Similar to oak woodland, the sparse eucalypt stand also showed a transient and patchy hydrophobic pattern, with widespread hydrophobic properties recorded in just 26% of the 61 measurement periods at 0-20 mm and 50-100 mm and 24% of occasions at 20-50 mm depth. In contrast, in dense eucalypt plantations, hydrophilic conditions were only observed on 41, 15 and 13% of occasions, at 0-20 mm, 20-50 mm and 50-100 mm depth respectively, with severe to extreme hydrophobic properties being dominant and widespread, forming a continuous surface area in 53, 55 and 70%, respectively, of occasions when hydrophobicity was present.

Hydrophobicity showed the same marked seasonal patterns at all three study sites. It was typically absent during late autumn and winter, and most severe and widespread during summer. After dry periods, hydrophobicity was more resistant to being broken down during rainfall events in eucalypt plantations and disappeared earlier in oak woodland. Also, when drier conditions were restored, hydrophobicity was re-established more quickly under eucalypt than under oak. Thus after the largest rainfalls in autumn 2011 and beginning of winter 2012, hydrophobicity required five months longer to reappear in oak than in the eucalypt stands.

In dense eucalypt stands, hydrophobicity increased in frequency and severity with soil depth (increasing from 44 to 59% of the monitored periods between 0-20 mm and 50-100 mm layers, $p<0.05$). Also, a greater number of rainstorms were required to reduce hydrophobicity levels in deeper soil. Extreme hydrophobicity was recorded on 18, 13 and 30% of occasions, respectively, at 0-20 mm, 20-50 mm and 50-100 mm. A similar pattern with depth occurred in the sparse eucalypt site, despite lower hydrophobicity severity and coverage (extreme hydrophobicity was recorded in 8, 13 and 15% of occasions, at 0-20 mm, 20-50 mm and 50-100 mm depth respectively). In contrast to eucalypt sites, hydrophobicity did not vary statistically with soil depth in oak woodland ($p>0.05$), although it showed a tendency to decrease in severity but increase in temporal frequency with soil depth (Figure 4.6).

Although hydrophobicity severity and spatial frequency varied with antecedent weather at all stands and at all depths, inverse relationships with storm rainfall and throughfall amount, although statistically significant ($p<0.01$), are weak (r never exceeding -0.31) and are not statistically significant in the case of maximum rainfall intensity ($p>0.05$). Particle size and organic matter content were weakly correlated with hydrophobicity. Hydrophobicity slightly increased with increasing sand content ($r=0.25$, 0.28 and 0.34 for increasing soil depths, $p<0.01$) and organic matter content at the subsurface ($r=0.14$, 0.16 and 0.22 for increasing soil depths, $p<0.01$), and was negatively correlated with silt ($r=-0.26$, -0.30 and -0.36 for deeper soil layers, $p<0.01$) and clay ($r=-0.15$, -0.18 and -0.23 for increasing soil depths, $p<0.01$) fractions.

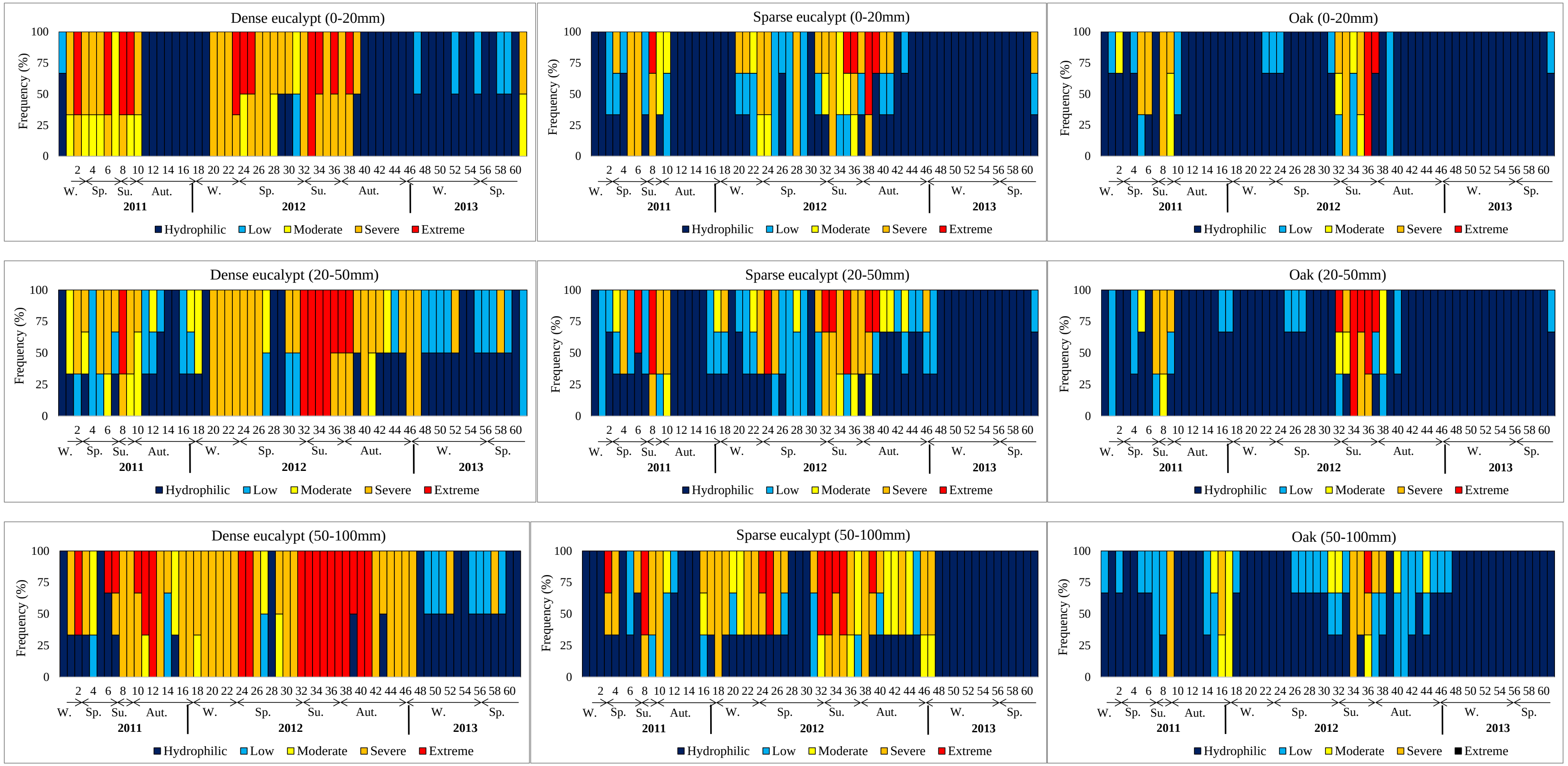


Figure 4.6 - Temporal variability of frequency distribution of hydrophobicity classes per woodland type and soil depth (0-20 mm, 20-50 mm and 50-100 mm) for the 61 measurement periods from 9th February 2011 to 14th April 2013.

4.4.3.3. Soil moisture content

Median surface soil moisture content (0-50 mm), measured under laboratory conditions for samples collected during monitoring periods, was similar between dense (15%) and sparse (18%) eucalypt stands ($p>0.05$), but both were significantly lower than at oak sites (29%) ($p<0.05$) (Figure 4.7).

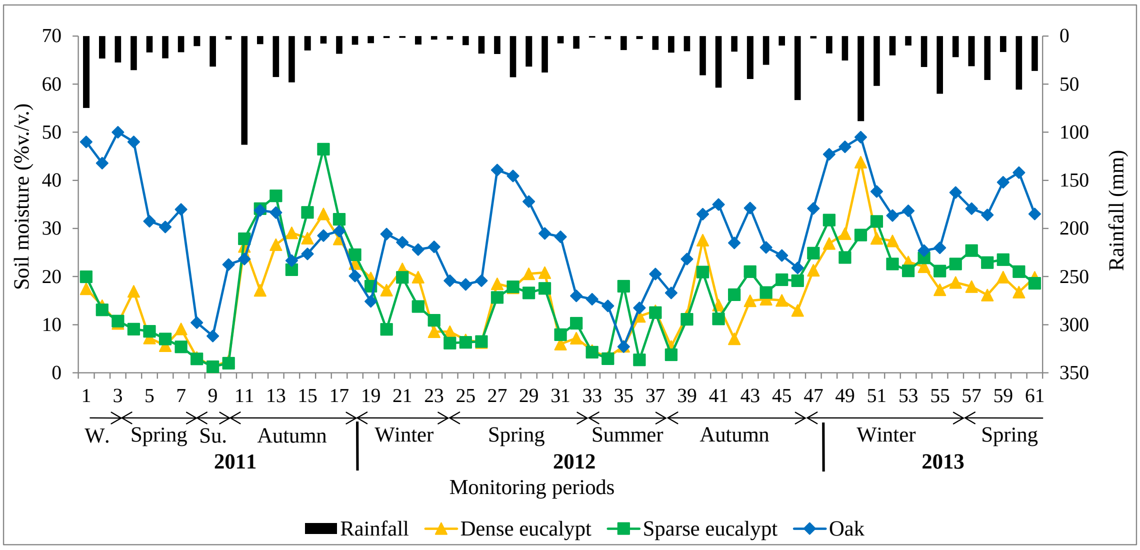


Figure 4.7 - Median surface soil moisture content per woodland type for the 61 measurement periods from 9th February 2011 to 14th April 2013.

During the study period, no significant difference on soil moisture content was found among the three plots at the dense and sparse eucalypt sites ($p>0.05$). However, under oak woodland, plot O2 had significantly higher values than the other two plots (O1: 29%, O2: 35% and O3: 25%) ($p<0.05$). In dense eucalypt stands, DE1 clear-felling in March 2012 (period 22) did not significantly affect soil moisture content, but it seemed to change the spatial patterns. Before logging, higher soil moisture content was measured in ED3, whereas after clear-felling it was observed in DE1, but differences became more alike with eucalypt regeneration in DE1. Despite not clearly noticed, thinning of 20% of O3 canopy cover (period 48) may slightly increase soil moisture content. In fact, soil moisture was generally lowest in plot O3 before thinning, whereas after it was greater than O1, but still lower than O2.

Soil moisture content increased significantly with preceding period rainfall amount and throughfall ($p<0.01$), although the relationships were not very strong (Table 4.2). It was substantially lower in summer than during the other seasons ($p<0.05$), with a similar median value (8%) for all woodland types. Soil moisture increased slightly from spring, to autumn and winter (21, 24 and 25%, respectively), but with variations between the two years. During spring, median soil moisture content was higher in 2013 (22%) than in both 2011 (16%) and 2012 (11%) ($p<0.05$). Through autumn, soil moisture was significantly higher in 2011 than in 2012 (28% vs 17%) ($p<0.05$). Over winter, median soil moisture reached highest values in 2013 (26 % compared with 19% in 2011 and 20% in 2012). Generally, higher soil moisture content was observed during autumn 2011 (median values of 27%, 33% and 27% for DE, SE and O, respectively), winter 2013 (median values of 23%, 24% and 36% for DE, SE and O, respectively) and spring 2013 (median values of 18%, 22% and 36% for DE, SE and O, respectively). Soil moisture content reached highest values of 37%, 32% and 49% in DE, SE and O in winter 2013, but the peak value of 47% in the SE site was attained in autumn 2011.

Overall, considering the results from all plots together, soil moisture content increased significantly with increasing rainfall and throughfall amounts, but the relationship were rather weak ($r=0.25$ and 0.20, respectively, $p<0.01$), even excluding the summers season due to the lowest throughfall percentages associated with driest conditions. Nevertheless, no significant correlation between soil moisture and rainfall was identified in oak woodland. Rainfall intensity was not significantly correlated with soil moisture content ($p>0.05$). Hydrophobicity decreased with soil moisture increase, but correlations were weaker at greater soil depth ($r=-0.51$, -0.52 and -0.42 for depths of 0-20 mm, 20-50 mm and 50-100 mm). Generally, soil moisture differences between runoff plots may be partially explained by topographic characteristics and soil properties, considering their significant influence despite the poor correlations. Soil moisture decreased with increasing slope angle ($r=-0.32$, <0.01) and was affected by particle size distribution, increasing with increasing silt ($r=0.20$, $p<0.01$) and clay ($r=0.09$, $p<0.05$) contents and decreasing with sand content ($r=-0.19$, $p<0.01$), although the weak correlations.

4.4.3.4. Overland flow

Overland flow was generated in most measurement periods (97, 92 and 89% of the occasions for dense eucalypt, sparse eucalypt and oak stands, respectively), although runoff coefficients represented less than 1% over the 2 years (Figure 4.8). Overland flow exceeded 1% of period rainfall on just 8, 4 and 3 occasions out of 61 for dense eucalypt, sparse eucalypt and oak sites respectively, but never exceeded 3%. Overland flow was significantly higher in the dense eucalypt plantation than in the sparse eucalypt and oak stands (overall values of 6.9 mm, 2.6 mm and 2.9 mm, respectively) ($p<0.05$).

Differences in the temporal pattern of overland flow were also observed between woodland stands. Dense eucalypt plantation plots generated greater percentage overland flow (medians of up to 2.2%) in rainstorms occurring in dry settings (late spring, summer and at the beginning of autumn), whereas in wet conditions it was lower than 1.0%. In the sparse eucalypt stand, overland flow varied less over the year, with maximum runoff coefficients of 0.5% and 1.2% in both dry and wet settings (mainly in spring, autumn and winter periods). In the dense eucalypt plantation, the highest percentage overland flow values were recorded in rainfall events that were moderate (4-23 mm and I_{30}= 3-16 mm h^{-1}) and in the sparse eucalypt stand highest percentage overland flow occurred in relatively small rainfall events (4-10 mm and I_{30}=3-6 mm h^{-1}). In contrast to eucalypt sites, overland flow in oak woodland was mainly produced after the wettest antecedent weather and soil moisture conditions, attaining higher values mainly after larger rainfall events (>10 mm), which were mostly experienced in winter and spring 2013, the wettest measurement periods in the 2-year study. Even under the wettest conditions, however, the runoff coefficient only reached 2.2% in the oak stand (but median values of three replicated plots did not exceed 0.6%), whereas following dry weather it did not exceed 0.4%.

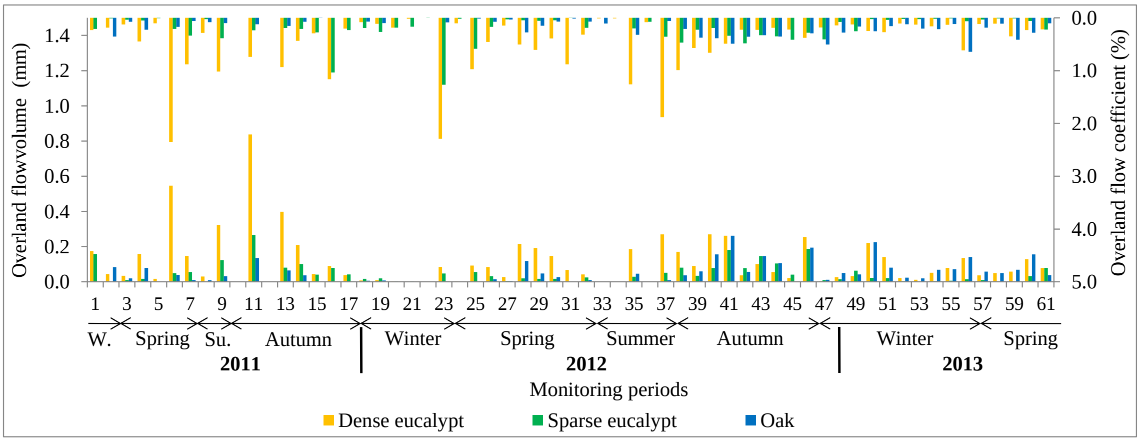


Figure 4.8 - Median overland flow, expressed as amount and percentage rainfall, per woodland type for the 61 measurement periods from 9th February 2011 to 14th April 2013.

Under dense eucalypt plantation, overland flow did not vary much between runoff plots, even after clear-felling ($p>0.05$), except immediately after disturbance. Before tree clear-felling (period 22), DE1 showed slightly higher overland flow amount than the other plots (DE1: 4.0 mm, DE2: 1.9 mm and DE3: 3.3 mm), whereas after that, the difference was more noticeable until period 36 (DE1: 1.3 mm and DE3: 0.9 mm). Immediately after harvesting, the clear-felled plot (DE1) showed the highest overland flow of the study period (2.3%) whereas in DE3 it did not exceed 1.0%. However, with faster vegetation regeneration after September 2012 due to rainfall increase after the dry period, overland flow in the harvested plot DE1 became lower than in the intact DE3 (2.3 mm vs 2.9 mm, respectively).

Contrary to dense eucalypt woodland, plots installed in sparse eucalypt and oak sites showed significant differences ($p<0.05$). In the sparse eucalypt stand, overland flow was higher on SE3, installed on intermediate vegetation density but with a greater number of trees nearby, showed higher overland flow than SE1 and SE2 (total overland flow: 5.9, 1.4 and 2.9 mm, respectively), associated with a higher number of overland flow events (56, 45 and 48, correspondingly, out of 61 events). In the oak site, overland flow was lower on O1 than at the O2 and O3 plots (2-year totals of 1.9 mm, 4.3 mm and 3.2 mm, respectively). The number of overland flow events showed a gradual increase with decreasing vegetation density (54 events in O3, 56 in O2 and 59 in O1, out of 61). The decrease of 20% in canopy cover on plot O3, between periods 48 and 49, however, did not significantly affect overland flow.

Overland flow increased significantly with period rainfall (amount and intensity) and throughfall (Table 4.2), but the strength of the correlations varied with woodland type. Dense eucalypt plantation exhibited stronger correlations between overland flow and rainfall variables than the other woodland types (DE: r=0.61 and 0.62, SE: r=0.44 and 0.34, and O: r=0.53 and 0.27 for rainfall amount and I_{30}, respectively, $p<0.01$). Oak woodland showed stronger correlations than eucalypt plantations between overland flow and throughfall amount (0.48, 0.46 and 0.60 for DE, SE and O stands, respectively, $p<0.01$), as well as rainfall in the previous 30 days (r=0.43 and 0.26 for O and SE, $p<0.01$). No significant correlation was found between overland flow and antecedent rainfall within dense eucalypt site ($p>0.5$).

Generally, overland flow correlated significantly neither with hydrophobicity or soil moisture content within woodland areas ($p>0.05$, Table 4.2). Separating monitoring periods into wettable and hydrophobic conditions at the surface did not produce significant correlations with overland flow volume or coefficient. However, considering individual woodland types, overland flow increased with soil moisture content in the oak and sparse eucalypt plantations, although correlation coefficients were weak (r=0.21 and 0.29, respectively, $p<0.05$).

A synthesis of significant correlations is shown on Table 4.2. A summary of statistical differences between hydrological properties between runoff plots is given on Table 4.3.

Table 4.2 – Spearman rank correlation coefficients between rainfall, throughfall and soil properties (* and ** represent correlations with 0.05 and 0.01 levels of significance; n=511).

	Throughfall	Hydrophobicity 0-20mm	Hydrophobicity 20-50mm	Hydrophobicity 50-100mm	Soil moisture	Overland flow
Rainfall amount	0.83**	-0.31**	-0.29**	-0.30**	0.25**	0.51**
I_{30}	0.57**	-0.13**	-0.10*	-0.09*	-0.01	0.51**
Throughfall	-	-0.20**	-0.22**	-0.16**	0.20**	0.45**
Hydrophobicity						
0-20mm	-0.20**	-	0.68**	0.42**	-0.51**	-0.03
20-50mm	-0.22**	0.68**	-	0.72**	-0.52**	-0.05
50-100mm	-0.16**	0.42**	0.72**	-	-0.42**	0.04
Soil moisture	0.20**	-0.51**	-0.52**	-0.42**	-	-0.01
Soil texture						
Sand	-	0.25**	0.28**	0.28**	-0.19**	0.25**
Silt	-	-0.26**	-0.30**	-0.36**	-0.20**	-0.23**
Clay	-	-0.15**	-0.18**	-0.23**	-0.09*	-0.23**
Organic matter	-	0.14**	0.16**	0.22**	0.04	0.15**
Bulk density	-	-0.06	-0.05	-0.07	-0.21**	-0.12**
Slope	0.09	0.07	0.014**	0.13*	-0.32**	0.02

Table 4.3 – Summary of statistical differences of soil hydrological properties between the three woodland types and between the runoff plots within the same site.

	Woodland type	**Plots within the same woodland type**
Throughfall	$p \geq 0.05$	$p \geq 0.05$
Hydrophobicity	$p<0.05$	ED: $p<0.05$ [0-20 mm ≠ 20-100 mm]
	[ED ≠ EO ≠ O]	EO: $p<0.05$ for EO1 and EO3 [0-20 mm ≠ 20-100 mm] but $p \geq 0.05$ for EO2 O: $p \geq 0.05$
Soil moisture	$p<0.05$ [O > (ED = EO)]	ED: $p \geq 0.05$ EO: $p \geq 0.05$ O: $p<0.05$ [O2 ≠ (O1 = O3)]
Overland flow	$p<0.05$ [ED > (EO = O)]	ED: $p \geq 0.05$ EO: $p<0.05$ [EO3 ≠ (EO1 = EO2)] O: $p<0.05$ [O1 ≠ (O2 = O3)]

4.5. Discussion

4.5.1. Spatio-temporal pattern of hydrological properties and woodland type

4.5.1.1. Throughfall

Despite the reported important role of vegetation structure and architecture in influencing throughfall amount (Návar, 1993; Levia and Herwitz, 2005; Levia et al., 2010; Livesley et al., 2014), no significant differences in throughfall were identified between the different woodland types in *Ribeira dos Covões*. Nevertheless, throughfall slightly increased from dense eucalypt, to oak and sparse eucalypt, following decreasing tree density. According to André et al. (2011) more horizontal branches in oak trees would favour drip development, enhancing throughfall. Differences in tree density and species, as well as dissimilarities in the stage of tree development between individual dense eucalypt plots and between woodland stands (Table 4.1), may explain the throughfall similarities found (Ferreira, 1996; Pypker et al, 2005; Barbier et al., 2009). For instance, the larger differences found within dense eucalypt plots did not show a significant influence on throughfall. Young forest have been reported to provide significantly lower canopy water storage capacity and higher direct throughfall relative to old-growth forest (Pypker et al, 2005). Barbier et al. (2009), measured an increase of 16% of net precipitation from young to adult evergreen forests. Ferreira (1996) reported throughfall decreases in *Eucalypt globulus Labill*. stands from 90 to 86% for trees 5 and 10 years in age. A 5% average increase in throughfall was measured during the dormant phase in the Belgian deciduous forest relative to the growing season (André et al., 2011).

The study performed in *Ribeira dos Covões* did not allow extrapolation of the influence of harvesting at the dense eucalypt site (due to theft) nor thinning in O3 plot. Nevertheless, these management activities are expected to increase throughfall. In southern France, tree thinning carried out to reduce 33% of the stem basal area of an evergreen *Q. ilex* coppice, caused a decrease of 31 to 20% in interception losses (Limousin et al., 2008).

In *Ribeira dos Covões* throughfall percentages were generally higher than those reported in literature dealing with similar woodland stands. In eucalypt plantations in *Ribeira dos Covões*, median throughfall was 98%, whereas Valente et al. (1997) reported 58-92% throughfall under *Eucalyptus globulus Labill*. stands elsewhere in Portugal, whereas a review by Llorens and Domingo (2007) indicated 85-88% under *E. globulus*.

The larger scrub cover in sparse eucalypt stand of *Ribeira dos Covões*, which extended above throughfall gauges, may be the reason for the slightly lower throughfall than that recorded in the dense eucalypt plantation (98 and 87%, respectively), with its limited underbrush cover (Table 4.1). However, since throughfall measurements were made ~30 cm above the soil surface, actual interception by scrub less than 30 cm high would be missed and throughfall would be smaller than the values recorded. Previous studies have, however, also reported interception losses declining under short vegetation compared with trees, due to lower aerodynamic roughness (Robinson et al., 2003). In shrubs and bushes mean relative throughfall of about 49% has been reported (Llorens and Domingo, 2007).

Despite, to the author' knowledge, no throughfall measurements having been previously undertaken in *Q. robur, Q. faginea* or *Q. suber* (the woodland species found in the oak stand within the catchment), the results from *Ribeira dos Covões* (average throughfall of 85%) are higher than those reported for *Q. cerris L*. (85-89%), *Q. pyrenaica*, (83-86%), *Q. coccifera* (55%) and *Q. ilex* (60-78%) (Llorens and Domingo, 2007).

Throughfall was found to be affected by rainfall amount and intensity as reported in previous studies (e.g. Ferreira, 1996; Gash, 1979; Shachnovich et al., 2008; André et al., 2011). No significant seasonal pattern of throughfall was observed over the study period, as reported in previous deciduous trees studies (Cape et al., 1991). However, generally lower throughfall values were measured in drier than wetter periods. For instance, rainfall of a particular amount in summer can be fully intercepted, whereas the same rainfall in winter can generate throughfall (periods 34 and 23). This may be related to antecedent vegetation moisture content and evapotranspiration rate, associated with antecedent weather conditions (rainfall and temperature) (Gash, 1979; Crockford and Richardson, 2000; Limousin et al., 2008). For the smallest rainfall events, throughfall represents water passing between canopy gaps (direct throughfall), since water hitting vegetation is retained, whereas for increasing rainfall volumes, additional indirect throughfall is generated from water dripping onto the ground, as a result of canopy storage capacity exceedance. Increased vegetation interception during drier seasons results from generally lower rainfall, which may be insufficient to saturate the canopy, and higher evaporation (Hewlett, 1969). In addition, during the summer, the interval between rainfall events is generally larger, leading to lower vegetation moisture content. In a north-central Portuguese pine and eucalypt forest, rainfall interception during discontinuous storms was twice as high as during continuous ones, due to evaporation of water retained in the vegetation canopy between rainfall events (Ferreira, 1996).

Throughfall results from *Ribeira dos Covões* must be interpreted as indicative. Throughfall measurements include the influence of trees canopy as well as scrub vegetation in eucalypt and oak woodland, leading to overestimation of water retention by trees when compared with other studies. Furthermore, a larger number of throughfall gauges should be used in order to perform a better assessment, better accounting for the spatial variation. Ziegler et al. (2009) reported that several trees could combine channel stemflow to common drip points on a trunk and large limbs, and, therefore, cause measured throughfall to exceed rainfall. Large spatial variability associated with throughfall has been reported elsewhere, attributed to precipitation patterns and structural characteristics of the trees (Carlyle-Moses et al., 2004; Shachnovich et al., 2008; Rodrigo and Ávila, 2001). Different number of measurements have been used to quantify throughfall, varying between 9 (e.g. Rodrigo and Ávila, 2001), 20 (Shachnovich et al, 2008), 38 (Carlyle-Moses et al., 2004), 94 (Keim et al., 2005) and 180 (Ziegler et al., 2009). Rodrigo and Ávila (2001) declared that the number of collectors should not be <30, in order to obtain a good estimate of throughfall.

4.5.1.2. Hydrophobicity

In *Ribeira dos Covões*, soil hydrophobicity was high and resistant to breakdown under eucalypt stands (particularly in the dense plantation), as widely reported (Doerr et al., 1996; Keizer et al., 2008; Santos et al., 2013). Hydrophobicity is caused by organic compounds, derived from living or decomposing plants or microorganisms, and it is intimately related with vegetation type due to exudate chemistry (e.g. Doerr et al., 2000). Different hydrophobic substances released by vegetation type may explain the greater resistance of hydrophobicity to break-down with rainfall events in eucalypt (greater in dense than open stands) than oak areas. This compounds type would also affect the time needed for new hydrophobic compound input in order to re-establish hydrophobicity after wet periods (e.g. Doerr et al., 2000; Doerr and Thomas, 2000), which increased from oak to open and dense eucalypt sites.

In dense eucalypt stands of *Ribeira dos Covões*, hydrophobicity disappeared after 113 mm (period 11), whereas Ferreira et al. (2000) found hydrophobicity persisted after 200 mm rainfall in schist soils farther north in Portugal. Furthermore, the recorded increase in the extension and severity of hydrophobicity under eucalypt stands with soil depth contrasts with the findings of Santos et al. (2013) in similar plantations in Portugal, though on schist soils. The increase in and persistence of hydrophobicity with soil depth under eucalypt stands can indicate that hydrophobic compounds are primarily released by root activity (Dekker and Ritsema, 1994; Doerr et al., 1998). However, considering the deepness of eucalypt roots, it is more plausible that hydrophobicity at 50-100 mm results from surface leaching compounds during storm events (Doerr et al., 2000). High surface hydrophobicity found at the eucalypt harvest site (ED1) could be due to eucalypt leaves and branches left on the ground, the breakdown of which would have led to hydrophobic compounds (Doerr et al., 2000; Robinson et al., 2003; Zavala et al., 2009). In sparse eucalypt site, hydrophobic conditions under abundant scrub cover, were also reported under similar climatic conditions, 50 km from the study site (Stoof et al., 2011; Walsh et al., 2012).

Under the oak woodland, the observed low severity and persistence of hydrophobicity accord with the findings of Cerdà and Doerr (2005) for *Q. coccifera* in south-eastern Spain. However, the similar hydrophobicity found between soil depths in *Ribeira dos Covões* is in contrast to the progressive decrease described for oakwood soils in northeast Spain (Badía et al., 2013).

The recorded differences in soil hydrophobic properties between woodland types in *Ribeira dos Covões* (dense eucalypt>sparse eucalypt>oak) may in part be linked to vegetation type and density, but could also be linked to soil texture differences. Hydrophobicity is more frequently associated with coarse-textured soils, since coarse particles are more susceptible to develop hydrophobicity due to a smaller surface area per unit volume compared with fine-textured soils (DeBano, 1991; Doerr et al., 2000; Cerdà and Doerr, 2007; Martínez-Zavala and Jordán-López, 2009; González-Peñaloza et al., 2013). This could enhance the hydrophobicity on the sandier eucalypt locations compared with the loamy oak woodland sites. Although not common in clay-rich soils, the type of clay has been reported as important in hydrophobicity formation (DeBano, 2000; Diehl, 2013; McKissock et al., 2002; Zavala et al., 2009).

Reported relationships between hydrophobicity and soil organic matter have been very inconsistent, and some authors suggest that the kinds of organic matter compounds (e.g. aliphatic and amphiphilic hydrocarbons structure, the presence of tannins, phenolic compounds, lipids and the humic/fulvic acids proportion) are more important than the amount (Doerr et al., 2000; Diehl, 2013; de Blas et al., 2010; McKissock et al., 2002; Jordán et al., 2013). According to Zavala et al. (2009), soil and vegetation parameters need to be considered together.

The seasonal hydrophobicity pattern characterized by greater severity and spatial extent in dry periods, as well as lower under wet settings, has been widely reported (Dekker and Ritsema, 1994; DeBano, 2000; Doerr et al., 2000; Santos et al., 2013) and is clearly linked to the antecedent rainfall pattern. The significant negative correlations found between hydrophobicity and antecedent rainfall were also recorded by Buczko et al. (2007), but not by Santos et al. (2013) for other eucalypt sites in Portugal.

4.5.1.3. Soil moisture

The higher soil moisture content recorded under oak than in the two eucalypt stands may be associated with higher water retention by the finer-textured soil overlying limestone bedrock compared with the coarser sandstone soils of the eucalypt areas, causing lower percolation (as unsaturated hydraulic conductivity results showed) and higher soil moisture content. Soil texture has been reported to influence the spatial variability of soil moisture particularly in wet conditions (Baroni et al., 2013). The higher soil moisture content under oak, however, could also be the result of: (1) more effective ponding by underlying bedrock in the shallower soil (<0.4 m on limestone as opposed to >3 m in sandstone), as found elsewhere by Maeda et al. (2006), Hardie et al. (2012) and Yang et al. (2012); (2) the lower slope angles (13-22º as opposed to 16-26º and 26-28º in dense and sparse eucalypt plots), which gives more opportunity for infiltration and therefore increased soil moisture as found elsewhere by Zhu and Lin (2011); (3) the lower position of oak plots on the hillslope (Table 4.1), leading to more effective moisture accumulation and retention than upslope (Kim, 2009; Ridolfi et al., 2003); and (4) the presence of a few relict stone walls in the oak woodland which may have increased water retention, as found elsewhere by Yang et al. (2012).

In addition to differences in soil properties and terrain characteristics, higher soil moisture under oak than eucalypt sites may be linked to factors driven by vegetation, such as transpiration and hydrophobicity (less intense and less frequent in oak woodland soil). Eucalypt trees are usually associated with greatest water demand (Robinson et al., 2003; Yang et al., 2012), leading to lower soil moisture content than oak woodland. Previous reports from Portugal, showed that daily transpiration from a mature *Eucalyptus globulus* Labill. stand varied between 0.5 and 3.6 mm day^{-1} during a spring-summer period (David et al., 1997). In south-eastern Australia, Forrester et al. (2010) reported a transpiration increase of eucalyptus plantations from 0.4 mm day^{-1} at age 2 years to a peak of about 1.6–1.9 mm day^{-1} in stands aged 5–7 years. Lower transpiration was reported in *Quercus ilex* L., in Catalonia, NE Spain, which ranged from 464 mm year^{-1} and 453 mm year^{-1} in valley and ridge-top locations of a forest catchment, respectively (Sala and Tenhunen, 1996).

In *Ribeira dos Covões*, the higher soil moisture content in oak than eucalypt stands, however, does not seem to result from greater water consumption by eucalypt trees, since no significant difference in soil moisture was found between dense and sparse eucalypt stands. Nevertheless, the high evapotranspiration rate of extensive scrub cover can be similar to that of eucalypt trees (Bellot et al., 2004; Hümann et al., 2011; Yang et al., 2012), which could lead to the absence of significant soil moisture differences in distinct eucalypt stands. The high evapotranspiration provided by the scrub cover may also counterbalance the higher soil water retention expected at the sparse than dense eucalypt stands, due to higher silt and clay contents (Table 4.1).

Harvesting (DE1) and thinning (O3) performed in wet periods seemed to enhance soil moisture content, as a result of higher throughfall. Nevertheless, lower soil moisture content would be expected if harvesting was performed in dry weather, because of higher exposure to insolation (Ferreira, 1996; Scherer and Pike, 2003; Vernimmen et al., 2007; Ensenbies et al., 2007). The litter layer also intercepts incoming radiation, reducing soil evaporation and increasing water retention capacity (Ogée and Brunet, 2002; Matthews, 2005; Savva et al., 2013). Greater litter thickness and lower soil bulk density may explain greater soil moisture content at the O2 plot compared with O1 and O3 plots. Differences in the litter layer could have masked the effect of different tree densities in the eucalypt areas.

Surface soil moisture content seemed to be strongly associated with hydrophobicity pattern. Generally, soil moisture was low when hydrophobicity was most severe and high when hydrophobicity was weak or absent. Soil hydrophobicity blocks water infiltration, which is usually restricted to preferential pathways provided by root holes and burrows, channels, cracks and stones (Urbanek and Shakesby, 2009; Wang et al., 2013). Such patchy infiltration leads to a heterogeneous soil moisture distribution (Dekker and Ritsema, 1994; DeBano, 2000; Doerr et al., 2000; Tumer et al., 2005). Stronger persistence of hydrophobicity under dense eucalypt stand could have led to a lower soil moisture content compared with the sparse eucalypt site, as well as lowest values under oak woodland.

In *Ribeira dos Covões*, hydrophobicity was absent above soil moisture contents of 33, 21 and 32% in dense eucalypt, sparse eucalypt and oak woodland, respectively (Figure 4.9). Similarly, extreme hydrophobicity was not recorded for soil moistures above 26, 18 and 21%, respectively, reinforcing the view of the highly resilient nature of hydrophobicity in dense eucalypt plantations. Differences in the critical moisture content for the existence of hydrophobicity between woodland types may be linked to variations in soil texture (Doerr et al., 2000) and soil organic matter (Tumer et al., 2005; Jordán et al., 2013), where the latter may be linked to species of trees and understorey vegetation. Previous studies have reported hydrophobicity for soil moisture contents of up to 22% in sandy loam soils (Doerr and Thomas, 2000), and as high as 38% in clayey soils (Dekker and Ritsema, 1994). Under eucalypt plantations in central Portugal, Santos et al. (2013) reported the dominance of strong and extreme hydrophobicity in schist soils when soil moisture content was below 14%, which is lower than for the *Ribeira dos Covões* findings.

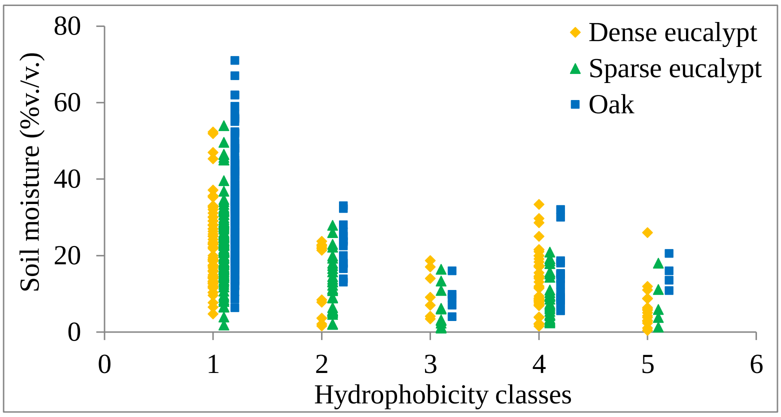


Figure 4.9 - Average soil moisture variability within hydrophobicity classes (1: wettable, 2: low, 3: moderate, 4: severe and 5: extreme hydrophobicity) for different forest types.

Temporal pattern of surface soil moisture was affected by variation in rainfall, as reported in previous studies (Bellot et al., 2004; Yang et al., 2012), as well as throughfall, as observed by Ferreira et al. (2000). However, no correlation between throughfall and soil moisture was identified by Shachnovich et al. (2008).

4.5.1.4. Overland flow

Runoff plots installed in *Ribeira dos Covões* recorded very low overland flow coefficients (<3%) in woodland sites. Generally, vegetation enhances infiltration, particularly in tree stands because of their comparatively deep root systems (Calvo-Cases et al., 2003; Hümann et al., 2011; Komatsu et al., 2011). Nevertheless, the underlying bedrock can have an important effect on slope hydrology, particularly influencing infiltration and overland flow (Hattanji and Onda, 2004; Zhang and Hiscock, 2010). Generally, coarse-textured soils associated with sandstone are usually highly permeable, allowing water to drain freely. High permeability of limestone soils has been also widely reported in areas of Mediterranean climate (e.g. Calvo-Cases et al., 2003; Cerdà, 1997). Although bedrock differences in the study catchment may mask the influence of woodland type, significant overland flow differences were found between dense and sparse eucalypt despite both being on sandstone, and no significant overland flow difference was identified between sparse eucalypt and oak stands, despite the latter overlying limestone. Spatio-temporal variation in overland flow pattern between woodland types is thought instead to be a consequence of hydrophobicity differences, since no significant throughfall difference was found between woodland stands, and soil moisture was higher in oak soils, where overland flow was lower.

In storm events following dry weather, the most likely cause of overland flow seemed to be infiltration-excess caused by hydrophobic soils. Infiltration-excess overland flow under hydrophobic conditions have been widely reported (e.g. DeBano 2000; Doerr et al., 2000; Hümann et al, 2011). Thus the greater severity of hydrophobicity in the dense eucalypt plantation is considered to be the reason for its greater overland flow (Figure 4.10), especially in larger rainstorms. In the sparse eucalypt stand, the moderate or severe and patchier hydrophobicity broke down more easily as a result of rainfall (see section 4.4.3.2), thereby explaining the lower overland flow than in the dense eucalypt plantations. Nevertheless, smaller rainfall events (3.7 mm and 9.5 mm in period 23 and 25) failed to break down soil hydrophobicity in the sparse eucalyptus (Figure 4.6), which may explain the higher percentage overland recorded in those periods (Figure 4.8). In oak woodland, the low or moderate hydrophobicity and its much patchier nature would explain why infiltration-excess overland flow responses were very small even after prolonged dry weather. Differences in the breakdown resistance of hydrophobic properties may be the reason for a stronger correlation between overland flow and rainfall in dense eucalypt plantation than in the other woodland types (see section 4.4.3.4).

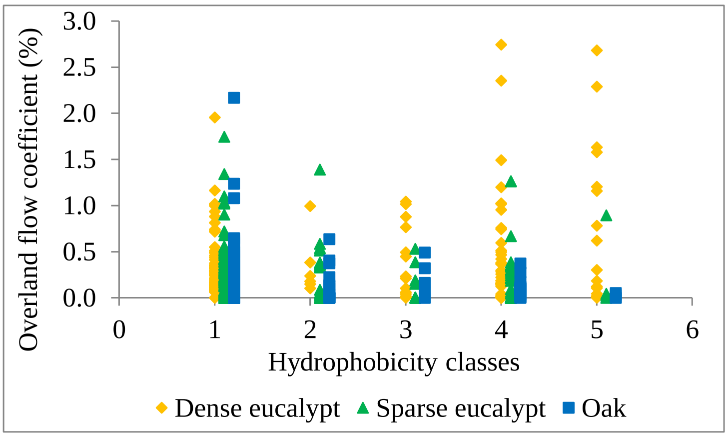


Figure 4.10 - Variation of overland flow coefficient according with surface hydrophobicity (1: wettable, 2: low, 3: moderate, 4: severe and 5: extreme hydrophobicity) for different monitored plots.

Even under extreme hydrophobic conditions, however, overland flow was minor. Thus, the maximum runoff coefficient in dense eucalypt plantations never exceeded 2.2%. This peak runoff is lower than the maximum of 10% measured in similar experimental plots under similar eucalypt stands in north-central Portugal following a long dry season, though for schist soils (Ferreira et al., 2000). The low overland flow under extreme hydrophobicity indicates the role of water sinks within the woodland soils. Given the relatively low soil moisture content in hydrophobic soils, infiltration would seem to occur: (1) in hydrophilic soil patches, linked to a discontinuous hydrophobic layer, particularly under oak and sparse eucalypt stands (Figure 4.6); and (2) via preferential flow routes provided by cracks and root holes, although stones in sufficient quantities may also promote infiltration (Urbanek and Shakesby, 2009). Several authors have reported the relevance of preferential flow patterns for water infiltration in hydrophobic soils (DeBano, 2000; Doerr et al., 2000; Buczo et al., 2006). In hydrophobic sandy and sandy loam soils elsewhere, >80% (Ritsema et al., 1997) and 86-99% (Tsukamoto and Ohta, 1988) of water movement has been attributed to preferential flow.

Limited overland flow under antecedent dry settings may be also associated with surface water retention, favoured by vegetation and litter, as well as micro-topographic concavities on hillslopes. Under these conditions, rainfall may stop before surface depressions had been filled. The longer concentration time required for continuous flow on long hillslopes compared with the duration of the most effective rain showers was stated by Yair and Raz-Yassif (2004) as the cause of the low efficiency of runoff processes on slopes.

In wet conditions, particularly in the dense eucalypt plots, it was unclear whether overland flow was promoted by hydrophobicity-linked infiltration-excess and/or saturation-excess mechanisms. The persistence of subsurface hydrophobicity, in combination with a thin hydrophilic soil layer, may prevent downward water flux through the soil matrix (Doerr et al., 2000). Any infiltrated water would tend to pond above the hydrophobic layer leading to surface soil moisture build-up and possible saturation (Doerr et al., 2000; Calvo-Cases et al., 2003). Under these conditions, ponded water in the surface saturated layer may be diverted laterally as subsurface lateral flow unless encountering a vertical preferential flow path, allowing it to reach soil at greater depth and perhaps enter the underlying rock.

During the wettest conditions, overland flow appears to be generated by saturation-excess in the sparse eucalypt and, particularly, oak woodland types, as the soils were hydrophilic rather than hydrophobic. In the sparse eucalypt stand, generation of saturation-excess overland flow may also have been favoured by greater bulk density and clay content of its soil (Table 4.1), and its steeper slopes (26-28º), as found elsewhere by Neris et al. (2013). Saturation overland flow was greatest in large rainfall events, when water detention by the surface micro-topography is exceeded leading to a greater downhill flux connectivity to develop (Yang et al., 2012). Surface topography may also enhance overland flow connectivity via local rills. Thus it was observed that during this study, a rill developed on plot SE3 creating a preferential surface path for overland flow, which may account for the significantly greater overland flow in that plot compared with in plots SE1 and SE2 (see section 4.4.3.4).

In the oak woodland, generation of saturation overland flow may have been favoured by the loamier and also shallower soil than in the eucalypt plantations (Table 4.1). These will enhanced ponding and lead to subsurface lateral flow, which was observed while digging the holes for the overland flow tanks at the O2 and O3 oak plots. Previous researchers have also remarked on the contribution of lateral subsurface flow in lower hillslope positions in view of the high soil moisture content after rainfall (Gautam et al., 2000; Ridolfi et al., 2003; Güntner and Bronstert, 2004). According to Lorz et al. (2007), subsurface water flow paths prevail where there is a uniform forest cover. The lack of water ponding where the pit for the collecting tank for plot O1 was excavated, may indicate deeper subsurface lateral flow associated with locally deeper soil, since this plot was installed a few metres downslope and at some lateral distance from the other plots. The impact of spatially heterogeneous distributions of soil thickness on rainfall–runoff processes was also reported elsewhere (e.g. Maeda et al., 2006).

Nevertheless, based on minor overland flow events during the study, the dominance of infiltration and/or subsurface lateral flow is evident. Even with high soil moisture content, plots showed an elevated permeability on limestone soil. Owing to high soil permeability, no seasonal variation was identified in overland flow measured on plot O1. However, since overland flow generated on plots O2 and O3 was affected by subsurface soil saturation and lateral flow, temporal differences were identified. The oak woodland results accord with the high infiltration capacities of limestone soils under Mediterranean climate reported in previous studies (Cerdà, 1997; Calvo-Cases et al., 2003).

Lower overland flow in oak compared with eucalypt sites could be also favoured by lower slope gradients (Table 4.1), despite no significant correlation being observed. A lower slope angle on plot O1 may have led to minor overland flow than the other runoff plots installed under oak stand (cumulative overland flow over the study period was 1.9 mm, 4.3 mm and 3.2 mm for plots O1, O2 and O3, respectivelly). On steep slopes, overland flow tend to increase due to the shorter residence time for water on the soil and reduced effectiveness of surface roughness in retaining water (Ferreira et al., 2012; Neris et al., 2013). This can be particularly important throughout, or immediately after, large rainfall events, when surface microtopography exceeds water retention capacity, leading to increase downhill flux connectivity (e.g. Yang et al., 2012). Topography has been considered the controlling factor on lateral flow only in wet conditions (Lv et al., 2013; Ridolfi et al., 2003).

Forest management activities can also affect overland flow generation. Under dense eucalypt plantation, plot DE1 had its highest runoff coefficient immediately after clear-felling. Such increases in overland flow and stream peakflows after logging have been widely reported elsewhere, where they have been linked to reduced infiltration capacities due to ground disturbance and soil compaction (Ferreira et al., 2000; Eisenbies et al., 2007; Robinson et al., 2003). In south-central Japan, partial plot thinning (43%) of a Japanese cypress forest led to an increase in runoff coefficient from 33 to 56% (Dung et al., 2012). At the catchment scale, Calder (1993) calculated a runoff increase of 3.3 mm for each percent of an area deforested, based on a world-wide database of hydrologic studies. Based on 94 experimental catchments throughout the world, Bosh and Hewlett (1982) estimated that partial tree thinning (by 20%) led to changes in annual streamflow increase lower than 10% in hardwoods and than 20% in scrub areas. Nonetheless, some studies have pointed out that such changes in catchment discharge are unlikely to be detected if the area affected constitutes less than 20-30% of the total forest cover (Scherer and Pike, 2003; Bathurst et al., 2011).

In *Ribeira dos Covões*, the fact that overland flow after clear-felling was not higher than 2.3% may be due to the thick ground cover of leaves, bark and small branches left in the harvested plot DE1, which would have enhanced water retention capacity and minimized any reduction in infiltration capacity due to splash effects. The enhancement of overland flow in DE1 was quickly reduced, first because of low rainfall in spring and summer and secondly with rapid regeneration of vegetation after September 2012, in response to the onset of the rainy late autumn-winter season. The timing of clear-felling may be a determining factor in overland flow impact, since felling performed during spring allows vegetation to regenerate before autumn rains, minimizing overland flow impacts, compared with late summer or autumn felling.

In oak woodland, canopy cover reduction in plot O3 (between periods 48 and 49) did not affect overland flow generation, which indicates the minor influence of vegetation on overland flow under wet conditions. Nevertheless, the removal of much of the canopy near the upper plot boundary, although not leading to increased overland flow, resulted in much water being retained in surface depressions and not reaching the plot outlet.

4.5.2. Potential implications for catchment streamflow

The low overland flow recorded in *Ribeira dos Covões* over 2-year period supports the widespread notion of high soil permeability associated with forest vegetation. Nevertheless, different woodland types have distinct effects on overland flow amount and on its temporal pattern. Dense eucalypt plantations are less suitable as a tree cover to encourage infiltration than sparse eucalypt and oak stands, as a result of great severity and resistance of soil hydrophobicity. However, the minor overland flow generated even under extreme soil hydrophobicity highlights the dominance of vertical water fluxes, favoured by preferential flow pathways. In oak woodland, and to a lesser extent in the sparse eucalypt stand, overland flow is mostly produced in prolonged rainfall events during wet weather conditions.

Based on *Ribeira dos Covões* results, it is arguable that dense eucalypt plantations would be most likely to contribute to flash floods during extreme storms that occur immediately after the summer, due to infiltration-excess overland flow favoured by greater severity and spatial cover of hydrophobicity. On the other hand, sparse eucalypt stands and particularly oak woodland, would contribute to large-scale floods mostly in wettest conditions, since overland flow in those forest types is typically produced by saturation-excess mechanisms. Nevertheless, even under saturated conditions, water interaction with the canopies, litter layers and enhanced surface roughness of woodland and forest areas may delay overland flow, slowing its transport down a hillslope thus lengthening the lag time and reducing the peak discharge in the stream network (Eisenbies et al., 2007; Hewlett, 1982).

On 25th October 2006, a rainfall event at Coimbra-Bencanta of 102 mm after a long dry summer, led to a flash flood in *Ribeira dos Covões* catchment. According to Brandão et al. (2001), rainfall events of 94 mm day^{-1} and 112 mm day^{-1} at Coimbra have return periods of 10- and 50-years, respectively. Although the contribution from woodland areas to this flood is unknown, based on overland flow measurements performed under local woodland, dense eucalypt plantations could have some contribution to this flood, whereas sparse eucalypt and oak sites could provide upstream overland flow sinks.

Nevertheless, the overland flow measurements undertaken in this study were conducted at a plot scale. It is known, however, that overland flow responses tend to diminish with increasing contributing area (van de Giesen et al., 2000; van de Giesen et al., 2005; Ferreira et al., 2011; Chamizo et al., 2012). For example, van de Giesen et al. (2005) recorded a decrease of 40–75% in overland flow from short (1.25 m) to long plots (12 m). On the other hand, Mounirou et al. (2012) reported similar runoff amounts from 50 and 150 m^2 plots, though both were significantly lower than the smallest plot (1 m^2) used. Cerdan et al. (2004), in turn, observed a strong decrease in mean runoff coefficients with increasing area in studies performed at larger scales: three times lower for 90 ha than 450 m^2, and ten times for 1100 ha than 90 ha. In an experimental study, Chamizo et al. (2012) found an optimal plot length of 20 m to determine runoff representative of a catchment.

Decreasing overland flow with increasing slope length is usually explained with greater opportunity for water infiltration on long than on short slopes (van de Giesen et al., 2005). It has also been attributed to increased soil heterogeneity within larger area, in terms of greater spatial variability in soil infiltration capacity (Cerdan et al., 2004; Mounirou et al., 2012), wettable patches and macropores, which can act as sinks for water (Calvo-Cases et al., 2003; Güntner and Bronstert, 2004; Nasta et al., 2009), as well as the temporal dynamics of the rainfall–runoff events (van de Giesen et al., 2005). These spots with enhancing infiltration capacity can provide important overland flow sinks, breaking flow connectivity (Calvo-Cases et al., 2003; Güntner and Bronstert, 2004; Nasta et al., 2009). In addition, the relatively little overland flow tends to be trapped by vegetation and litter and retained in microtopographic concavities on the hillslope. However, flow connectivity may be enhanced by rill development, as observed in plot SE2.

Nevertheless, some authors have argued that spatial variability only has a scale-related effect on total runoff during relatively short rainfall events (van de Giesen et al., 2005; Mounirou et al., 2012). In *Ribeira dos Covões*, considering the discontinuous pattern of the rainfall and the small amounts of overland flow generated under woodland land-use, the generation of sufficiently continuous overland flow able to reach valley floors and channels would be rare, particularly under dry conditions. This was particularly obvious at the sparse eucalypt site, where overland flow under dry conditions was mostly generated by lower rainfall events. Under these conditions, rainfall stopped before surface depressions had been filled. Thus, much overland flow generated on upper slopes is retained and/or infiltrated somewhere downslope, thus never reaches the channel. The longer concentration time required for continuous flow on long hillslopes compared with the duration of most effective rain showers was also stated by Yair and Raz-Yassif (2004) as the cause for the low efficiency of runoff processes on slopes. Nevertheless, with continuous rainfall, surface depressions may eventually reach saturation, leading to a continuous flow transferred downslope. Under these conditions, field measurements showed larger overland flow amounts (particularly in late winter and spring seasons of 2013). However, stone walls, even when small as in this study, present barriers to overland flow delivery, limiting significantly the amount of overland flow reaching the valley floor.

Previous studies also have been reporting that slopes behave as a mosaic of runoff generation and run-on patches, whose size depends on slope morphometric characteristics, lithology, differences in soil thicknesses and climate (Calvo-Cases et al., 2003; Ridolfi et al., 2003; Güntner and Bronstert, 2004; Komatsu et al., 2011; Lorz et al., 2007). These variables control the hydrological discontinuity between different parts of the same slope and between slopes, channel network and catchment outlet. The scale effect is of the utmost importance in this process due to the size of the contributing area and the number of opportunities for water infiltration and retention (Merz and Bárdossy, 1998; Güntner and Bronstert, 2004).

Vegetation intercepts and detains water within the canopy delaying or preventing some of it from reaching the ground. Vegetation, and particularly trees, can mitigate peak flow by maintaining soil moisture deficit through evapotranspiration over days or weeks, thereby resulting in increased potential for soil storage and infiltration capacity during frequent, relatively low intensity storms (Eisenbies et al., 2007). Although the minor overland flow measured in the woodland areas of *Ribeira dos Covões* catchment supports the protective role of forest land-use during storm events, the highest daily rainfall in the monitoring period was only 48 mm, which does not exceed a 2-year return period (Brandão et al., 2001). Overland flow responses in more extreme events can only be surmised. It is clearly possible that in such extreme events overland flow from woodland areas will be much greater and will also more readily be transferred to downslope areas, since interception by vegetation and surface water retention capacities provided by litter and micro-topographic concavities will be exceeded. Thus, some studies have emphasized the limited storage capacity of forested terrain during larger storms and its minor role in flood protection (Bathurst et al., 2011; Eisenbies et al., 2007). Nevertheless, even under saturated conditions, forest floor roughness represents a barrier for overland flow passage.

The role of woodland type on flood events, however, clearly needs further investigation. Additional monitoring in *Ribeira dos Covões* would need to be carried out in order to monitor larger storm events and improve understanding of the role of woodland on overland flow under these conditions. Furthermore, the impact of woodland types on overland flow should also be performed at a larger scale, in order to understand its influence on catchment scale. In *Ribeira dos Covões*, streamflow measurements have been carried to assess the role of woodland areas at the sub-catchment scale. This information would be particularly important for mixed land-use catchments.

Woodland is the dominant land-use in *Ribeira dos Covões* catchment, followed by urban surfaces, which in some places interrupts woodland patches. Urbanization in recent years seems to have promoted increased catchment discharge, which is expected to continue in view of the character of future urban development already approved (Ferreira et al., 2013). Considering the small amount of overland flow generated in local woodland, this land-use can provide potential overland flow sinks for such flow emanating from upslope impermeable urban areas. A discontinuous pattern of urban and woodland land-uses can interrupt flow connectivity over the landscape and minimize the detrimental hydrological impacts of urbanization (Ferreira et al., 2015). Nevertheless, the infiltration of urban surface runoff through preferential flow routes, particularly under woodland areas, especially under dry settings when soil hydrophobicity is widespread, may represent a problem for groundwater contamination (Selker et al., 1996; Pitt et al., 1999).

Furthermore, forestry management activities can also play an important role on overland flow and influence the role of woodland areas on flood protection. Timber harvesting may enhance overland flow due to the higher throughfall, decreased evapotranspiration and lower resistance to water run-on promoted by vegetation removal, and soil compaction caused by heavy machinery (Scherer and Pike, 2003). Nevertheless, results from *Ribeira dos Covões* showed no significant change in overland flow with total or partial plot harvesting (ED1 and O3), but increased overland flow coefficients were attained immediately after harvesting. This was attributed to the retention of logging slash on the soil, which can enhance surface detention. The importance of logging slash in harvested areas for interception has also been noted by other researchers (e.g. Shakesby et al., 2013; Robinson et al., 2003; Prats, 2013). Small areas covered would generate little overland flow, particularly if harvesting is carried out on upper hillslopes. On the other hand, large clear-felled areas would provide high quantities of overland flow that might reach the channel. Chang (2003) reported that small canopy openings on upper slopes can cause a smaller impact on water yield than when they occur on lower slopes. Some studies, however, have pointed out that changes in catchment discharge are unlikely to be detected if the area affected is <20-30% of the total forest cover (Scherer and Pike, 2003: Bathurst et al., 2011). In a review by Eisenbies et al. (2007), studies are cited where a harvesting impact on stormflow was only significant at relatively low volumes (0.1-1 mm) and others where no differences were observed for stormflows >10 mm. Calder et al. (1992) calculated a runoff increase of 3.3 mm for each percent of area deforested, based on a world-wide database of hydrologic studies.

Despite the impact of harvesting on overland flow was not an original objective of this study, the results from plots DE1 and O3 suggest that the impact of clear-felling on overland flow depends on its timing. Harvesting performed during spring and summer allows vegetation to regenerate before autumn rains, minimizing overland flow impacts, compared with autumn harvesting, given the size and frequency of rainfall events.

In *Ribeira dos Covões*, woodland is the most dominant land-use, followed by urban areas, some of them located upslope. Urbanization in recent years seems to have promoted increased catchment discharge, and this is expected to continue in future taking into account the character of urban development already approved (Ferreira et al., 2013). Considering the greater overland flow generated in urban areas (e.g. Mulliss et al., 1996; Konrad and Booth, 2002; Huang et al., 2008) and the high infiltration capacities of woodland, this land-use may provide sinks for overland flow generated in comparatively impermeable urban areas. The flow disconnectivity provided by a mosaic of different land-uses may minimize the detrimental hydrological impacts of urbanization (Ferreira et al., 2012d) and enhance the safety of the resident population downslope of woodland areas, at least during small and average storm events.

Despite woodland capacity to generate limited overland flow and to provide potential overland flow sinks from upslope land-uses, it is also prone to contribute into catchment streamflow. Through dry settings, widespread hydrophobicity, particularly dense eucalypt areas due to great severity and resistance of switching to hydrophilic properties, has led to increased overland flow and could contribute to flash floods. In wet weather conditions, long-lasting rainfall events during saturated soil conditions, particularly in oak woodland areas, enhance overland flow and can contribute to large-scale floods. Anyway, woodland areas may slow down overland flow due to great surface roughness and thus lengthen the lag time and reduce peak discharge in stream network. Usually woodland and forest streams have a delayed response time because of water interactions with the canopy, litter layer and increased surface roughness, in addition to any influence of soils and topography (Hewlett, 1982; Eisenbies et al., 2007).

The importance of sustainable management of forest areas in retaining and reducing overland flow may be important to protect downslope urban areas. The understanding of seasonal variability of overland flow and its spatial distribution as a result of soil properties, topographic position and geographic location in catchment, in particular within wooded areas, is of the utmost importance to identify landscape sinks and sources. This information is crucial for integrated planning and management of catchments undergoing urban development, to minimize hydrologic impacts. Further investigation should be carried out in order to improve understanding of the appropriate sizes and locations of woodland areas within peri-urban catchments, in order to minimize the hydrologic impacts of urbanization and protect downslope urban cores from flood hazard.

4.6. Conclusions

In the urbanizing catchment of *Ribeira dos Covões* in central Portugal, permeable woodland soils on sandstone and limestone produced overland flow representing less than 3% of the incident rainfall, based on measurements performed on small (16 m^2) plots over 2 years of monitoring. A dense eucalypt stand generated significantly higher overland flow than either sparse eucalypt or oak woodlands, which differed only slightly. Although the underlying bedrock can also influence hydrological processes, woodland type appears to be far more important, given the differences in soil hydrological properties and overland flow generation recorded on dense and sparse eucalypt stands, as they are both located on sandstone.

In dry conditions, hydrophobicity-linked infiltration-excess overland flow was the dominant means of downslope water movement. This process was particularly important in dense eucalypt plantations, where hydrophobicity was more extreme, spatially contiguous and resistant to breakdown with rainfall than was the case in the other two woodland types. Under hydrophobic conditions, overland flow strongly increased with rainfall amount and intensity, but overland flow coefficient did not exceed 2.2%. In contrast, in the sparse eucalypt plots, moderate hydrophobicity was easily broken down, and percentage overland flow was greatest in smaller rainfall events (overland flow coefficient <0.5%), when the soil was not rendered wettable. The weak hydrophobic properties observed in oak woodland plots led to a maximum overland flow coefficient of 0.4% in storms following dry antecedent weather.

In periods of wet weather, saturation overland flow occurred most readily in oak woodland followed by sparse eucalypt stands. Relatively high soil moisture contents maintained throughout wet periods enhanced overland flow by saturation, so that runoff coefficients reached 1.2% and 2.2% on the sparse eucalypt and oak woodland plots, respectively. On the latter, saturation was favoured by the shallow soil overlying limestone, its loamy texture and subsurface lateral flow, whereas in sparse eucalypt stand, saturation was favoured by the high bulk density and clayey nature of the soil. In both woodland types, overland flow strongly increased with rainfall amount and soil moisture. In the dense eucalypt plantation, overland flow did not exceed 1.0% of the rainfall in wet weather.

Interception by the different tree canopies was not significantly different. It is thought to have been important in reducing overland flow responses only during small rainfall events following antecedent dry weather, as interception was low in percentage terms during large events and wet periods due to canopy saturation. In addition, surface roughness, associated with the litter layer promoted water retention and decreased lateral flow connectivity.

Important implications of this study for managing peri-urban catchments are that patches of semi-natural and managed woodland are critical in order to retain rainfall, promote infiltration and act as sinks for overland flow from upslope. In urbanized catchments, the lack of rainfall interception and the size, and often contiguity, of areas covered by impermeable surfaces tend to promote rapid overland flow and the possibility of flooding. Authorities concerned with catchment management and urban planning, therefore, should try to incorporate such patches in any development proposal in order to reduce the total runoff-generating area and provide sinks for runoff generated on impermeable urban surfaces upslope. Thus, the most satisfactory compromise is likely to be a mosaic of diverse land-uses designed to disrupt overland flow connectivity. Identifying the best arrangement of such patches while maximizing the use of land for urban development should now be a research priority. A second research need is for field data on overland flow responses within this mosaic in more extreme, potentially flood-producing rainstorms than occurred within the 2-year monitoring period of this study.

CHAPTER 5

INFLUENCE OF THE URBANIZATION PATTERN ON STREAMFLOW OF A PERI-URBAN CATCHMENT UNDER MEDITERRANEAN CLIMATE

ABSTRACT

Population growth and improved living standards are leading to patchy urban sprawl and land-use change in peri-urban catchments. In order to understand better the impacts on peak flows and in the response and recession times of the storm hydrograph, a monitoring network was installed in a small peri-urban catchment (620 ha) located in Coimbra, central Portugal. The network comprised five rainfall gauges and eight water level recorders, in order to provide information on the hydrological response to rainstorms of catchments and sub-catchments of different size and urban patterns (extension, impervious surface cover, distance to the stream network and water management strategies), overlying either sandstone or limestone areas. The results showed both the importance of weather, season and lithology on catchment hydrological response and the increase of runoff coefficients with percentage urban area. However, urban areas located closer to the stream network showed higher contributions to the streamflow due to lower water infiltration opportunities. This included greater peak flows and lower response times, especially where the storm drainage system diverts the overland flow from impervious areas directly to the stream or nearby soils. However, some urban features (e.g. houses and walls constructed in valley bottoms) may provide surface water retention, breaking the connectivity between hillslope urban surfaces and the stream network. In contrast, continuous urbanization enhances overland flow and streamflow peaks, though may be reduced through adopting particular land-use pattern and urbanization style, in order to enhance water infiltration opportunities. Hydrological monitoring of peri-urban areas can provide crucial information to develop planning strategies that improve the hydrological sustainability of urban areas and minimize the flood hazard.

Keywords: urban areas, runoff, peak flow, flow connectivity, storm drainage system

5.1. Introduction

The proportion of urban residents across the globe increased from 29% to 47% between 1950 and 2000, and are forecasted to reach 56% by 2020 (UNESCO, 2006) and 70% by 2050 (UNPD, 2008). In Europe, urban population attained 75% in 2006, and is expected to increase to 80% by 2020 (EEA, 2006). Nevertheless, the lower living costs, easy mobility/transport and the demand for improved quality of life, have been leading people to move outside the city to peri-urban areas (Ravetz et al., 2013). It has been been argued that peri-urban areas, comprising a mixture of natural forest or agricultural lands and urbanized areas, usually with less than 20000 inhabitants, with an average density of at least 40 persons per km^2, may become the dominant urban form of the twenty-first century (Braud et al., 2013; Ravetz et al., 2013).

Urbanization involves radical changes to the environment, including hydrological processes. These impacts have been studied through statistical analysis of long data records, monitoring of paired catchments (similar catchments with different land-uses) and by predicting changes through modelling. Results report decreased evapotranspiration and infiltration, as well as increased runoff (e.g. Kundzewicz, 2008; Ying et al., 2009; Kalantari et al., 2014). These lead to hydrograph shape changes, linked to greater peak discharge (e.g. Semadeni-Davies et al., 2008), reduced time of concentration and recession period (Graf, 1977; Baker et al., 2004; Huang et al., 2008) and lower baseflow (e.g. Simmons and Reynolds, 1982; Konrad and Booth, 2005; Wheater and Evans, 2009). These lead to increased magnitude and frequency of floods (Moscrip and Montgomery, 1997; Burns et al. 2005; Haase, 2009) and shorten recurrence intervals on urban streamflow (e.g. Hollis, 1975; Chen et al., 2009). However, the size of hydrological impacts is not clearly related to the percentage impervious surface. The existence of a threshold level of urbanization above which hydrological changes are noticed is not consensual. Some studies have been reporting urbanization influences on streamflow regime above 3-5% impervious surface (Yang et al., 2011), while others identified a minimum of 20% (Brun and Band, 2000).

The nature of hydrological changes varies greatly with the biophysical characteristics of the catchment, such as geology, lithology, climate and soil properties, as well as anthropogenic activities, which affect land-use change history and the percentage and distribution of impervious area (e.g. Boyd et al., 2003; Konrad and Booth, 2005; WMO/GWP, 2008). Each landscape contains different combinations and arrangements (distribution and size) of pervious and impervious surfaces (buildings, roads and other paved areas), which affect the amount of runoff produced and the speed at which it is delivered to other parts of the catchment (Parikh et al., 2005; Jacobson, 2011).

Since 1960, many studies have focussed on urban hydrology, but few have studied peri-urban areas, particularly under Mediterranean climate. Although studies performed on peri-urban areas confirm many of the accepted theories regarding to urbanization impact on hydrological regime, they highlight the complexity involved in isolating land-use change impacts in a real catchment with diverse land-uses and hydrological pathways (Perrin et al., 2001; Braud et al., 2013). The complexity of spatial pattern within peri-urban areas, the irregular rainfall regime of Mediterranean climate and the combination of artificial and natural flow pathways represent additional challenges to urban hydrology (Miller et al., 2014). Thus, it is important to understand the impact of different urbanization patterns on runoff and flow connectivity.

This chapter aims to assess the impact of a Portuguese peri-urban area on catchment hydrology. The specific objectives are to: 1) assess the streamflow response of a catchment undergoing urbanization process; 2) investigate the seasonal influence of the Mediterranean climate on catchment discharge; 3) quantify the streamflow delivery from different contributing areas, characterized by different land-use arrangements and their contribution to catchment hydrology; 4) explore the role of different urbanization styles on flow connectivity and stream discharge. Knowledge of the influence of different urban mosaics on peri-urban catchment hydrology is important to landscape managers and should guide urban planning in order to restrict flow connectivity and reduce flood hazard.

5.2. Study Area

The study focuses on *Ribeira dos Covões*, a small catchment (6 km^2) located nearly 2 km away from the *Coimbra* city centre, one of the main cities in central Portugal (Figure 5.1). The catchment is somewhat elongated in shape, draining S-N into the large floodplain of the *Mondego* river.

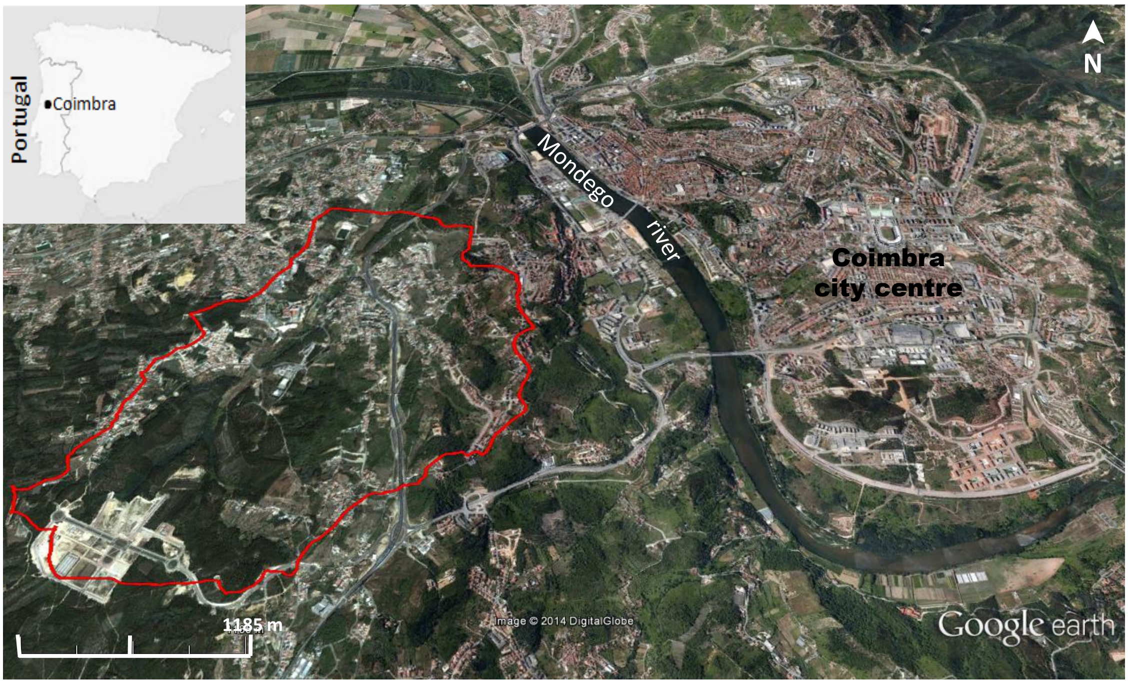


Figure 5.1 - Location of *Ribeira dos Covões* catchment in Portugal and in relation to *Coimbra* city centre (adapted from Google Earth, 2013).

The area has a Mediterranean sub-humid climate, with an annual average temperature of 15°C, an average annual rainfall of 892 mm of rainfall and a strong contrast between dry summer and winter conditions. The catchment experiences a progressive wet-up period from about October to December and thereafter maintains very moist conditions until late spring. It is a well-drained catchment (drainage density of 3.1 km km^{-2}), supplied by a dendritic pattern with a perennial 3rd order stream (Strahler, 1957) and ephemeral tributaries (Figure 5.2a).

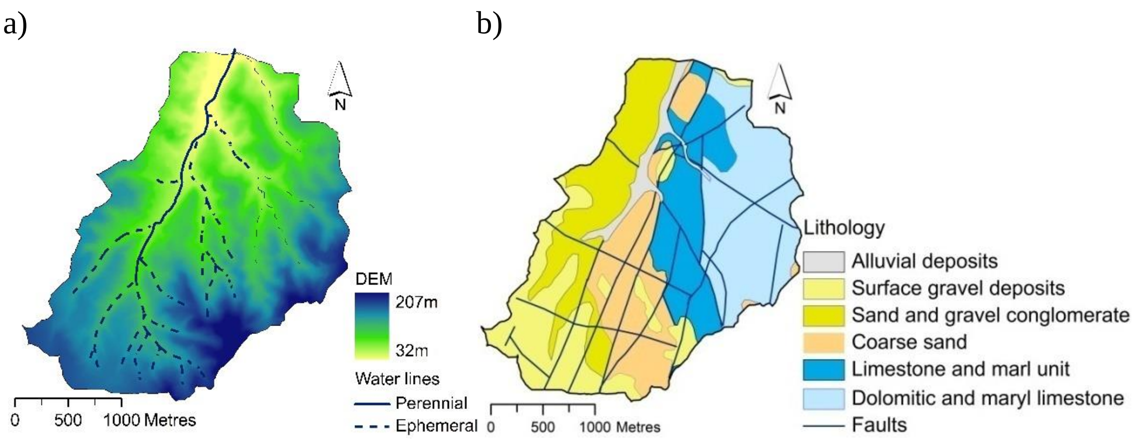


Figure 5.2 - Catchment physical characteristics: a) digital elevation model and stream network, b) lithological units and faults.

From the geological point of view, the study site is located in the *Orla Meso-Cenozóica Ocidental*, characterized by sandstone and limestone hills and broad shallow valleys with abundant alluvium. *Orla* is characterized by important aquifer systems, related to the detrital and carbonate formations. The sequential organization of sedimentary rock loads to multi-layer aquifer systems, usually of karstic and porous nature. Generally, karstic aquifers have limited auto-regulation capacity, evidenced by large variations in flow rate of the important springs between the rainy and dry seasons (Almeida et al., 1999). The *Ribeira dos Covões* catchment is characterized by contrasting geology, marked by areas of 1) sandstone, mostly represented by sand and gravel conglomerate and deposits from Paleogene/Neogene, with variable depth but not exceeding 25 m; 2) limestone formations on the east side, represented by limestone and marl units from Cretaceous, with mean soil depth of 7-8 m, and dolomitic and marl limestone of the Jurassic, which soil depth mostly ranges between 0.1 m and 0.4 m; and 3) alluvial deposits of the Quaternary age, whose depth may reach 5 m (Pato, 2007). The lithological units are interrupted by some geological faults (Figure 4.2b). Soils are mainly represented by Cambisols (medium and fine-textured materials) and Podzols (derived from sandstone rock).

Topography of *Ribeira dos Covões* catchment ranges from 30 m to 205 m (Figure 5.2a). Slopes average is 11º, but steep slopes (from 17-31º) represent 10% of the area, and hillslope gradient reaches 36º in few locations.

The catchment went through major land-use changes and an increasing urbanization process for the last half century as a result of the proximity to Coimbra city center. People living in Coimbra municipality increased 150%, from 98027 in 1950 to 143396 in 2011, while in Antanhol, São Martinho and Santa Clara parishes, where *Ribeira dos Covões* is located, population doubled, from 14315 to 26632 inhabitants (INE, 1950; INE, 2011). The study catchment covers 16% of the mentioned parishes area, but based on aerial photographs and urban cores location, it is estimated that people in the study site increased from 2500 to 7200 inhabitants. This led to the conversion of a rural area with few dispersed urban cores (before 1958) to a discontinuous urban fabric. In 1993, a new Master Plan considered the study catchment as part of the Coimbra urban area, encouraged continuous urbanization and triggered a new urban consolidation phase (Tavares et al., 2012).

Between 1958 and 2007, land-use changes in *Ribeira dos Covões* involved the conversion of agricultural fields (from 48% to 4%) to urban (from 8% to 32%) and forest areas (from 44 to 64%) (Figure 5.3). After 2007, some deforestation occurred to build a major road, an enterprise park and to expand some existing urban cores. These changes led to urban areas covering 40% of the catchment in 2012. This urbanization trend is expected to continue, based on urban projects already approved.

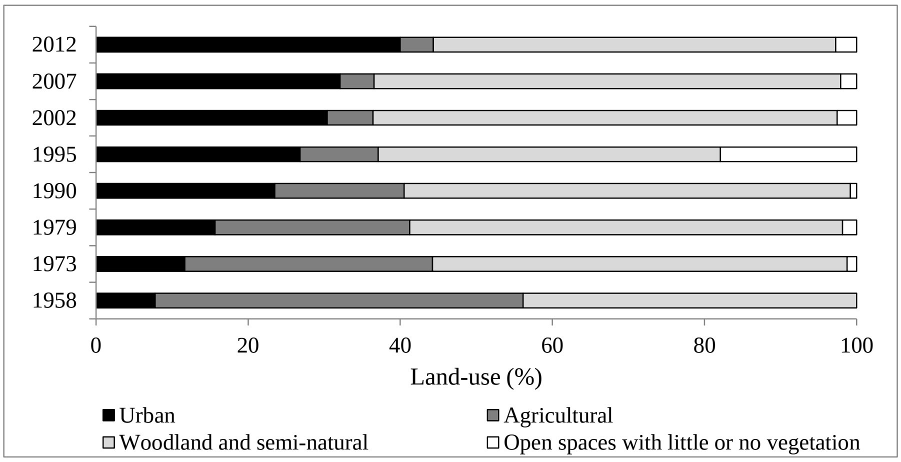


Figure 5.3 - Variation of land-use cover between 1958 and 2012 (the largest open space in 1995 was a result of forest fire).

Urbanization has involved large areas of paved surfaces interrupting woodland and often semi-abandoned agricultural terrain. Urban settings vary from older discontinuous buildings and structures (<25 inhabitants km^{-2}), comprising mostly detached houses surrounded by gardens and delimited by walls, but also recent well-defined urban cores, comprising apartment block (9900 inhabitants km^{-2}) (Tavares et al., 2012). The area also contains educational and health facilities, including a central hospital and some small industrial facilities. Much of the urban area is located in the valleys but also in upslope sites, mostly along ridges including the catchment boundary (Figure 5.4).

Within the urban areas, separate drainage systems transport domestic waste water into a treatment plant located outside the catchment, whereas the stormwater (including from roofs, streets and concrete paved area) generated in the most recent urban cores is piped to the main river and/or its tributaries. Where urban infrastructures and derelict urban land are surrounded by agriculture fields, however, stormwater just dissipates in these areas.

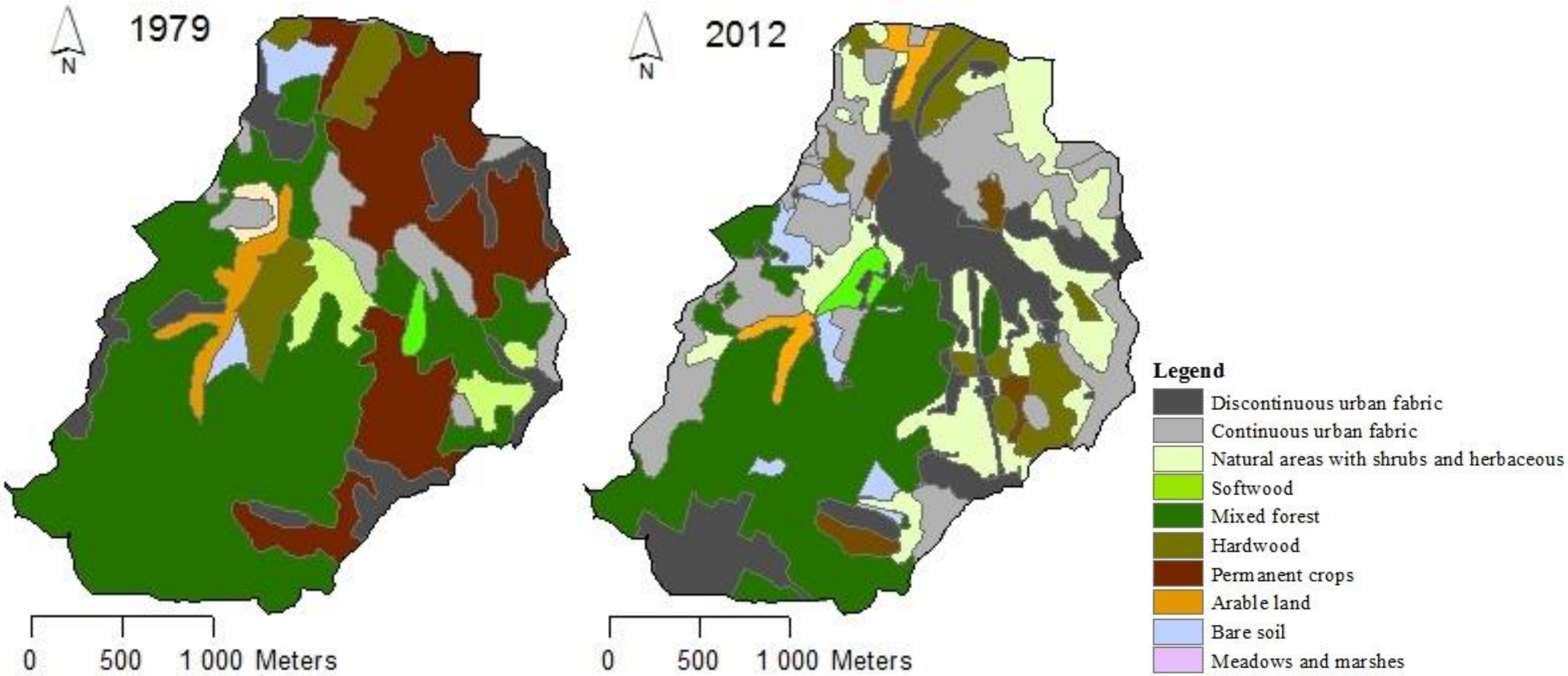


Figure 5.4 - Spatial differences in land-use between the initial discontinuous urbanization process (1979) and the current continuous urbanization phase (2012) of *Ribeira dos Covões* (adapted from Pato, 2007, Corine Land Cover, 2007, and Google Imagery, 2012).

5.3. Methodology

5.3.1. Research design

The hydrological response of the *Ribeira dos Covões* catchment was assessed via a monitoring network. In late 2005, a weir was constructed at the catchment outlet (*ESAC*) to measure stream discharge. This involves a 90º V-notch weir for the lower flows and a concrete rectangular section for greater discharges. Water level in the pool behind the weir has been continuously recorded using a float-operated Thalimedes Shaft Encoder (OTT Hydromet) with integral data logger. However, several construction problems only allowed reliable water level data collection from October 2008 onwards.

Daily climatic data, including rainfall, temperature, wind and solar radiation were provided by the Coimbra/Bencanta weather station, integrated in the national meteorological network (12G/02UG, from IPMA), located 0.5 km north of the study area. Although spatial variation of rainfall was later found to be minor, three raingauges were installed across the study catchment in February 2008. These tipping-bucket raingauges (Rain-O-Matic from Pronamic, 0.2 mm resolution) were connected to a continuous recording data logger (Onset HOBO).

In October 2010, the hydrological network was extended by installing eight additional water-level recorders (Odyssey, ~0.8 mm resolution), to provide sub-catchments discharge data (Figure 5.5). Sites took into account land-use and lithology, local suitability and accessibility. The purpose and characteristics of each sub-catchment were as follows:

- *Espírito Santo* measures the streamflow response of a highly urbanized sub-catchment overlying sandstone; it was installed in an asymmetrical section, delimited by a cement wall and an irregular compacted soil slope.
- *Quinta* provides data for a large sandstone area, mostly dominated by forestry; it was settled in a natural channel of rectangular shape.
- *Iparque* was sited at the outlet of the detention basin constructed downstream of the enterprise park area.
- *Covões* drains an area of sandstone and limestone, mostly dominated by forest but with downslope urban cores; the monitored channel cross-section comprises a straight cement wall on one side and an irregular herbaceous slope on the other.
- *Ribeiro da Póvoa* provides discharge data from most of the sandstone part of the catchment; it was installed in a current concrete rectangular section;
- *Mina* provides discharge data from an ephemeral watercourse overlying limestone that also receives stormflow from a section of the recent constructed major road; it was installed in an existing concrete trapezoidal channel.

- *Porto Bordalo* measures the discharge of three ephemeral streams on limestone (including *Mina* sub-catchment); it was sited in a current concrete trapezoidal channel.
- *Drabl* provides discharge data from an extensive limestone area (including *Porto Bordalo* and *Mina* sub-catchments), with a large urban cover downslope; it was installed in an existing stone trapezoidal channel.

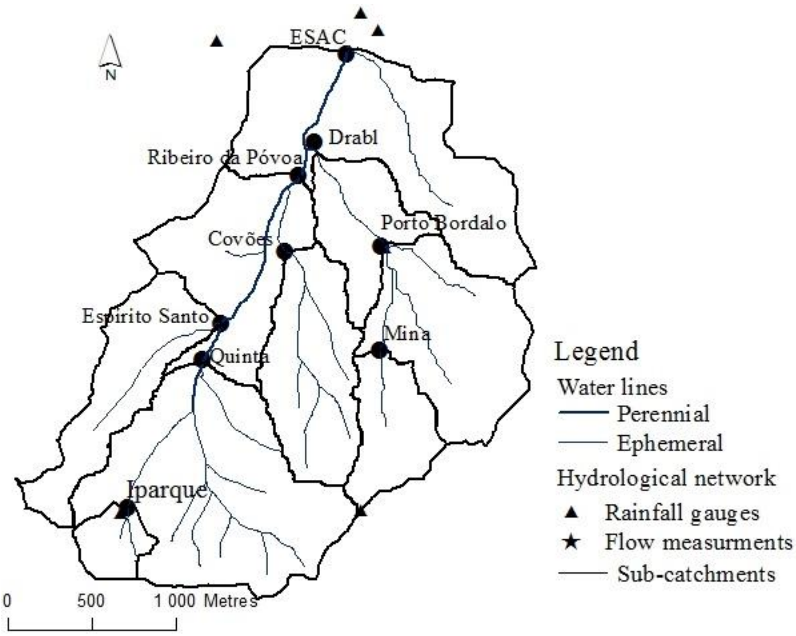


Figure 5.5 - Hydrological network installed in *Ribeira dos Covões* catchment.

Vandalism (equipment damage and theft) restricted data acquisition, particularly at the *Iparque* and *Mina* gauging stations. Destruction of raingauges led to the installation (in different sites) of three additional double tipping-bucket raingauges (Davis Tipping-bucket Rain Collector, coupled to Odyssey rain gauge loggers, 0.2mm resolution) in January 2011, and two more in June 2011.

Equipment maintenance was carried out at least every 3 months. Manual measurements of streamflow were made to calibrate and validate equipment results. In each gauging station, water height was measured manually with a ruler, whereas flow velocity was measured with a float and a chronometer for low flows (<7 L s^{-1}), or with an ultrasonic transit time flow meter (Vórtice) for greater discharges, following Bedient and Huber method (1987).

5.3.2. Characterization of drainage area

A detailed analysis of sub-catchments area was accomplished using cartographic information, aerial photographs and field visits. Characterization included drainage area, slope gradient, soil type, land-use and percentage impervious surface. Slope gradient was derived from a digital elevation model (DEM) with 5 m × 5 m pixel size, prepared using contour and elevation points (supplied by *Instituto Geográfico Português* - IGP). The DEM was processed to fill null cells, to calculate flow directions and delimit drainage areas of all the gauging stations, based on Spatial Analyst Tools available on ArcGIS 10 software.

Land-use data from 2007 were available from Corine Land Cover (5 m × 5 m resolution), and cartographic information as regards to impermeable surfaces was provided by IGP. However, since these information was not available for recent years, it was manually updated through the analysis of aerial photography using available Google Earth imagery (29/07/2009, 20/03/2011 and 13/06/2012) and field observations. Land-use and urban feature polygons were drawn for 2009, 2011 and 2012, with Google Earth tools, and exported to ArcGIS 10. Detailed information on urban features encompassed: 1) impermeable surfaces, including buildings, swimming pools, walls, roads, car parks, courtyards, driveways and pavements; 2) semi-permeable surfaces, including paths, compacted bare soil linked to parking and construction sites, as well as gardens covered by semi-permeable materials such as geotextiles; 3) permeable surfaces, mostly gardens; and 4) water detention basins, comprising structural flood measures but also sites where runoff is retained due to walls and roads embankments. The percentages of impermeable, semi-permeable and permeable surfaces in each catchment were calculated by dividing the area of such features by the respective catchment area. Description of the storm drainage system within the study site was not provided in time by the responsible institution, so it was based on observation during field visits.

5.3.3. Data analysis

Catchment hydrological response was analysed over five hydrological years (October 1 to September 30) (Palutikof et al., 1996), from 2008/09 to 2012/13. Analysis of discharge from the extended gauging station network was performed for three hydrological years 2010/11 to 2012/13.

Until December 2010, rainfall data was provided by the Bencanta/Coimbra national meteorological station (12G/02UG), because of vandalism with the installed raingauges. After January 2011, rainfall data was provided by the new raingauges installed. Spatial differences in rainfall records were investigated through Mann-Whitney U test ($p<0.05$), using IBM SPSS Statistics 22 software. Since no significant difference was identified, weighted average rainfall results were assumed uniform for the entire catchment. Weighted average rainfall was calculated from the gauges' area of influence, determined by Thiessen Polygons on ArcGIS 10 software. During periods of missing data, due to equipment malfunction/failure, weighted average was adjusted considering the available rainfall records. Data quality was checked by storage rainfall gauges installed adjacent to the recording ones. Long-term rainfall records (INMG, 1971-2000) were used to calculate rainfall probability and recurrence periods of rainstorms. Potential evapotranspiration was calculated based on Thornthwaite and Mather method (Thornthwaite and Mather, 1955), considering the climatic data from the Bencanta/Coimbra station.

Stage-discharge rating curves for each gauging station were derived from field measurements of water level and discharge. The quality of the rating curves was assessed through the calculation of the Perarson's rank correlation, Root Mean Square Error (RMSE) and Nash-Sutcliffe model efficiency coefficient (E) between measured and calculated flow. Streamflow records, calculated from the rating curves, were manually checked, validated, corrected or removed, based on field measurements. Missing daily values were replaced by interpolation based on discharge relation between all stations for the corresponding month. In order to compare data from drainage areas of different sizes and identify possible impact of land-use on the discharge, specific flows (L km^{-2} s^{-1}) were calculated by dividing all the data by the drainage area. These values also enabled runoff coefficients to be calculated.

Baseflow and storm flow components were separated, through the application of a mathematical low-pass digital filter developed by Lyne and Hollick (1979), considering the improvements suggested by Nathan and McMahon (1990). The constant used in the filter was assumed to be 0.925, based on a visual inspection of several data sets which indicated that this value of the filter parameter was that yielded the most acceptable. The baseflow index (BFI), defined as the ratio between baseflow and total streamflow (Nathan and McMahon, 1992), was calculated for all the gauging stations based on daily streamflow data.

Differences in flow magnitude of all the gauging stations were assessed through the calculation of annual and monthly runoff coefficients (ratio between total discharge and rainfall), as well as individual storm event analysis. A storm event was defined by the time interval between the beginning of the rainfall and the stop of storm flow. Rainfall events that did not promote a rise in streamflow were not considered for the individual storm event analysis. The study was performed for the January 2011 to September 2013 period, which had time resolution of rainfall data (5-minutes interval), comprising 310 storm events. For individual storm events several rainfall and hydrograph parameters were calculated. The rainfall characteristics considered were the depth, duration and intensity - mean hourly intensity and maximum intensities observed in 5 and 15 minutes (these maximum values were converted into mm h^{-1}) and 1-hour. The hydrograph parameters considered were: 1) storm runoff, 2) peak flow discharge, 3) response time, defined as the time lag between the centroid of the rainfall and peak flow (Lana-Renault et al., 2011), 4) recession time, which corresponds to the time interval between peak flow and the time when storm flow cease, and 5) runoff coefficient, defined as the ratio between stream runoff and rainfall. Differences in response and recession times between different gauging stations were investigated with Kruskal-Wallis test, at 0.05 significance level. Antecedent Dry Period (sum of rainfall over a defined period of days) was calculated for 7, 14 and 30 days prior to a storm event (API_7, API_{14} and API_{30}). The relation between rainfall and hydrograph parameters were analysed through Spearman's rank correlation coefficient (r), in IBM SPSS Statistics 22 software. The relation between annual runoff coefficient and the characteristics of the drainage area (area, mean slope, urban area extent and impermeable surfaces percentage) were also assessed. For the 2010/11 hydrological year, urban area and percentage impermeable surfaces were derived from the March 2011 aerial photograph, whereas for the 2012/13 and 2013/14 hydrological years it was based on June 2012 aerial photograph. Between these years, no land-use change was observed.

5.4. Results and analysis

5.4.1. Drainage area characterization

The gauging stations installed in *Ribeira dos Covões* have catchment areas ranging from 15 ha (*Iparque*) to the full catchment size (620 ha, *ESAC*). Variations in topography, lighology and land-use of the catchments are summarized in Table 5.1. *Iparque* and Mina gauging stations were abandoned due to vandalism problems (theft).

Table 5.1 – Summary of statistical differences of soil hydrological properties between runoff plots (S.: sandstone; L: limestone; A. alluvial).

Streamflow gauging station name	Contributing area (ha)	Topography			Lithology (%)			Hydrology		
		Min-Max altimetry (a.s.l.)	Dominant aspect	Slope (◦): Mean (Min.-Max.)	S.	L.	A.	Stream classification	Stream order	Drainage density (km km^{-2})
ESAC (outlet)	615	32-205	NW-E	10 (0.0 - 36)	56	41	3	Perennial	3	3.1
Drabl	152	48-207	NW-W	11 (0.1-31)	3	95	2	Ephemeral	2	2.6
Porto Bordalo	113	71-207	NW-W	12 (0.1-31)	2	98	0	Ephemeral	2	2.4
Mina*	35	99-207	E-NE	12 (0.2-27)	5	95	0	Ephemeral	1	1.4
Ribeiro da Póvoa	345	50-207	E-NW	9 (0.0 - 30)	84	12	4	Perennial	2	3.2
Covões	65	65-203	NE-NW	11 (0.0-30)	36	62	1	Ephemeral	1	4.1
Espírito Santo	56	79-165	E-SE	8 (0.1-26)	97	0	3	Ephemeral	1	1.9
Quinta	150	86-207	E-SE	9 (0.1 - 31)	100	0	0	Ephemeral	2	3.5
Iparque*	15	133-163	E	4 (0.2-15)	100	0	0	Ephemeral	1	2.7

*Abandoned because of vandalism/theft

Although all catchments are dominated by forest (Figure 5.6), *Espírito Santo* and *Drabl* showed the largest urban cover (46-48% and 47-53%) (Figure 5.7). Between 2007 and 2012, land-use changes were noticed all over the catchment, though only minor changes were recorded in *Espírito Santo* and *Covões* (2% and 3% increase of the urban areas, respectively). Major land-use change was recorded in *Iparque* sub-catchment (in upslope sandstone area), where 97% of the forest area was clear-felled for the enterprise park construction. Nevertheless, the majority of this area is still in an initial build-up stage, largely covered by compacted bare soil, considered as semipermeable area (Figure 5.7). These changes led to an enlargement of the urban area from 6% to 25% in *Quinta* drainage area, although most of it is still compacted bare soil (semipermeable) (Figure 5.7). Under limestone land-use changes were mainly associated with the new major road construction (Figure 5.8).

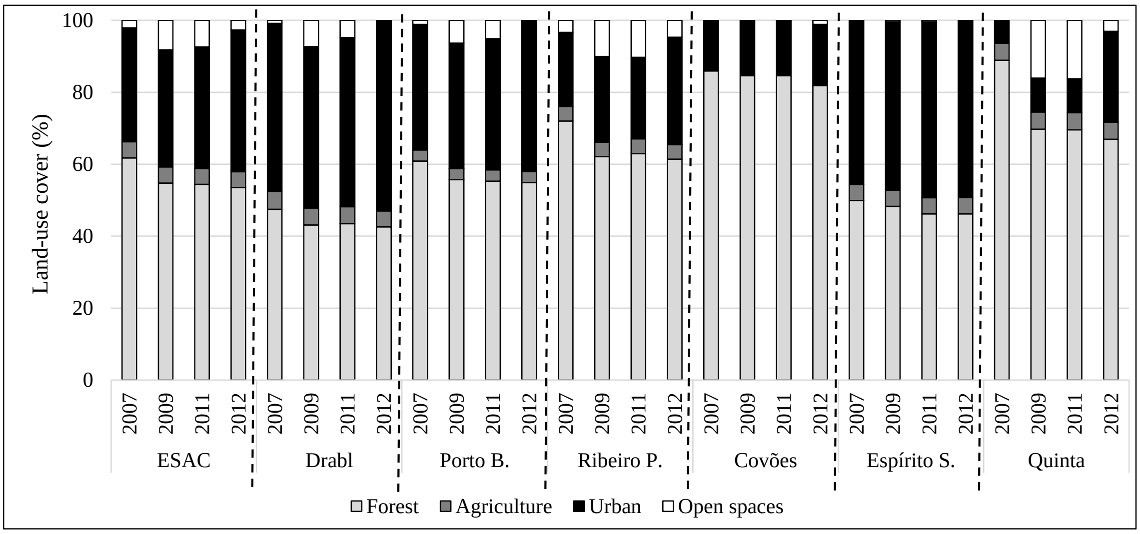


Figure 5.6 - Land-use changes within studied drainage areas, between 2007 and 2012.

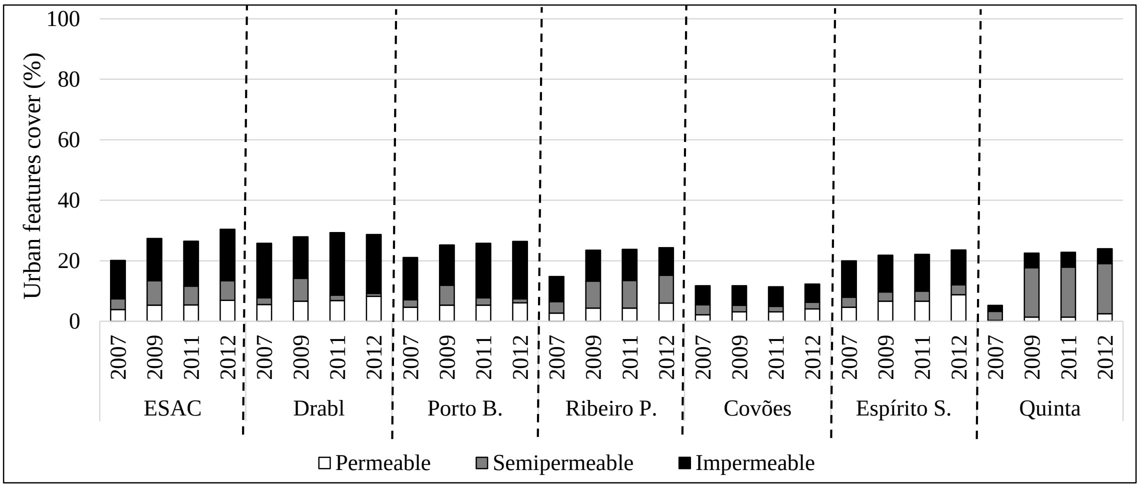


Figure 5.7 - Variation in the different types of urban cover in monitored drainage areas of *Ribeira dos Covões*, between 2007 and 2012 (Corine Land Cover, 2007; Google Imagery, 2014).

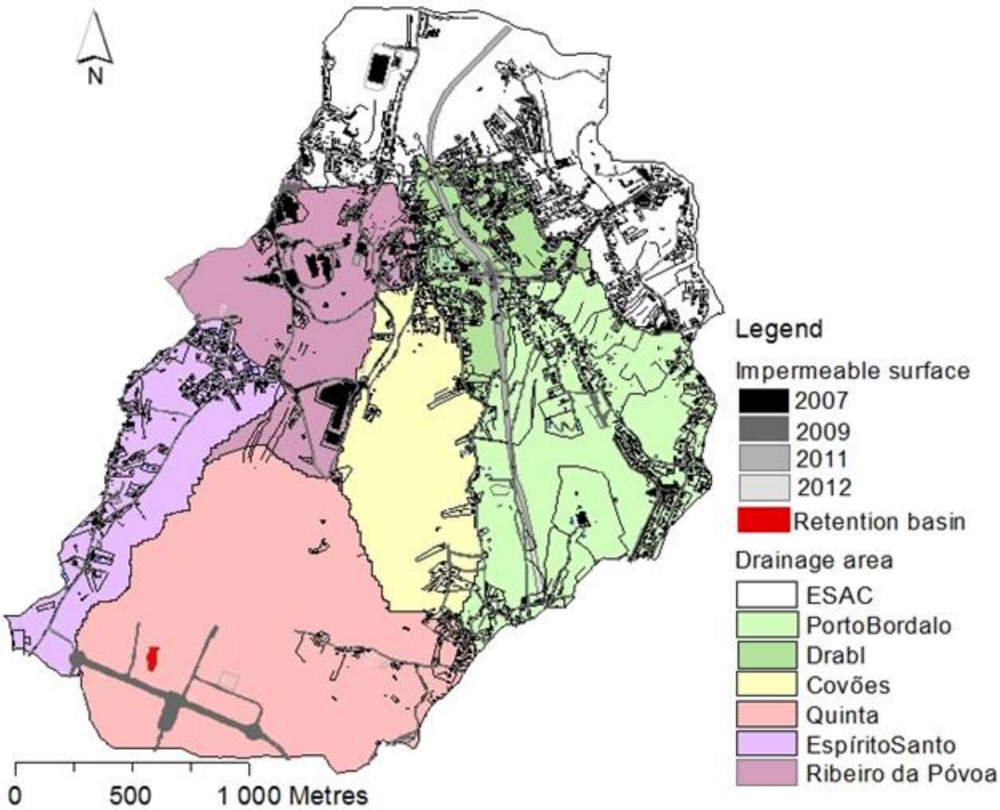


Figure 5.8 – Location of the urban impermeable surface in *Ribeira dos Covões* catchment (adapted from IGP, 2007, and Google Earth Imagery, 2012).

Between 2007 and 2012, urban land-use increased from 32% to 40% across *Ribeira dos Covões* catchment, but impermeable surfaces (e.g. paved areas) enlarged from 20% to 33%, displaying the urban consolidation process undergoing the recent years (Figure 5.8). Impermeable surfaces were mostly located in the north part of the catchment. Within *Ribeiro da Póvoa* (56% of the catchment area), in 2007, impermeable surfaces represented 43% of its urban drainage area, whereas in 2012 they covered 37% of the area. Most of these impermeable surfaces were located downslope, between *Ribeiro da Póvoa* and the upstream gauging stations (38-27%, between 2007 and 2012) and in *Espírito Santo* (56-49%) urban drainage area. Inside *Drabl* drainage area (25% of the catchment), 44-41% of the impermeable surfaces were concentrated in the small downslope area, between these and *Porto Bordalo* gauging stations (39 ha, 26% of the *Drabl* area). This high urban intensity contrasts with the upslope *Porto Bordalo* drainage area, where the impervious surfaces were dispersed across the valley bottom and in the upslope W side (Figure 5.8). Nevertheless, the most recent urban cores constructed in *Porto Bordalo* and *Drabl* drainage areas (limestone) are characterized by townhouses and flats (Figure 5.9a and 5.9b), whereas in upslope sandstone areas, the urban areas include larger permeable areas, such as gardens (Figure 5.9c and 5.9d). The different urbanization styles reflect differences in the extent of permeable and semipermeable surfaces within the drainage areas.

a) b)

c) d)

Figure 5.9 - Different types of urban areas across *Ribeira dos Covões* catchment: a) recent urban cores with greater population density in NE side, b) townhouses characterized by intensive soil sealing in E, and older urban cores with c) lower population density and d) isolated houses.

Across the catchment, management of storm runoff differs with age and location of the urban core. In the smaller and dispersed urban nuclei located in upslope areas, storm runoff was routed downslope (enhanced by the slope gradient and/or driven by the storm drainage system) to forest and/or agricultural soils, at different distances to the stream network. Increasing distance to the stream provides more infiltration/retention opportunities, leading to generally low runoff coefficients and greater response time to rainfall events. On the other hand, urban areas located downslope are characterized by a greater intensity of impervious surfaces, with road runoff collected in gutters and quickly delivered into downslope watercourses or nearby soils. The stream network represents a mix of semi-natural (with soil banks but partially straightened) and channelized sections. Open artificial channels contribute the stream for a few metres before *Porto Bordalo* gauging station and for a larger distance immediately after *Ribeiro da Póvoa* station. The stream section between *Porto Bordalo* and *Drabl* stations is piped, flowing beneath the soil surface. Along the main stream and larger tributaries crossing urban areas, some hydraulic infrastructures were built in order to by-pass the storm runoff from roads, for example. At the outlet of the enterprise park, under construction area in upslope catchment, a detention basin has been created to minimize downstream flood peaks. This structure consists of a 3650 m^2 basin with three small pipes (Ø= 0.20 m) that allows a perennial water flow downstream, but with a peak flow delay during storm events.

5.4.2. Climate during the monitoring period 2008-13

Climate during the years 2008/09 to 2012/13 showed the typical Mediterranean pattern, with hot and dry summers, as well as cool and wet winters (Figure 5.10). During the study period, rainfall between June and August represented 2-11% of the annual rainfall, similar to the average of 8% (INMG, 1971-2000). There were great differences, however, between the very dry 2011/12 (551mm, recurrence period of 17 years) and very wet 2012/13 (947 mm, 3 years return period) (Figure 5.11). These annual differences were also reflected in potential evapotranspiration differences (greater in 2011/12 and lower in 2012/13), typical of the Mediterranean environments (Figure 5.12). Rainy days varied from 89 days in 2008/09 to 200 days in 2012/13 (Table 5.2). Low rainfall intensities of <2 mm day^{-1} were dominant. Maximum daily rainfall ranged from 27 mm in 2008/09 and 2011/12 to 74 mm in 2009/10. These maximum daily intensities were not associated with the greatest hourly intensities, which varied between 10 mm in 2012/13 and 58 mm in 2009/10, respectively. However, based on the duration and mean hourly rainfall intensity of isolated storm events, observed between October 2010 and September 2013, none exceeded two years return period.

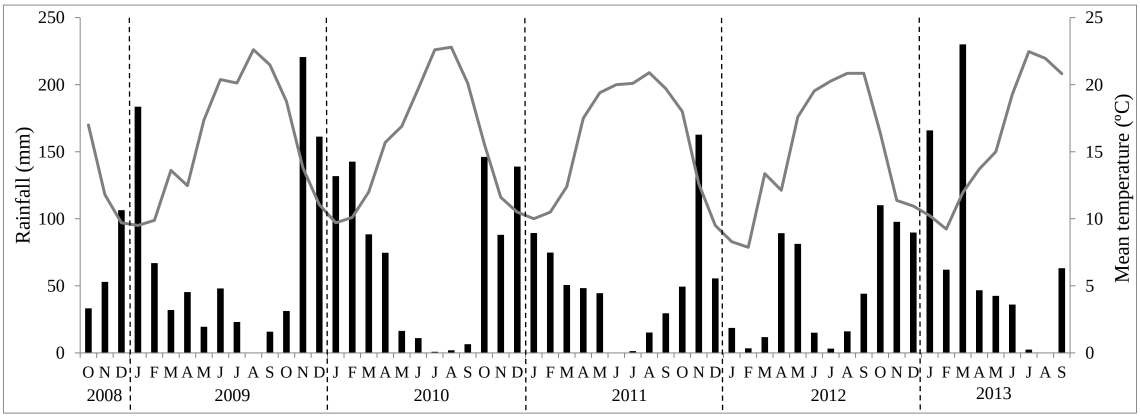


Figure 5.10 - Monthly rainfall and temperature pattern between 2008/09 and 20012/13 hydrological years.

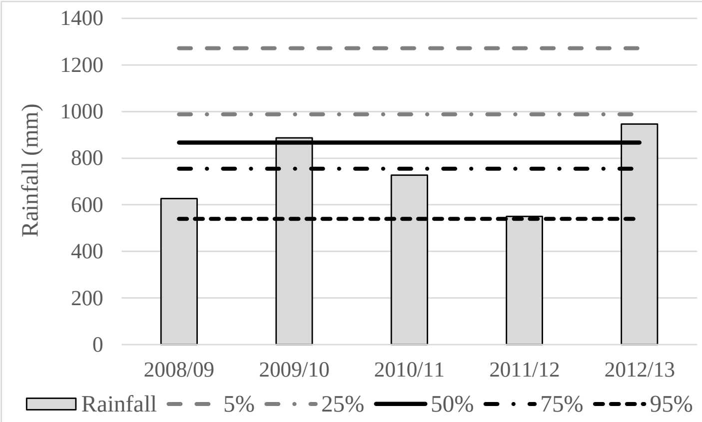


Figure 5.11 - Annual rainfall over the study period and comparison with the occurrence probability based on 1971/2000 annual records (INMG, 1971-2000).

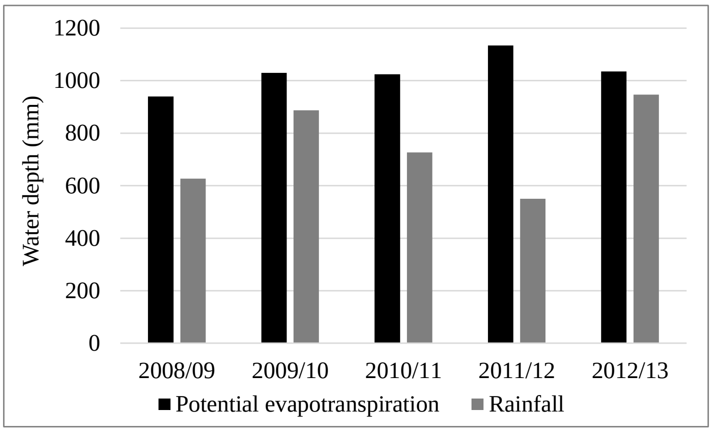


Figure 5.12 - Annual rainfall and potential evapotranspiration over the study period.

Table 5.2 – Summary of daily and maximum hourly rainfall through the study period.

	Number of days						Maximum (mm)	
	> 0 mm	<2 mm	2-10 mm	10-25 mm	25-50 mm	>50 mm	Daily	Hourly
2008/09	*89*	39	38	24	1	0	27	15
2009/10	*117*	48	61	22	5	1	74	58
2010/11	*131*	70	45	22	3	0	35	11
2011/12	*121*	78	40	15	1	0	27	16
2012/13	*200*	112	68	27	3	0	48	11

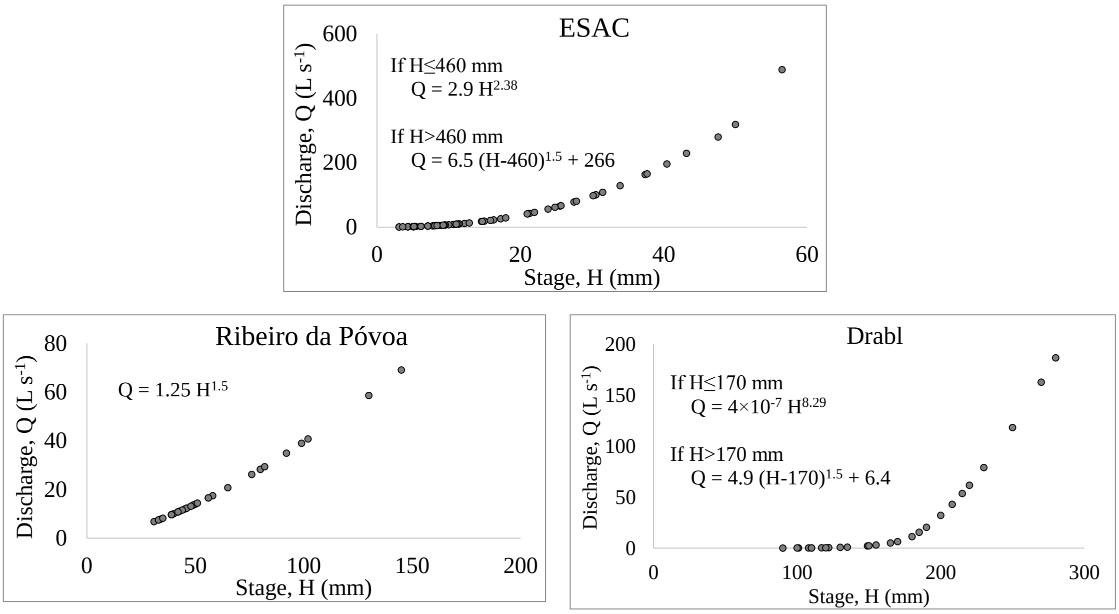
5.4.3. Catchment hydrology

5.4.3.1. Rating curves

The rating curves established for each gauging station were defined by composite equations (Figure 5.13), except for *Ribeiro da Póvoa*. The equations gave good fits to the stage-discharge data as measured by Pearsons´ rank correlations and Nash-Sutcliffe model efficiency coefficients, which ranges between 0.86-1.00 and 0.77-1.00 (Table 5.3). Although many flow measurements (varying from 25 to 68), high flow measurements were few.

Table 5.3 – Predictive accuracy of the rating curves results for individual gauging stations, based on field flow measurements.

Gauging station	Number of measurements (n)	Pearsons' rank correlation (r^2)	Root Mean Square Error (RMSE)	Nash-Sutcliffe model efficiency coefficient (E)
ESAC	68	1.00	3.75	1.00
Ribeiro da Póvoa	36	0.87	10.34	0.79
Drabl	27	0.99	4.15	0.85
Porto Bordalo	25	0.99	4.24	0.98
Covões	13	0.93	3.01	0.93
Espírito Santo	36	0.86	6.10	0.77
Quinta	33	0.99	11.74	0.99



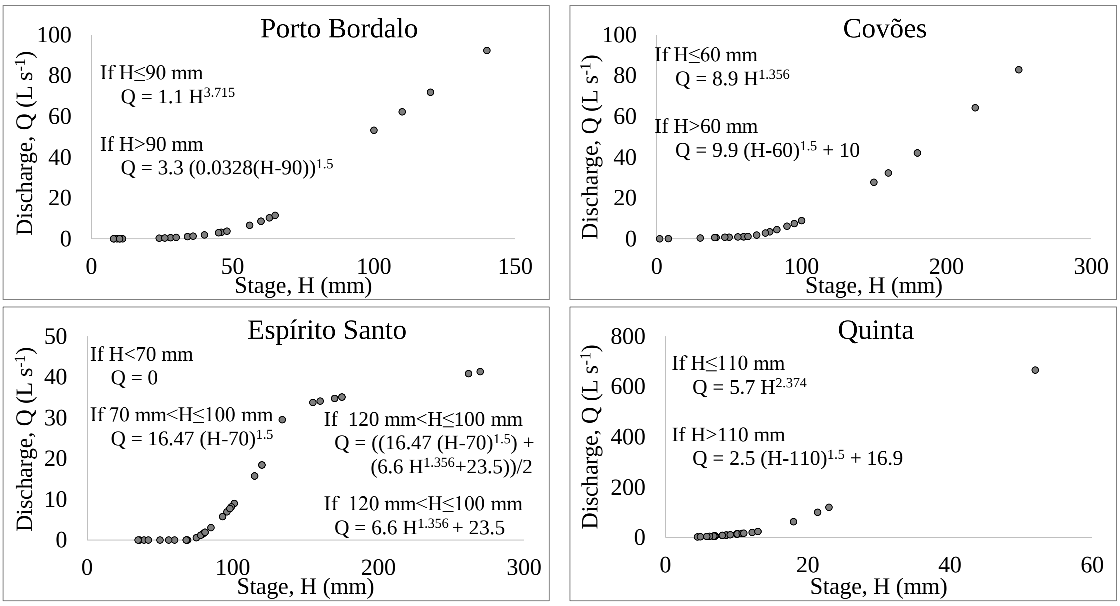


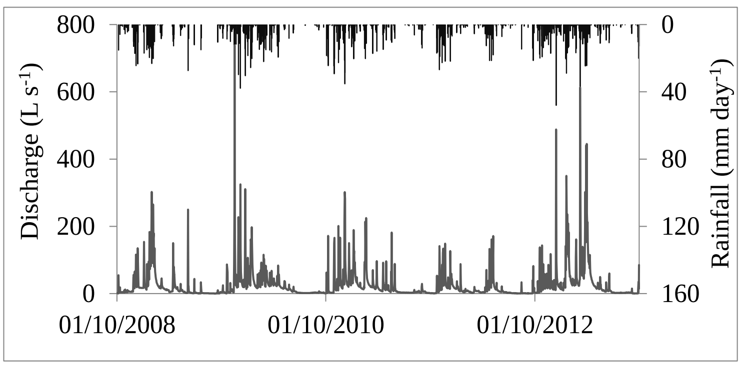
Figure 5.13 - Rating curves for individual gauging station, based on data (dots) acquired during field work (locations shown in Figure 5.5).

5.4.3.2. Streamflow

5.4.3.2.1. Temporal pattern of catchment discharge

Ribeira dos Covões discharge responded to rainfall through the five studied hydrological years, particularly to rainfall amount ($r=0.941$, $p<0.01$) (Figure 5.14a). On average, runoff rate was 0.4 mm day^{-1}, but mean daily winter values were ten times higher than in summer (0.06 and 0.60 mm day^{-1}). The highest recorded peak flow was 738 L s^{-1} on 16th November 2009, as a result of the maximum daily rainfall intensity recorded in the study period (74 mm). In the other studied hydrological years, peak flows were perceived in winter and spring seasons (wettest periods) (Figure 5.14a).

a)



b)

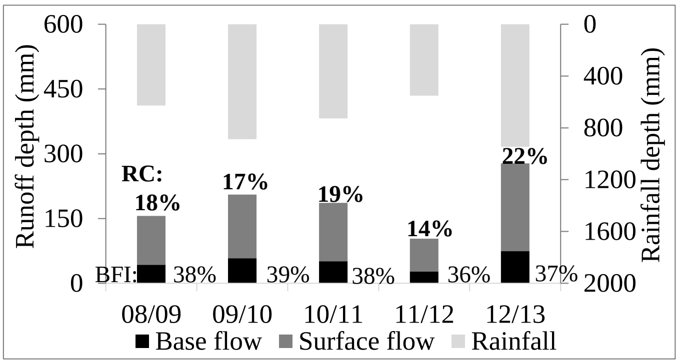


Figure 5.14 - Temporal variation of *Ribeira dos Covões* discharge between 2008/09 and 2012/13 hydrological years: a) daily hydrograph and b) annual variation.

Annual runoff varied from 14% in the driest year (2011/12) to 22% in the wettest (2012/13) hydrological year (Figure 5.14b). Most of the catchment discharge was storm flow (61-64%), whereas annual BFI ranged between 36 and 39% (Figure 5.14b). Despite annual BFI and rainfall patterns displayed similar tendencies, no significant correlation was found between these two variables ($p>0.05$). In fact, despite a greater annual runoff coefficient in 2012/13, BFI was slightly lower than in the previous 3 years (Figure 5.14b).

The seasonal rainfall pattern was clearly reflected in the river regime (Figure 5.14a), with summer flows representing 3-7% of the annual flow. Increasing flow responses to rainfall over the wet period are shown by the rise in runoff coefficients from October until February (median values of 8% and 27%, respectively) (Figure 5.15a). Through spring, monthly runoff coefficients slightly decreased (23% in March to 19% in May) and reached minimum median values at the end of the summer (6% in September). Nevertheless, this temporal pattern was not always the same as the observed for monthly BFI. In fact, baseflow component increased with the rainfall amount, through the wet season ($r=0.584$, $p<0.01$), but reached highest values in summer (median values of 56 - 79%). In addition, BFI became stable over the spring (~60%), whereas runoff coefficient started to decline (Figure 5.15). The lowest BFI attained 27-18% of the catchment discharge, at the end of dry period. Inter-annual variability between monthly runoff coefficients were greatest in February, April and August, as a consequence of greater rainfall differences (Figure 5.10).

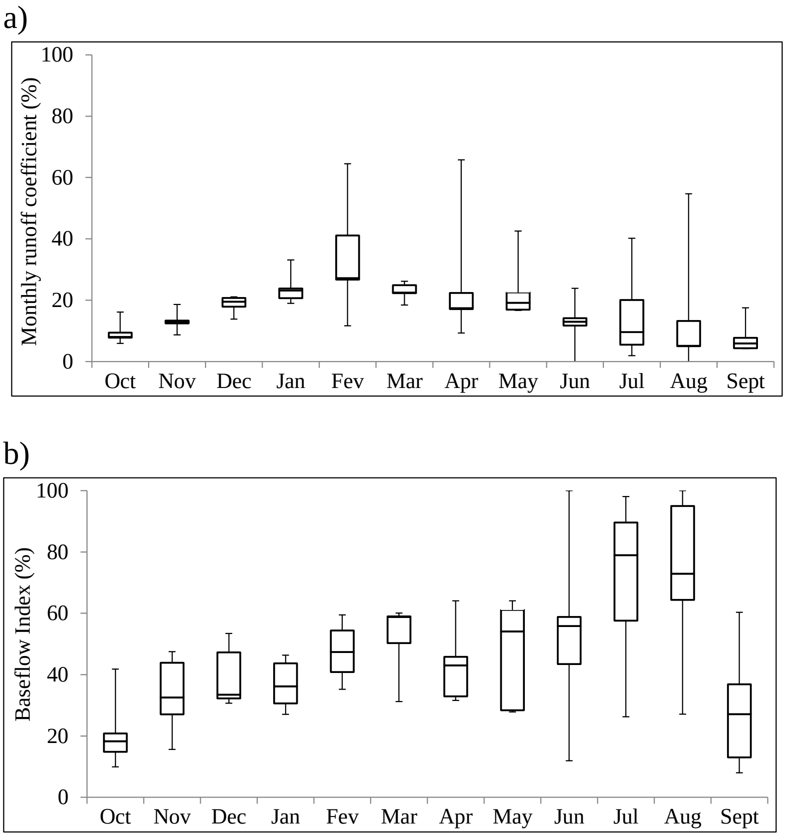
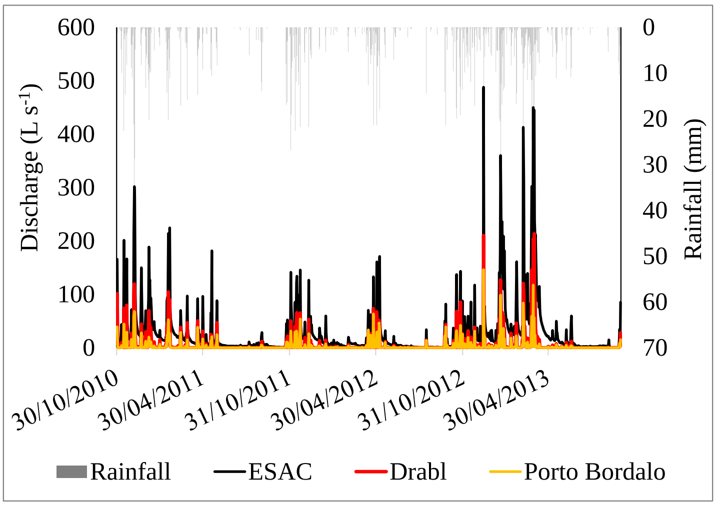


Figure 5.15 - Box plot showing the monthly variation of a) runoff coefficient and b) baseflow index in *Ribeira dos Covões* catchment outlet, for hydrological years 2008-2013.

5.4.3.2.2. Contributions from upstream sub-catchments

At all the gauging stations installed across *Ribeira dos Covões* catchment discharge followed the rainfall pattern (Figure 5.16), with lower values in summer, increasing through autumn and reaching higher values in winter and spring. Flows were always greater in the wettest 2012/13 hydrological year, whereas lower values were measured in the driest 2011/12, except in *Covões*, which recorded the lowest value in 2010/11 (Figure 5.16a). In general, flow increased with drainage area ($r=0.992$, $p<0.01$) and was correlated with hillslope position (total flow depth and altimetry: $r=-0.793$, $p<0.05$). *Espírito Santo* and *Covões*, with the smaller drainage areas (56 ha and 65 ha), presented lower runoffs (13-23 mm year^{-1} and <10 mm year^{-1}, respectively), whereas *ESAC*, representing the catchment outlet, recorded annual runoff of 200 mm. Nevertheless, *Covões*' peak flow (attained 91 L s^{-1}), slightly greater than in *Quinta* (87 L s^{-1}) which drains a larger area (150 ha). *Ribeiro da Póvoa* (outlet of sandstone), with a larger drainage area than *Drabl* (outlet of limestone), showed highest peak flow (257 L s^{-1} and 214 L s^{-1}). However, despite all these peak flows being measured in late winter 2012/13, they were not reached at the same time (distinct days in January and March). In *ESAC* and *Porto Bordalo* for instance, the highest flows were observed in December 2012 (488 L s^{-1} and 146 L s^{-1}). Nevertheless, *ESAC*, *Ribeiro da Póvoa* and *Drabl* gauging stations, located down the catchment and with larger contributing areas, typically presented peak flows in nearby days. Generally, greater discharges were always measured in late autumn, winter or beginning of spring seasons (Figure 5.16).

a)



b)

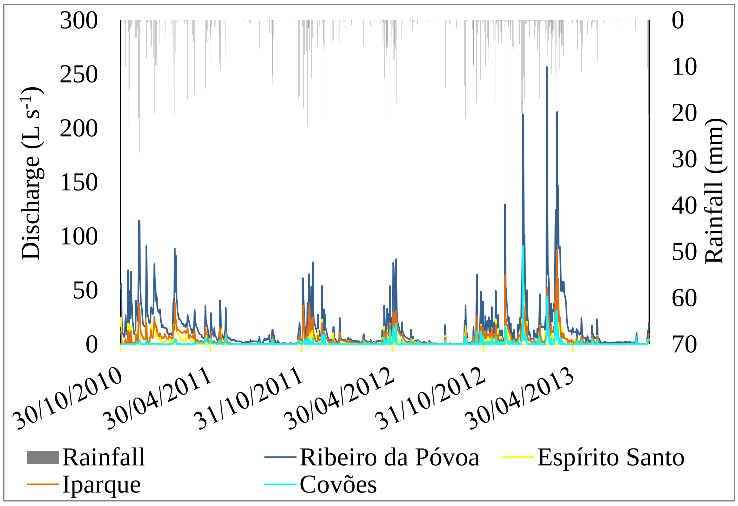
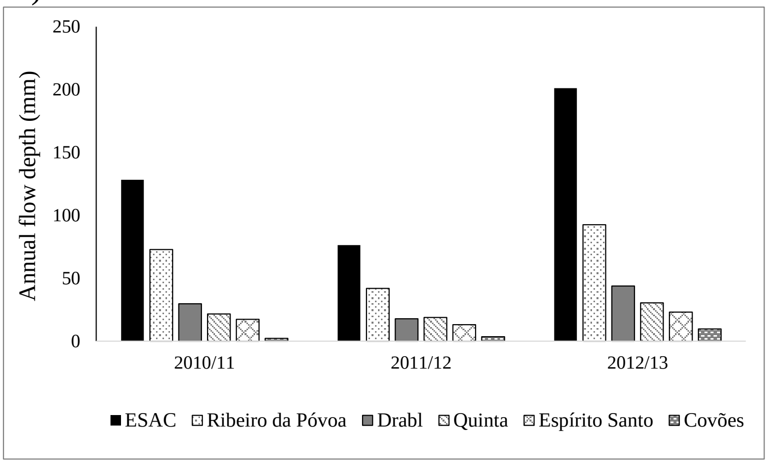


Figure 5.16 - Temporal variation of different gauging stations discharge between end of October 2010 and September 2013: a) ESAC outlet and limestone drainage areas (*Drabl* and Porto Bordalo), and b) sandstone dominated drainage areas - *Ribeiro da Póvoa*, Espírito Santo, *Iparque* and *Covões* (note scale differences).

Although the runoff increased from up to down slope the catchment (Figure 5.17a), storm runoff coefficients did not follow this tendency. Storm runoff coefficient was highest in *Espírito Santo* (20-21%) (Figure 5.17b). *ESAC* and *Ribeiro da Póvoa* revealed similar storm runoff coefficients (9-13% and 9-12%, respectively), slightly lower than *Drabl* (13-18%). The lowest storm runoff coefficients were found in *Covões* and Porto *Bordalo* (3-9% and 11%), followed by *Quinta* (9%) (Figure 5.17a). Annual storm runoff coefficient did not correlate significantly with the mean slope of the drainage areas, urban areas or impermeable surfaces cover (p>0.05). The general expansion of the urban areas by 6% through the study period showed a slight impact on storm runoff coefficient of *ESAC* (increased from 12.5% in 2010/11 to 13.4% in 2012/13) (Figure 5.17b). In *Covões*, however, a 2% urban expansion led to a storm runoff increase from 3 to 9%. In *Drabl*, *Ribeiro da Póvoa*, *Quinta* and *Espírito Santo*, the storm runoff coefficients were similar over the three hydrological years (18%, 11%, 9% and 21%), despite the urban enlargement of 8%, 6%, 16% and 2% (Figure 5.6).

a)



b)

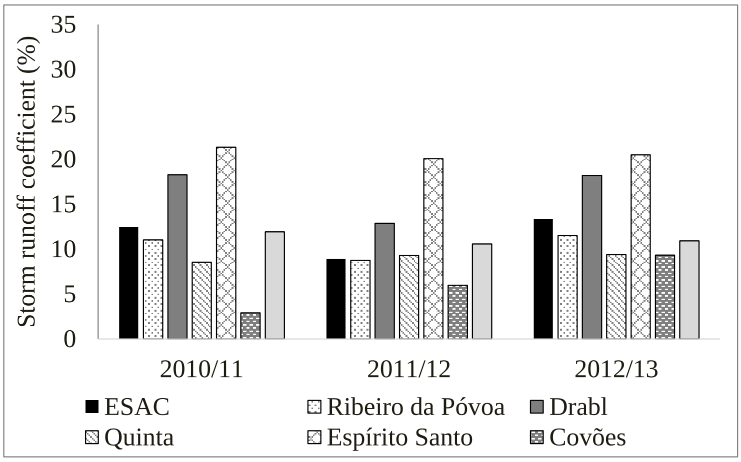


Figure 5.17 – Annual a) runoff and b) storm runoff coefficients variation in the monitored gauging stations, between late October 2010 and September 2013.

Flow was perennial at ESAC gauging station and experienced only a minor number of days without flow in *Ribeiro da Póvoa* and *Drabl* (28 and 12, respectively), recorded in the driest year of 2011/12. All the other gauging stations showed greater number of days without flow, reaching 25 and 22 days in the upstream *Quinta* and *Espírito Santo*, overlying sandstone, and 245 days in *Porto Bordalo* and *Covões*, totally or largely overlying limestone (Figure 5.18). Only in the most upstream gauging stations (*Quinta* and *Espírito Santo*), was the number of days without flow greater in 2012/13, following the driest year. All the gauging stations experienced lower annual BFI in the driest 2011/12 year (1% to 36%) and greater values in 2010/11 year (2% to 46%) (Figure 5.19a). In 2012/13, despite being the wettest hydrological year of the study period, BFI was 1-10% lower in the stream network than in 2010/11 (greater losses in *Covões*), due to the antecedent dryness, apart from *Porto Bordalo* which always showed very low BFI (2%). A clear difference was observed in the BFI between gauging stations installed in different lithologies: in limestone areas (*Porto Bordalo*, *Drabl* and *Covões*) it did not surpass 5% of the annual discharge, whereas in sandstone dominated areas (*Quinta*, *Espírito Santo*, *Ribeiro da Póvoa* and *ESAC*) it ranged between 20% and 40% (Figure 5.19a). In *Drabl*, the low BFI seems to contrast with the reduced number of days without flow, which is due to the maintenance of a very small flow (median summer flow of 0.03 L s^{-1}).

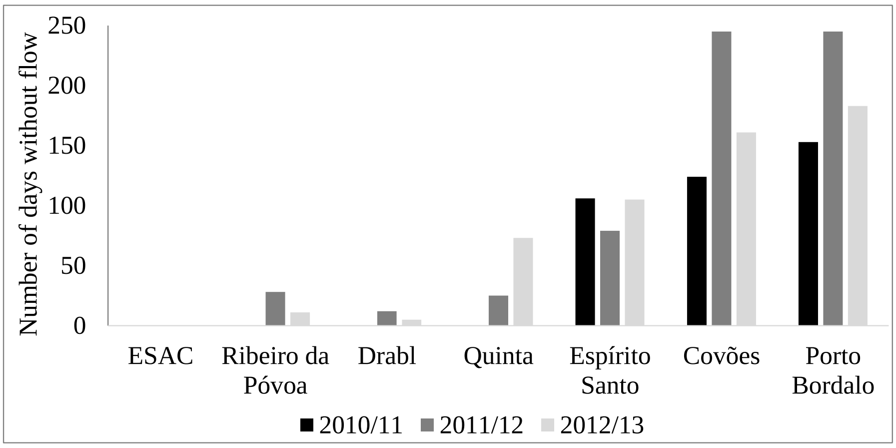


Figure 5.18 - Variation in the number of days without flow for the monitored gauging stations between years.

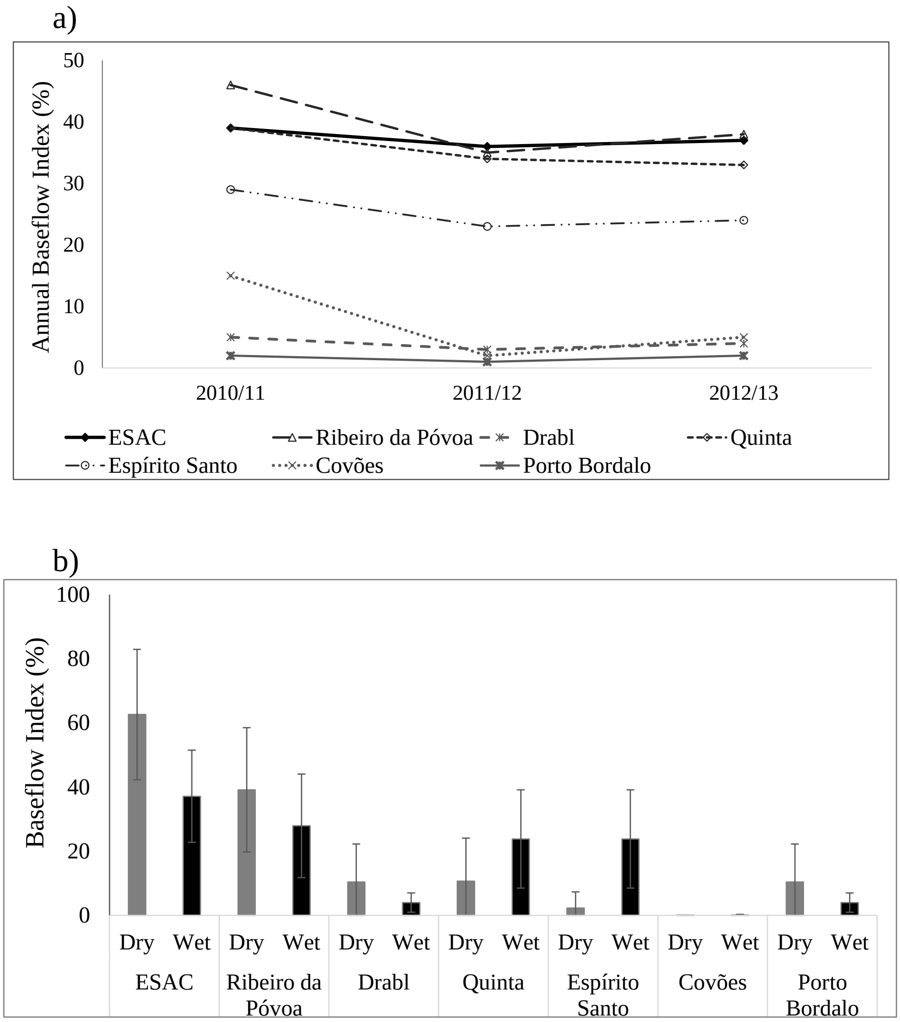


Figure 5.19 - Baseflow index variation for individual gauging stations over the study period: (a) annual and (b) seasonal mean and standard deviation values.

The majority of the no flow days were observed in the driest season. Baseflow represents a larger proportion of the summer flow than wet season flow (Figure 5.19b). Only in *Quinta* and *Espírito Santo*, upstream gauging stations on sandstone, was the BFI larger in wet periods (24% of the discharge). In *Covões* gauging station the increase of BFI during the wet season was minimal. Through the wet period, BFI was similar between 1) *Quinta* and *Espírito Santo* (with similar topography and lithology, see Table 5.1), 2) *Drabl* and *Porto Bordalo*, fully overlaying limestone, and 3) *Ribeiro da Póvoa* and *ESAC* (downslope gauging stations, both mostly overlaying sandstone). BFI did not significantly correlate with catchment area, but it increased with decreasing mean slope ($r=-0.839$, $p<0.05$). *Quinta* and *Espírito Santo*, located at greatest altitudes, were the only gauging stations which showed significant correlations between montly BFI and rainfall ($r=0.472$ and 0.449, respectively, $p<0.01$).

Annual variation on stormflow was also observed (Figure 5.20). In most of the gauging stations storm runoff coefficient increased during the rainy season, from late September/October until February – May, but decreased through spring and summer months. Monthly differences on storm runoff coefficients were greater in *Espírito Santo* and *Drabl*, ranging between no (or almost) flow in summer and 55%-41% of the rainfall in late winter/beginning of spring. However, in *Ribeiro da Póvoa* and *Covões*, storm runoff coefficients displayed lower annual differences, marked by lower increase through the wet season (*Ribeiro da Póvoa:* 5% - 14% and *Covões*: 3% - 9%, from October until May) and high values in the summer (median values for the three months of 20% in *Ribeiro da Póvoa* and 7% in *Covões*).

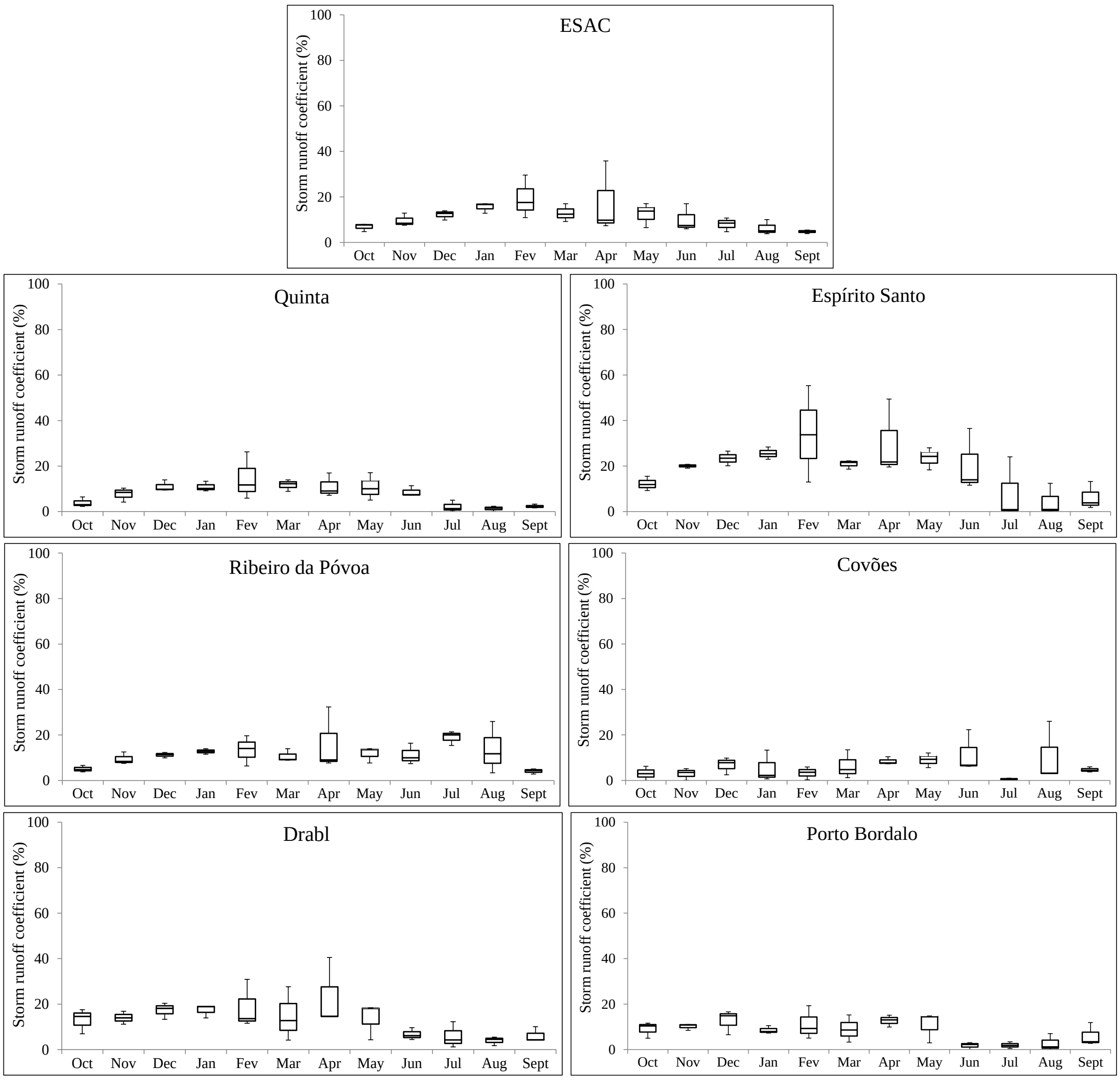


Figure 5.20 - Box-plots of monthly storm runoff coefficients measured between 2010/11 and 2012/13 in different gauging stations.

Based on the discharge data from three hydrological years, 51% of the catchment outlet discharge was supplied by *Ribeiro da Póvoa* flow, which covers 56% of the catchment area (largely overlaying sandstone) (Figure 5.21a). *Drabl*, encompassing 25% of the catchment area (dominated by limestone), delivered 23% of its annual discharge. The remaining 26% of the catchment flow was provided by the downstream drainage area (bellow *Drabl* and *Ribeiro da Póvoa* drainage areas, covering 19% of the catchment). This downslope area contributed 45% of the outlet baseflow (Figure 5.21b). Nevertheless, *Ribeiro da Póvoa* supplied the majority of the catchment baseflow (53%), since *Drabl* had a minor contribution (2%). Nevertheless, *Drabl* has a larger contribution to the catchment stormflow (35%), despite the important supply from *Ribeiro da Póvoa* (50%) (Figure 5.21c).

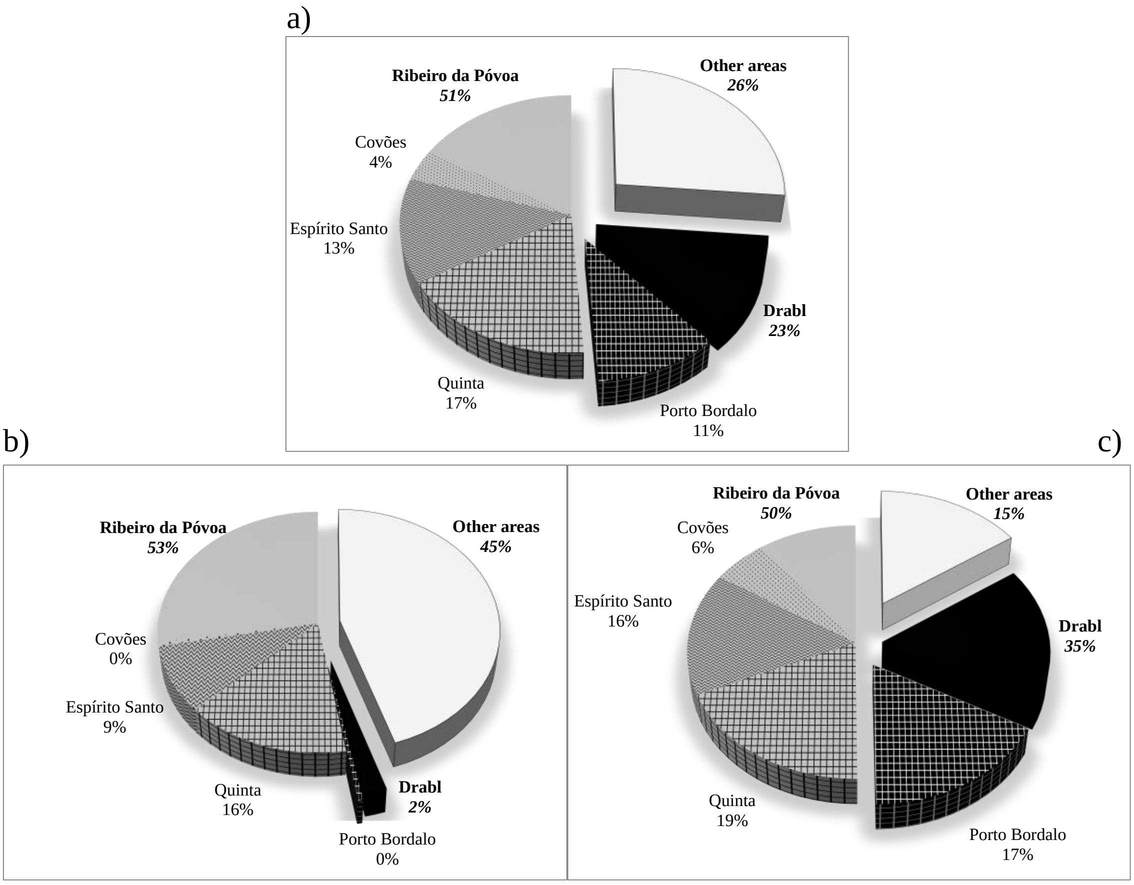


Figure 5.21 - Mean contribution of different gauging stations discharge (between 2010/11 and 2012/13) for the catchment flow (a) and its base (b) and storm (c) components. *Covões*, *Quinta* and *Espírito Santo* were included in *Ribeiro da Póvoa* discharge, and Porto Bordalo was included in *Drabl* (see Figure 4.6).

Most of the *Ribeiro da Póvoa* flow (68%) was supplied by the upstream gauging stations (*Quinta*: 34%, *Espírito Santo*: 26% and *Covões*: 8%), which comprised 78% of the drainage area (*Quinta*: 43%, *Espírito Santo*: 16% and *Covões*: 19%). However, these areas only delivered 48% of *Ribeiro da Póvoa* baseflow (*Quinta*: 30%, *Espírito Santo*: 17% and *Covões*: 1%) and 26% of its storm flow (*Quinta*: 5%, *Espírito Santo*: 9% and *Covões*: 12%), pointing out the importance of the downslope contributing area to supply baseflow (52%), but also storm flow (74%), despite its smaller drainage area (32% of

Ribeiro da Póvoa area). Within *Drabl*, 48% of its flow was delivered by *Porto Bordalo*, which covers 74% of its drainage area. *Porto Bordalo* provided 20% of *Drabl*' baseflow and 49% of its stormflow. This results highlight the prominence of the remaining 26% of the *Drabl*' downslope drainage area (below *Porto Bordalo*) on flow supply, particularly stormflow.

In sub-catchments overlying limestone, stormflow encompassed the majority of the flow, with median values ranging from 62% to 86% during wet periods (increasing from *Covões*, to *Drabl* and then to *Porto Bordalo*). In summer, stormflow was even greater in *Drabl* and *Porto Bordalo* flows (86% and 100%), but it was lower in *Covões* (50%), partially overlying sandstone (36% of the drainage area). Over sandstone lithology, stormflow encompassed a considerably lower fractions of the total discharge, with median values ranging between 27% to 45% during the wet seasons, but from 16% and 31% in the dry seasons (increasing from *Ribeiro da Póvoa* to *ESAC*, *Quinta* and *Espírito Santo*).

5.4.3.2.3. Spatio-temporal response during storm events

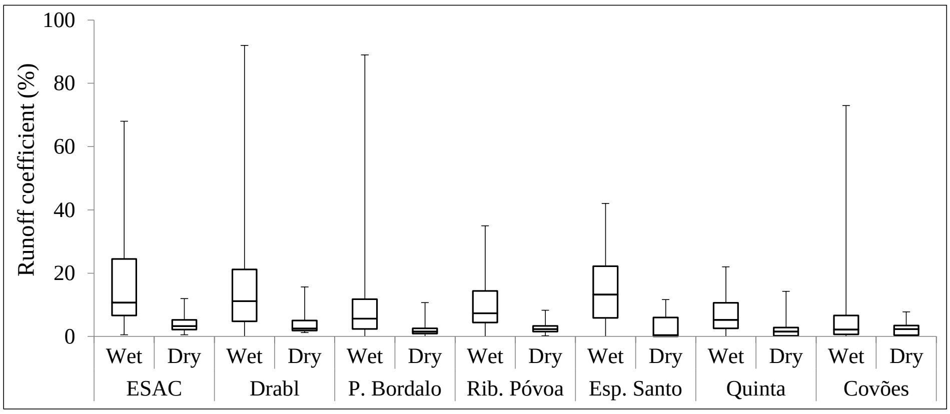
Storm event analysis indicated that only a small threshold amount of rainfall was required to generate runoff all over the catchment. During wet season, only 0.3 mm of rainfall was necessay after several antecedent storm events (API_7 >25 mm), whereas under summer conditions 0.7 mm was necessary with less antecedent rainfall (API_7 >7 mm or API_{14} >13mm). The seasonal climate pattern greatly influenced the runoff and storm runoff coefficients associated with individual storm events. Storm **runoff coefficients** were higher during the wet (median values ranged from 2% in *Covões* to 15% in *Espírito Santo*) than dry seasons (from 0.3% in *Quinta* to 7% in *Espírito Santo*), particularly in *Porto Bordalo* and *Quinta* gauging stations (6% vs 0.4% and 6% vs 0.3%, respectively) (Figure 5.23a). However, largest summer storms were only 14 mm of rainfall, whereas in wet periods it attained 29 mm. Runoff coefficients increased with: 1) storm rainfall (r ranged between 0.121 and 0.362 for the different gauging stations, $p<0.05$); 2) maximum 15-minute rainfall intensity (r ranged between 0.150 and 0.301 for different gauging stations, $p<0.05$), except in *Porto Bordalo* and *Drabl*, which always exhibited greater stormflow throughout the year; and 3) antecedent rainfall (correlation with API_7 ranged between 0.228 and 0.563 for the different gauging stations, $p<0.01$, but correlations with API_{14} and API_{30} were also found for the same level of significance).

At the end of winter (late March 2013), immediately after the largest rainfall period (API_7 >50 mm and API_{30} >160 mm) the greatest storm runoff coefficient reached 70% of the rainfall in the fully limestone areas (*Porto Bordalo* and *Drabl*), 52% in *Covões*, partially covered by limestone (62%), 39% at the catchment outlet (ESAC, 41% overlying limestone), 37% of the largely urbanized sandstone area (*Espírito Santo*) and, 14% and

10% in *Quinta* and *Ribeiro da Póvoa*, covered by more than 60% of forest under sandstone (Figure 5.22b).

During the summer, the highest storm runoff coefficients were attained in the largest urbanized catchments, but did not surpass 18% in *Espírito Santo* and 11% in *Drabl*, as a result of the greatest rainfall intensities (6-10 mm h^{-1}, in 5-minutes interval). In this summer storm, storm runoff coefficient only reached 8% in *Porto Bordalo*, overlaying limestone, 6% in *Quinta* and *Covões*, with the largest forest cover, and 3% in *ESAC* and *Ribeiro da Póvoa*, the largest drainage areas, mainly overlying sandstone. Nevertheless, median storm runoff coefficients over three years of study did not show a significant correlation with drainage area, mean slope, land-use or percentage impervious area (Figure 5.22b).

a)



b)

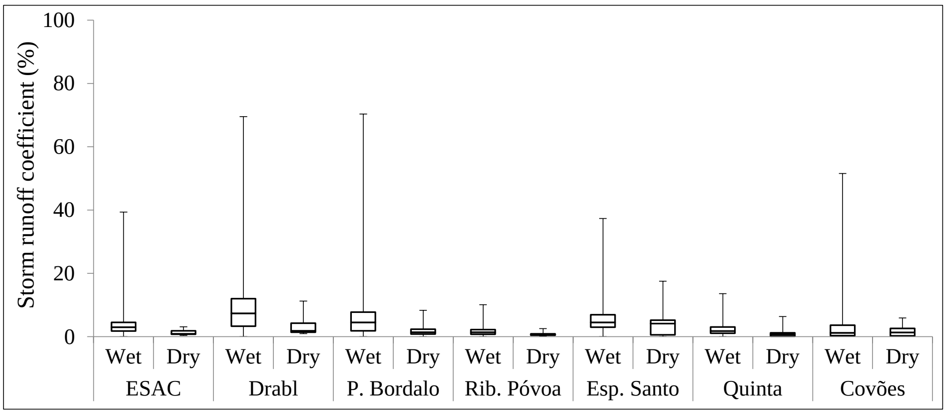


Figure 5.22 - Box plot showing the (a) runoff coefficient and the (b) storm runoff coefficient differences between individual storm events observed under dry and wet periods, for all the monitored gauging stations.

The higher storm runoff in limestone than sandstone areas, was also supported by the differences in **peak flows** (Figure 5.23). Despite the smaller drainage area of *Drabl*, median peak flow was 50% higher than in *Ribeiro da Póvoa*. Even the smallest drainage area under limestone (*Porto Bordalo*) displayed marginally higher peak flows than the largest sandstone *Ribeiro da Póvoa* (37 L s^{-1} vs 26 L s^{-1}), despite the slightly great urban cover in the later (Figure 5.6). *Drabl* and *Ribeiro da Póvoa* provided 89% of the median peak flows of *ESAC*, but this contribution falls to 50% during the highest storm event. These results stresses the importance of downslope catchment area, embracing 12% of the catchment urban area, to increase the magnitude of the largest floods. Within limestone areas, *Porto Bordalo*, covering 74% of *Drabl* drainage area, supplied 66% of median peak flows in *Drabl*. However, contrary to the observations in *ESAC*, during greatest storm events, the runoff contribution from *Porto Bordalo* increased to 74% of the *Drabl* peak flow, perhaps denoting a greater overland flow connectivity in the upslope drainage areas during largest storms. Within *Ribeiro da Póvoa*, the greater peak flows were observed in *Quinta*, which represents the largest area. However, *Espírito Santo* with slightly lower area than *Covões* but greater urban cover, showed somewhat higher peak flows (Figure 5.23). Nevertheless, considering the normalized discharge (divided by the drainage area), *Quinta* and *Covões* showed similar median peak flows (0.2 L km^{-2} s^{-1}), but *Espírito Santo* attained higher values (0.3 L km^{-2} s^{-1}). Nonetheless, during the largest storms, the discharges from *Quinta*, and particularly *Covões*, increased deeper than in *Espírito Santo* (peak flow of 2.3 L km^{-2} s^{-1}, 2.9 L km^{-2} s^{-1} and 3.5 L km^{-2} s^{-1}, respectively).

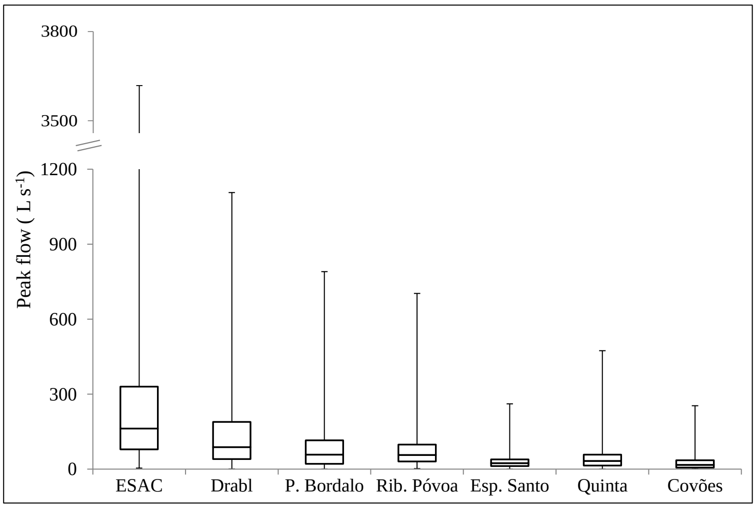
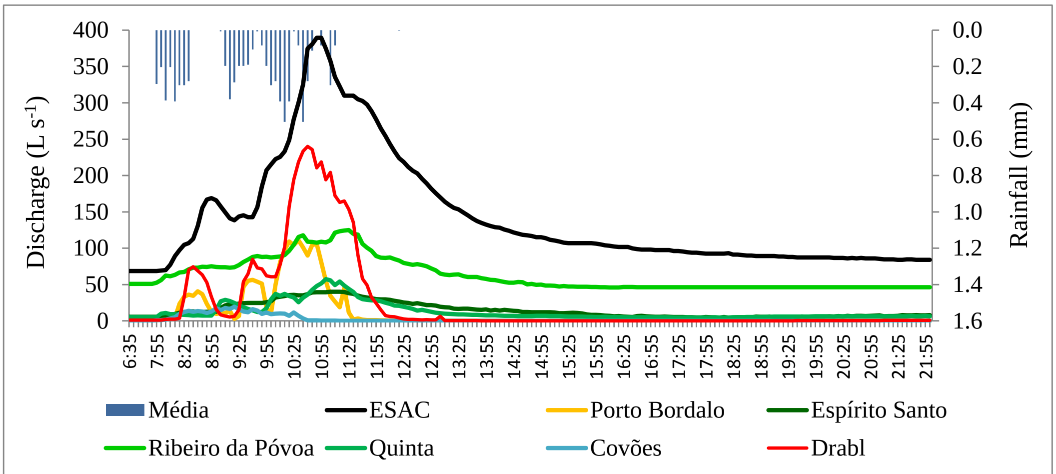


Figure 5.23- Spatial variability of peak flows measured during individual storms within *Ribeira dos Covões* catchment.

Results demonstrate the increase of overland flow connectivity during largest storms within all the drainage areas, but particularly within *Covões* and *Quinta*. Nevertheless, the lower peak flows in *Quinta* exhibits the delaying effect of the runoff promoted by the detention basin installed at the outlet of the enterprise park construction area. Generally, the peak flow increases significantly with: 1) rainfall depth (r ranged between 0.482 and 0.656 for the different gauging stations, $p<0.01$); 2) maximum hourly rainfall intensity (r ranged between 0.463 and 0.605 for the different gauging stations, $p<0.01$); and 3) antecedent rainfall (correlation with API_7 ranged between 0.159 and 0.452 for the different gauging stations, $p<0.01$, but correlations with API_{14} and API_{30} were also found for the same level of significance).

The differences in the hydrographs produced by similar rainfall patterns during different seasons, particularly on peak flows, may be observed in Figure 5.24 and Figure 5.25. For similar rainfall events with 7.2-7.5mm (Figures 5.24a and 5.24b), peak flows were over 2 times higher under antecedent wet conditions, except in *Covões* where it decreased (31 L s^{-1} vs 20 L s^{-1}). In terms of storm runoff coefficient there were only a slight increase in *Porto Bordalo*, *Espírito Santo* and *Covões* (<1.25 times), whereas at the other gauging stations the increase was 4-8 times higher, and 11 times higher at the ESAC outlet.

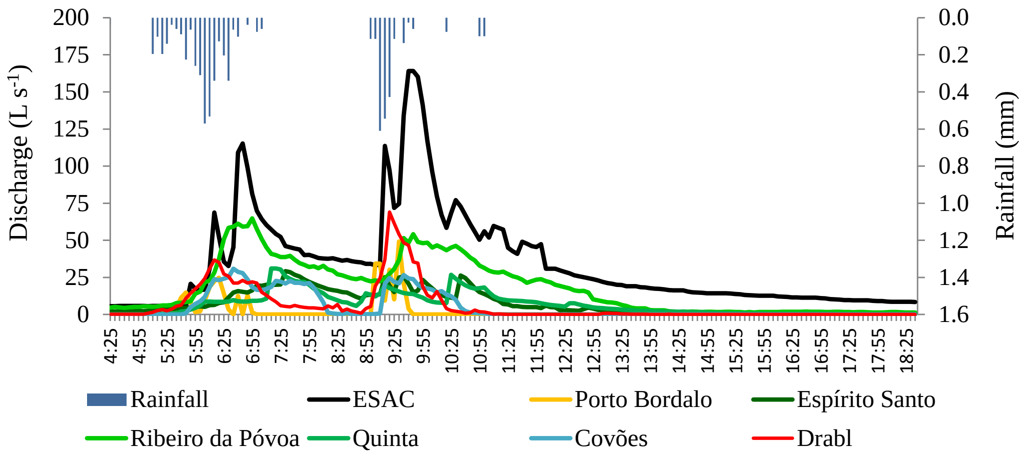
a)



	ESAC	Drabl	P. Bordalo	Rib.Póvoa	Esp. Santo	Quinta	Covões
Storm runoff coef. (%)	9.0	6.5	1.7	5.7	2.2	3.6	0.5
Runoff coef. (%)	28.0	11.7	7.6	8.7	15.8	5.0	9.0

Figure 5.24- Individual storm hydrographs to show the impact of antecedent weather conditions on the peak magnitude of the seven gauging stations: a) storm of 7.5 mm in late winter (10/04/2013) (AP_{I7}=15 mm, API_{14}=91 mm, API_{30}=179 mm), b) storm of 7.2 mm during summer (07/06/2012) (AP_{I7}=0.7mm, API_{14}=0.7 mm, API_{30}=12.7mm).

b)

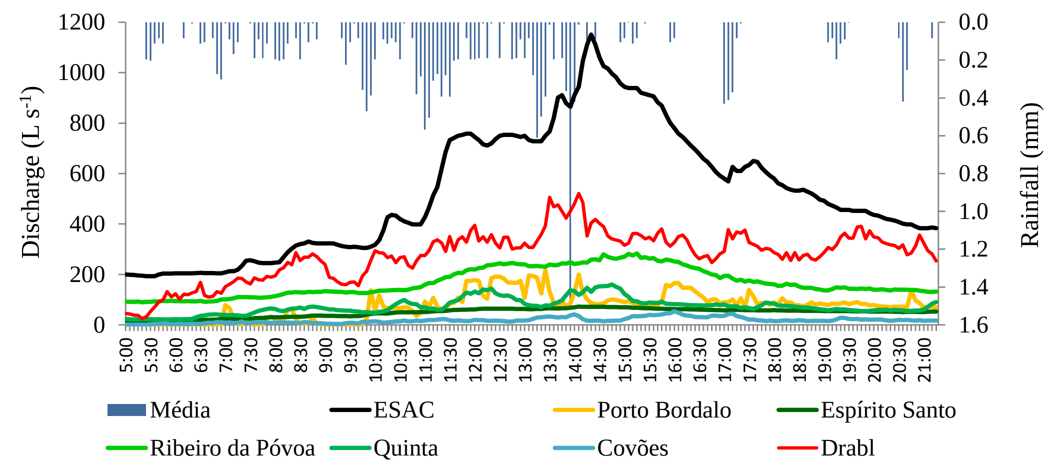


	ESAC	Drabl	P. Bordalo	Rib.Póvoa	Esp. Santo	Quinta	Covões
Storm runoff coef. (%)	0.8	1.4	1.5	0.7	2.3	0.9	0.4
Runoff coef. (%)	1.0	1.8	1.5	0.5	0.4	0.1	0.1

Figure 5.24 (cont.) - Individual storm hydrographs to show the impact of antecedent weather conditions on the peak magnitude of the seven gauging stations: a) storm of 7.5 mm in late winter (10/04/2013) (AP_{I7}=15 mm, API_{14}=91 mm, API_{30}=179 mm), b) storm of 7.2 mm during summer (07/06/2012) (AP_{I7}=0.7mm, API_{14}=0.7 mm, API_{30}=12.7mm).

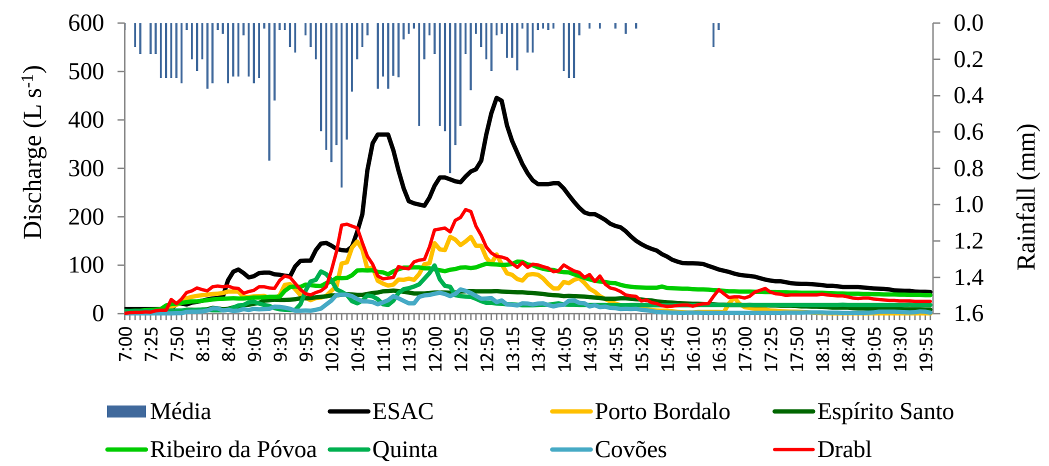
Comparing storm events with similar rainfall amount (22 mm vs 20 mm) observed in autumn and in late winter (Figures 5.25a and 5.25b), the differences in peak flows were not so accentuated as in previous example, with winter peak flow 1.4-2.6 times higher than in autumn. The increases in storm runoff coefficients from autumn to winter were minor, except in *Covões* where it increased 6 times. This may be a result of lower rainfall intensity in the winter event (mean rainfall intensity was only 1.3 mm h^{-1} compared with 2.4 mm h^{-1} in the autumn event).

a)



	ESAC	Drabl	P. Bordalo	Rib.Póvoa	Esp. Santo	Quinta	Covões
Storm runoff coef. (%)	4.7	11.1	7.3	1.9	3.2	3.4	3.0
Runoff coef. (%)	25.0	51.7	19.6	11.8	25.2	13.7	8.7

b)



	ESAC	Drabl	P. Bordalo	Rib.Póvoa	Esp. Santo	Quinta	Covões
Storm runoff coef. (%)	7.6	12.1	4.5	2.5	4.0	3.5	0.5
Runoff coef. (%)	21.9	29.9	6.0	11.4	17.8	10.2	3.4

Figure 5.25 - Individual storm hydrographs to show the impact of antecedent weather conditions on the peak magnitude of the seven gauging stations: a) storm of 22.4 mm observed during autumn (11/11/2011) (API_7=19 mm, API_{14}=64 mm, API_{30}=100 mm), and b) storm of 19.9 mm recorded in late winter (30/03/2013) (API_7=83 mm, API_{14}=105 mm, API_{30}=202 mm).

Ribeira dos Covões catchment showed a flashy response during rainfall events, with peak flows being reached in less than one hour. Generally, limestone areas were characterized by quicker flow responses, requiring, in most cases, less than 20 minutes to reach the peak flow, whereas in sandstone dominant areas it needed twice as long (except in *Espírito Santo*) (Figure 5.26). Within limestone areas, *Drabl* took five minutes more to reach peak flow than the upstream *Porto Bordalo* sub-catchment (median **response time** of 10 minutes), which covers 74% of the *Drabl* area. *Covões*, with a smaller area mostly on limestone, recorded the fastest response time, with a median value of 5 minutes. This drainage area, however, included downslope impermeable surfaces (Figure 5.5). In *Espírito Santo*, with more than twice the urban cover of *Covões*, peak flows were reached in a median time of 15 minutes. In fact, *Espírito Santo* and *Drabl* showed similar response times (p>0.05), may be because, despite the lithology, they have similar land-uses (Figure 4.7). The largest drainage areas of *Ribeiro da Póvoa* and *ESAC* had similar response times (p>0.05), with peak flows being reached in a median time of 40 minutes. *Quinta* experienced greater response times than at all the other gauging stations (p<0.05), with a median value of 50 minutes. This is because the recent enterprise park drains into a constructed detention basin, about 800 m upstream of *Quinta* gauging station. Field observations, however, revealed that during larger storms the flow exceeds the drainage capacity of the stream, thus some streamflow run-off into woodland land.

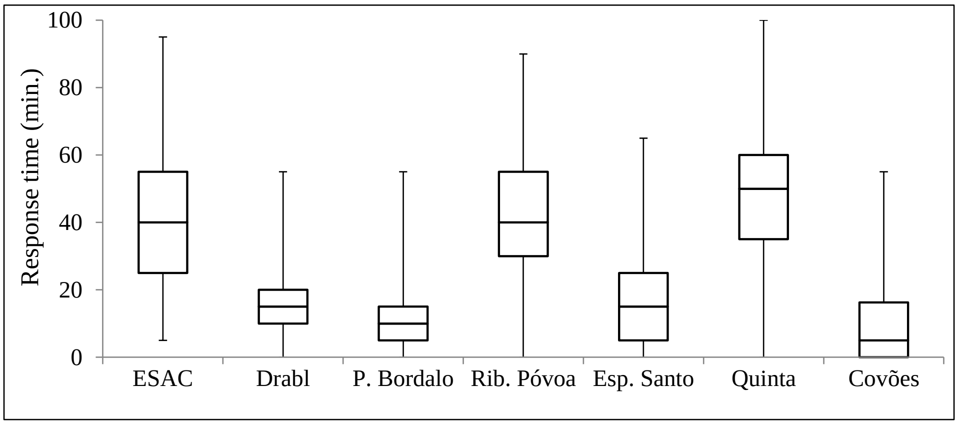


Figure 5.26 - Differences in response time during storm events for the catchment (ESAC) and sub-catchments.

Recession time ranged, in median, from 3h in *Porto Bordalo* (p<0.05), with the smallest drainage area fully overlying limestone, to 7h for the overall catchment (*ESAC*) (p<0.05) (Figure 5.27). *Ribeiro da Póvoa*, located 750 m upstream of *ESAC*, draining the second largest area, mostly on sandstone, showed a median recession time of 6h. Nevertheless, for largest rainstorms at the end of winter, *ESAC* and *Ribeiro da Póvoa* stormflow sustained for more than 1 day. In *Drabl*, *Covões*, *Quinta* and *Espírito Santo* recession times were similar and showed median values of 4h (p>0.05). Generally, the recession time increased with rainfall amount (r ranged between 0.163 and 0.432 for the different gauging stations, p<0.01) and maximum hourly intensity (r ranged between 0.178 and 0.393 for the different gauging stations, p<0.01), as well as with the runoff (r ranged between 0.150 and 0.436 for the different gauging stations, p<0.01) and baseflow component (r ranged between 0.148 and 0.470 for the different gauging stations, p<0.01). But no significant correlation was found between recession time and antecedent rainfall

(API_7). The recession time, as well as the response time, did not seem to be affected by season, but only 7% of the 310 individual storms analysed occurred during the summer.

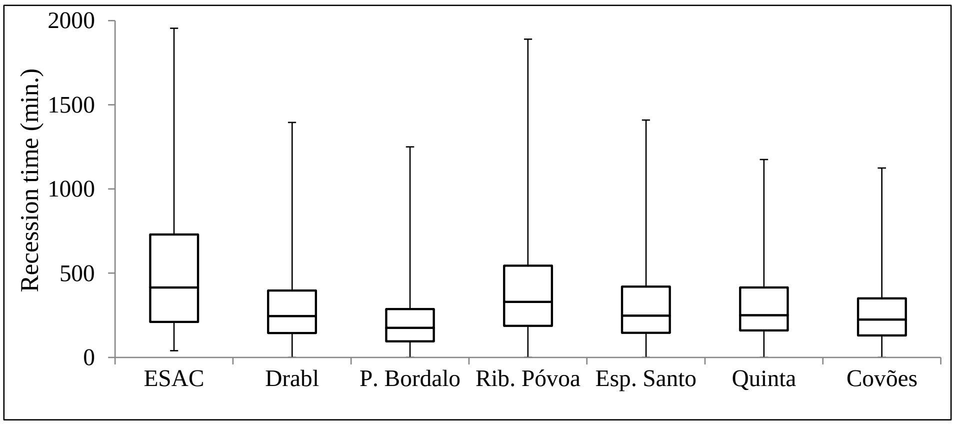


Figure 5.27 - Differences in recession time of storm events for the ESAC catchment and its sub-catchments.

5.5. Discussion

5.5.1. Hydrological response of catchment to weather and climate

Rainfall seems to be the main driver of *Ribeira dos Covões* streamflow. Nevertheless, previous studies performed under Mediterranean conditions also reported the importance of temperature on runoff, due to its influence on potential evapotranspiration (Lacey and Grayson, 1998; Rose and Peters, 2001; Lana-Renault et al., 2011). Rainfall and temperature also influence baseflow (e.g. Lacey and Grayson, 1998), which represents an important component of the catchment annual discharge (37-39%). Rainfall has positive and negative effects on baseflow in different seasons, as a result of baseflow recharge factors which affect groundwater discharge to streams. Over the year, BFI increases during wetting (autumn) and wettest (winter) months, but reached highest values during the summer (37% and 63% in wet and dry seasons), as a consequence of the antecedent recharge. Only in September was there a substantial decrease of BFI (Figure 5.15b), due to lower rainfall and higher water losses promoted by greater evapotranspiration (resulting from higher summer temperatures), which leads to a drop in groundwater level. The impact of climatic factors on the water table fall was greatest during the driest hydrological year (2011/12), when BFI attained the lowest annual value (36%) (Figure 5.14b). Decreased groundwater level as a result of driest conditions may be also linked with enhanced groundwater pumping, for irrigation uses. Based on field observations, 32 wells for irrigation purposes were identified in *Ribeira dos Covões*, mainly located in the agricultural SE and SW parts of the catchment (overlying sandstone) and in the valley bottom. In Makaha valley, Hawai, between 1971 and 1991, groundwater pumping was estimated to reduce streamflow by 19-22%. Subsequent additional pumping linked to the use of a new irrigation well leaded to a 36% reduction on streamflow (Mair and Fares, 2010).

Quinta drainage area, located in upslope sandstone, showed an almost continuous flow over the year, provided by several active springs, which supplied 16% of the catchment baseflow (Figure 5.21b). Only during the driest summer of 2011/12 were there a few days without flow, as well as in the subsequent hydrological year (Figure 5.18).

Generally, the low BFI of *Ribeira dos Covões* (36%-39%) is typical of catchments with low storage capacity (Braund et al., 2013), i.e. high evapotranspiration loss (Figure 5.12), but also linked to deep water infiltration. The great infiltration results from the generally deep soil and the easy infiltration of rainfall provided by abundant carbonates and sandstones. In addition, the deep filled valley on which the catchment is located may lead to subsurface flow under the gauge, which contributes for the low annual runoff coefficients (14-22%) measured.

The seasonal variability of rainfall has a noticeable impact on streamflow discharge, which increases during the rainy seasons and is restricted in summer. Dry soils in summer lead to a small streamflow response, low storm runoff coefficients (Figure 5.17), as typically observed under Mediterranean conditions (Lana-Renault et al., 2011). Lower storm runoff coefficients in September/October (beginning of the rainy season) have been attributed to the rainfall being used to recharge catchment soil moisture (García-Ruiz et al., 2008; Lana-Renault et al., 2011). As a consequence, during dry conditions, infiltration-excess overland flow is the only active runoff process, occurring in response to short and intense rainstorms, mostly over degraded areas (compacted soils with limited vegetation cover) and on hydrophobic soils.

In *Ribeira dos Covões*, hydrophobicity was identified within woodland areas and abandoned agricultural fields (Chapter 3). The impact of hydrophobicity on soil matrix infiltration capacity and enhanced overland flow have been reported at the hillslope scale (e.g. Ferreira, 1996) and at catchment level (Ferreira et al. 2000), particularly in *Ribeira dos Covões*, as discussed on Chapter 3. However, results from stream gauging stations show a limited impact of infiltration-excess from hydrophobic soils at the sub-catchment scale. During summer months, infiltration-excess overland flow promoted by hydrophobic soils lead to a slight increase in the storm runoff coefficients measured in *Ribeiro da Póvoa* and *Covões* (Figure 5.20), with the largest woodland areas, mainly covered by pine and eucalypt, linked to greatest soil hydrophobic conditions (e.g. Doerr et al., 2000). Nevertheless, the low impact at the sub-catchment scale, may be a result of the bypass of run-on water through preferential flow paths to deep soil layers, typical of vegetated hydrophobic soils (Dekker and Ritsema, 1994; Doerr et al., 2000), but also due to enhanced evapotranspiration and great surface water interception and retention of the limited rainfall amount typical of summer storms, which may be not enough to fill the surface depressions and run-off freely (Darboux et al., 2001). Grayson et al. (1997) also found that vertical flow is the controlling factor for the dry state of the soil. However, during dry periods, in *Ribeira dos Covões*, streamflow abstraction for private reservoirs and field irrigation was observed in sandstone areas. This may reduce the already limited streamflow which reaches the gauging stations, masking the hydrophobicity impact on catchment discharge. This was seen, for example, within *Quinta* drainage area, where a landowner diverts the streamflow into a tank with a capacity of approximately 100 m^3, placed 500 m upslope the gauging station.

Overland flow also occurred in wet periods during larger rainfall events, demonstrated by the significant positive correlation between runoff and rainfall intensity during storm events. The influence of this runoff process was clearly noticed in 16th November 2009, during the largest rainfall event of the study period (Figure 5.14a). However, during the wetting-up and drying-down transition periods, the hydrological response was variable, with infiltration-excess and saturation runoff processes occurring at the same time in different parts of the catchment, depending on the depth of the water table (which could be a pershed water table on slopes) before the event and the storm characteristics (depth and intensity).

Saturation overland flow was more prone in late winter and beginning of spring, as a result of greater soil moisture content, favoured by water table rise. Soil saturation was observed in some valley bottoms, particularly under sandstone and catchment downstream. This led to greater storm runoff coefficients from individual late winter/spring storms 2-19 times higher than in summer (Figure 5.22). Soil saturation was also observed in shallow soils (<0.4 m) of the limestone hillslopes (Ferreira et al., 2014), accompanied by subsurface lateral flow (Figure 5.28a). Subsurface saturation restricts deeper percolation and enhances the flow above that layer (Dahlke et al., 2012). Macropore flow can be a major process controlling the hydrologic response of a catchment to storm events (Peters and Ratcliffe, 1998). Nevertheless, subsurface lateral flow was also observed within sandstone areas, particularly in upslope areas (Figure 5.28b). Subsurface flow has been reported to be an important component of the catchment hydrology (McDaniel et al., 2008; Buda et al., 2009).

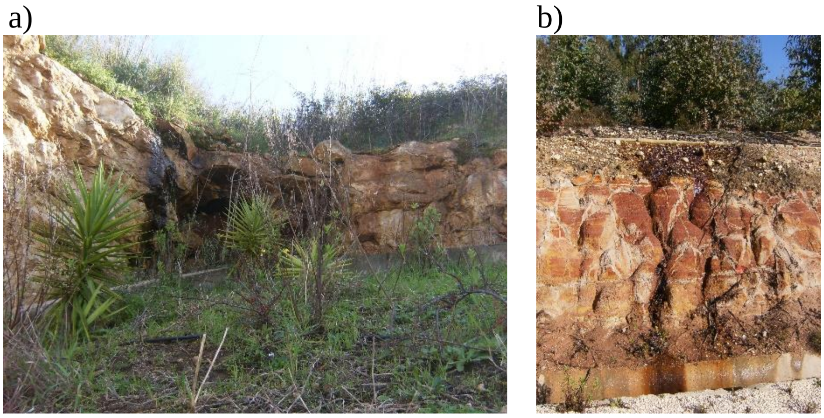


Figure 5.28- Subsurface lateral flow observed in a) limestone shallow soils and b) upslope sandstone.

In *Ribeira dos Covões*, analysis of individual storm events also showed increased storm runoff coefficients with greater antecedent soil moisture, as a consequence of enhanced flow connectivity over the hillslope and between the hillslope and the stream network. This is indicated by the significant positive correlations between storm runoff coefficient and the antecedent precipitation index. In addition, storm size has an effect on the occurrence of water ponding as well as on flow connectivity. With smaller storms, patches of saturation (or near-saturation) were smaller and the degree of connectivity was markedly lower, resulting in smaller trench responses. The location and extension of saturated areas varies through time, with antecedent soil moisture. These variable source areas have been identified in previous studies in other climatic settings (Troendle, 1985; Easton et al., 2008; Dahlke et al., 2012; Cheng et al., 2014).

Flow connectivity is not confined to overland flow but may be also established at the subsurface, depending on soil moisture distribution. This pattern is influenced by topography, which controls the dynamics of isolated patches of saturation, defining the hillslope hydrological system and the catchment response (Famiglietti et al., 1998; Zehe et al., 2005). Meerveld and McDonnell (2006) demonstrated that the connectivity between subsurface saturation patches was a necessary prerequisite for exceeding the rainfall threshold needed to drive sub-surface lateral flow in a Mountain catchment of Georgia, USA. A study performed by Hopp and McDonnell (2009) in a hillslope of Georgia, showed that significant lateral subsurface stormflow (>1 mm) only occurred when more or less well connected hillslope-scale areas of saturation or near saturation (within 95% relative saturation) developed at the soil–lithology interface, if the input exceed the topography-related threshold to induce spilling that leads to connection. Recent studies have shown that during autumn wetting (Harpold et al., 2010) and wet (winter) periods (McDaniel et al., 2008) near-stream areas connect with hillside saturated areas if the transient water table in the hillslope establishes whole-slope hydraulic connectivity. Reduced hillslope connectivity restricts the generation of saturation overland flow to small portions of the study area during the heavy rainy season (Haga et al., 2005). Srinivasan and McDowell (2009) found that disproportionately large runoff amounts are contributed by less than 10% of the catchment area.

Although no significant seasonal difference being observed in the response time of storm events analysed in *Ribeira dos Covões* catchment, rapid streamflow response was observed during near-saturation conditions in previous studies performed under Mediterranean climate, due to greater flow connectivity (Hopp and McDonell, 2009; Nasta et al., 2013).

5.5.2. Lithological influence on the streamflow regime

Lithology plays an important role on *Ribeira dos Covões* discharge, mainly due to baseflow regulation. Median annual BFI did not surpass 5% on limestone areas (*Porto Bordalo*, *Drabl* and *Covões*), whereas in sandstone it ranged between 25-33% in upstream tributaries (*Espírito Santo* and *Quinta*, respectively) and 37-38% in downstream areas (Figure 5.19a). These differences indicated the perennial regime of most of the sandstone areas, which contrasts with the ephemeral regime of the streams draining the limestone areas.

In the study site, seasonal variability on BFI was also affected by the lithology. On limestone BFI was twice as high in the dry than wet season, whereas in sandstone it was twice as high under wet conditions. These seasonal changes promoted by the lithology did not correlate with differences in the number of days without flow. Downstream gauging stations showed a continuous (at the outlet) or almost uninterrupted flow over the year, despite the great difference in the baseflow levels between sandstone and limestone areas (mean annual baseflow of 47 mm in *Ribeiro da Póvoa* and 5 mm in *Drabl*). In upstream areas, limestone gauging stations (*Porto Bordalo* and *Covões*) showed nearly twice as many days without flow than the sandstone stations (*Espírito Santo* and *Quinta*). However, larger number of active springs within *Quinta* drainage area provided more days with flow than *Espírito Santo* (Figure 5.18). Only in later summer did the flow from springs cease. Spring locations may be favoured by the presence of geological faults (Figure 5.2a).

Differences in baseflow were driven by the water table position within the distinct lithological units. Water table was closer to the surface in topographic lows, and seems to follow the hillslope relief under sandstone areas, whereas in limestone it seems to be deeper. Under limestone, typical rock fragmentation may provide deep water infiltration and horizontal movement (Almeida et al., 1999), as observed in *Ribeira dos Covões* (Figure 5.28). The multilayer aquifer systems associated with the limestone hillslopes, may provide water storage capacity through the rainy season. However, the limited water storage in superficial deposits and the thin soils of limestone areas, lead to rainfall conversion into storm runoff which enters directly to the stream via overland flow, exhibiting a lower baseflow component in the stream discharge. This could be also favoured by the lower woodland cover under limestone areas, leading to lower evapotranspiration losses than in sandstone areas.

Greater silt and clay soil contents in limestone leads to lower permeability than sandstone soils (Ferreira et al., 2012c), enhancing storm flow which reaches the stream network. This may partially explain the higher storm runoff coefficients and greater peak flows measured in limestone areas during individual rainfall events. Median storm runoff coefficients reached 2.6% and 3.4% for *Drabl* and *Porto Bordalo*, whereas in sandstone dominated areas they were <1.5% (Figure 5.22). *Drabl* also reached median peak flows twice as high as at *Ribeiro da Póvoa*, despite draining half size of the area (Figure 5.23). In addition, peak flows in *Drabl* (reached after 10 minutes) were quickly transferred downstream and contributed to the *ESAC* peak flow (Figure 5.26).

Despite the above stated differences between baseflow among limestone and sandstone areas, the impact of lithology on the recession time was not noticeable (Figure 5.27). This may be a result of the influence of different land-use and several topographic characteristics, such as relief, elevation, length of stream network and drainage density (Zecharias and Brutsaert, 1988; Nathan and McMahon, 1992; Lacey and Grayson, 1998). The similar recession time between *Drabl* and *Covões* may be due to similar lithology, altimetry and mean slope (Table 5.1). *Drabl* and *Espírito Santo* have similar land-uses (Figure 5.6), *Drabl* and *Quinta*, as well as *Espírito Santo* and *Covões* drains areas with similar size, *Espírito Santo* and *Quinta* are both located in upstream sandstone, with similar altimetry, and *Quinta* and *Covões*, drain the largest woodland areas. This suggests the dominance of overland flow on storm runoff.

5.5.3. Impact of land-use and urbanization pattern on streamflow

During the study period, land-use, and particularly urban areas, did not seem to be a significant factor controlling the streamflow response, possibly due to climate variability. Although previous studies have identified the land-use as a critical variable in the examination of stream discharge (e.g. Tang et al., 2005; Galster et al., 2006; Loperfido et al., 2014), other researchers reported the dominance of the weather settings and the catchment characteristics on the hydrological response within urbanizing catchments (Rose and Peters, 2001; Braud et al., 2013). Some methods have been devised to separate the influence of climate and land-use on the hydrology (Semadeni-Davies et al., 2008; Franczyk and Chang, 2009), but these methods require long data records and are not appropriate if the land-use changes were already happening during the hydrological measurements response, as in *Ribeira dos Covões*.

Although the limited discharge records preclude consideration of long-term hydrological trends, some comments may be inferred as regards to the land-use change in *Ribeira dos Covões*, and specifically to urbanization impact on storm hydrographs and baseflow component. At the catchment scale, there was not a clear change tendency on annual runoff coefficients through the study period, linked to the urbanization pattern, but runoff coefficient was greater in late 2012/13 (22% of the rainfall). Nevertheless, the slightly higher rainfall between 2012/13 than 2009/10 (Figure 5.11), reflected in a 5% increase on annual runoff coefficients (Figure 5.14) may be indicative of the urbanization influence (6% increase in the urban area and 5% increase of the impermeable surfaces), particularly noticing the minor decrease on annual BFI. Urbanization has been widely reported to enhance runoff and reduce baseflow components of the stream discharge (Shuster et al., 2005; Zhang and Shuster, 2014). However, in *Ribeira dos Covões* the decreasing BFI was more a result of the lower recharge in the antecedent dry year than a consequence of the urbanization, particularly considering the larger aquifer beneath the study site.

During the study period, greatest peak discharge across the catchment was also observed in 2012/13 (Figure 5.16), demonstrating a twice higher magnitude than in previous years, greatest than rainfall peak increase. However, the comparison of storm events observed between January 2011 and September 2013 did not show increasing peak flows and storm runoff coefficients over time (Figure 5.29). Nevertheless, the relationship between the urban increase and these streamflow variables may not be noticed for storm events with small return period, as the ones observed during the study period (<2 years). Hollis (1975) reported that paving over 5% of the landscape did not affect flood peaks with a return period of one-year. However, increasing runoff and peak discharges with urbanization have been reported in studies performed in USA (e.g. Cook and Dickinson, 1985; Rose and Peters, 2001).

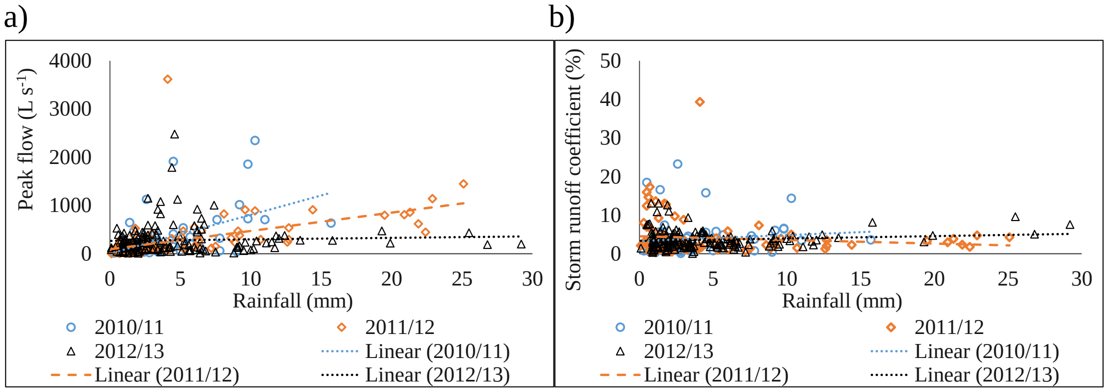


Figure 5.29 – Relationship between rainfall amount and a) peak flow, and b) storm runoff coefficient, of storm events observed between 2010/11 and 2012/13, at the catchment outlet.

Since increasing urban area in the last few years did not seem to affect the peak flows in *Ribeira dos Covões* catchment, the greatest peak observed in 2012/13 may be a result of greater flow connectivity enhanced by greater soil moisture, as discussed in section 5.4.3.2., associated with the higher rainfall of that year. Larger time series and a multiple regression approach may be useful to explore this in future work.

Based in all gauging stations results, if the hydrological impact of different lithological units (discussed in 5.5.2 section) are considered, runoff coefficient increased with urban and impermeable surfaces cover (Figure 5.30). *Quinta* and *Covões* with the largest woodland areas (>80%) of the sandstone and limestone sides, respectively, showed the lowest runoff coefficients (14% and 7% over the study period), apart from *Porto Bordalo*. Lower runoff in woodland areas may result from higher transpiration losses and greater water interception and retention (e.g. Mahmood et al., 2010; Wang et al., 2013). Surface roughness, characteristic of woodland land-uses, increases soil irregularities and cavities and therefore depression storage capacity, creating opportunities for water infiltration, delaying or eliminating overland flow transfer to downstream (Appels et al., 2011; Rodríguez-Caballero et al., 2012). Vegetation can create a mixture of run-off and run-on sites, determined by soil wetness in semiarid environments, of utmost importance to interrupt hydrological connectivity (Appels et al., 2011; Castillo et al., 2003).

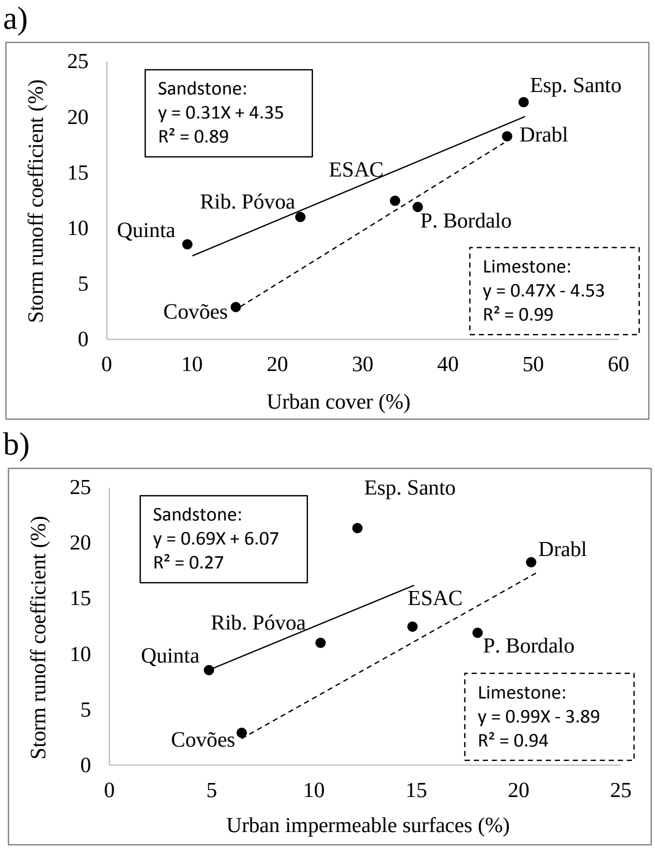


Figure 5.30 - Linear relations between storm runoff coefficients over three years and the mean (a) urban area and (b) impermeable surfaces cover, within *Ribeira dos Covões* drainage areas.

Impermeable surfaces seems to control the runoff during dry periods, since despite the generally lower runoff coefficient than in the wet season, the largest surface flow was measured within the most urbanized areas, *Espírito Santo* and *Drabl*. In this highly urbanized areas, the winter flow was 2-4 times higher than in dry periods, whereas in the other drainage areas, less urbanized, the seasonal difference in the measured flows was greater, and reached flows 21 time higher during wet period's storms than summer flows in *Quinta*.

Impermeable surfaces have been widely reported to generate overland flow and to increase hydrological connectivity (Tang et al., 2005; Meijía and Moglen, 2009). However, in sandstone areas, despite the runoff coefficient increased with the urban area, the correlation with the impermeable surfaces was rather weak (Figure 5.31b). This may be attributable to differences in the urbanization pattern, particularly in *Espírito Santo* and in the overall catchment (*ESAC*), which affect flow connectivity over the landscape. *Espírito Santo* drains a small area with greatest urban cover (Figure 5.6). Within this urban area, mostly represented by older houses, the storm runoff from the impermeable surfaces was dispersed in soils between the impermeable urban surfaces or downslope agriculture and woodland areas. The absence of storm drainage systems are typical in oldest urban cores. In urban areas, the location in the landscape between overland flow delivery and the stream network seems to be an important parameter affecting the flow connectivity and the catchment discharge.

Over the study period, despite the great urbanization within *Quinta* (urban areas increased from 9 to 25%), mainly associated to the upstream enterprise park construction, storm runoff did not increase (9%, Figure 5.17b). This may be attributed to the minor surface sealing of the under construction enterprise park (70% of the area was bare soil, Figure 5.7). In addition, overland flow generated in the impermeable surface could infiltrated in nearby soils or was diverted to the detention basin. Nevertheless, the detention basin was designed to reduce the flood peak by temporarily storing the excess stormwater and then releasing the water volume at allowable rates over an extended period (Ravazzani et al., 2014). Apart from the enterprise park, the remaining urban cores established within *Quinta* were mostly dispersed in upslope woodland and/or agricultural fields, enhancing the infiltration opportunities before overland flow could reach the stream network. On the other hand, in *Covões*, the 2% enlargement of the urban area during the study period (Figure 5.6) led to a storm runoff coefficient increase from 3% to 9% (Figure 5.17b). However, the new impermeable surfaces were mostly in downslope locations, where the stormwater from roads and rooftops (released on sidewalks) was partially routed to the stream channel.

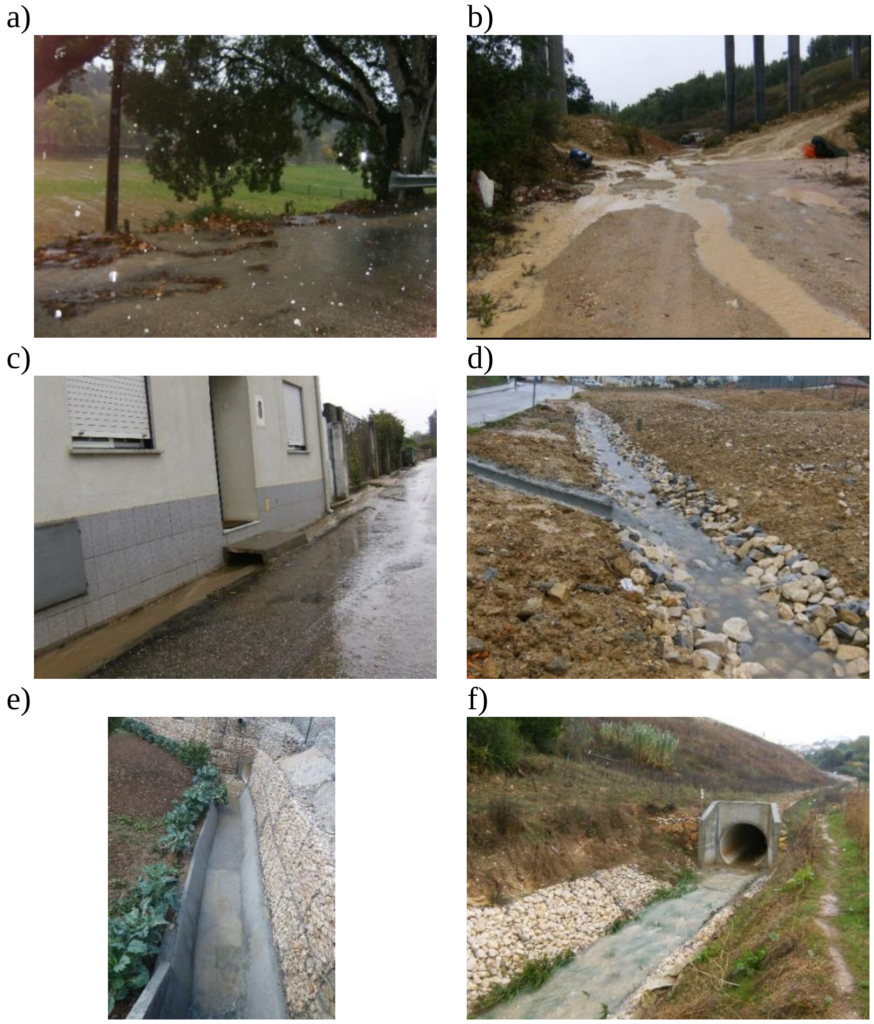


Figure 5.31 - Contrasting stormwater management strategies: a) overland flow runs freely to downslope agricultural or b) woodland soils; c) storm drainage systems collect and deliver overland flow into the stream network, downslope section of *ESAC* catchment and d) downslope *Drabl*; and e) stream channelization within downstream *Porto Bordalo* and f) *Drabl*.

Although impermeable surfaces generate overland flow, several urban features may obstruct water passage to downslope, breaking the flow connectivity. Surface water retention may occur due to: 1) tanks used to store channelized streamflow for irrigation purposes (Figure 5.32a); 2) surface depressions promoted by soil movement in construction areas (Figure 5.32b); and 3) embankments such as roads constructed above natural terrain level (Figure 5.32c), houses and walls constructed in topographic lows (Figure 5.32d).

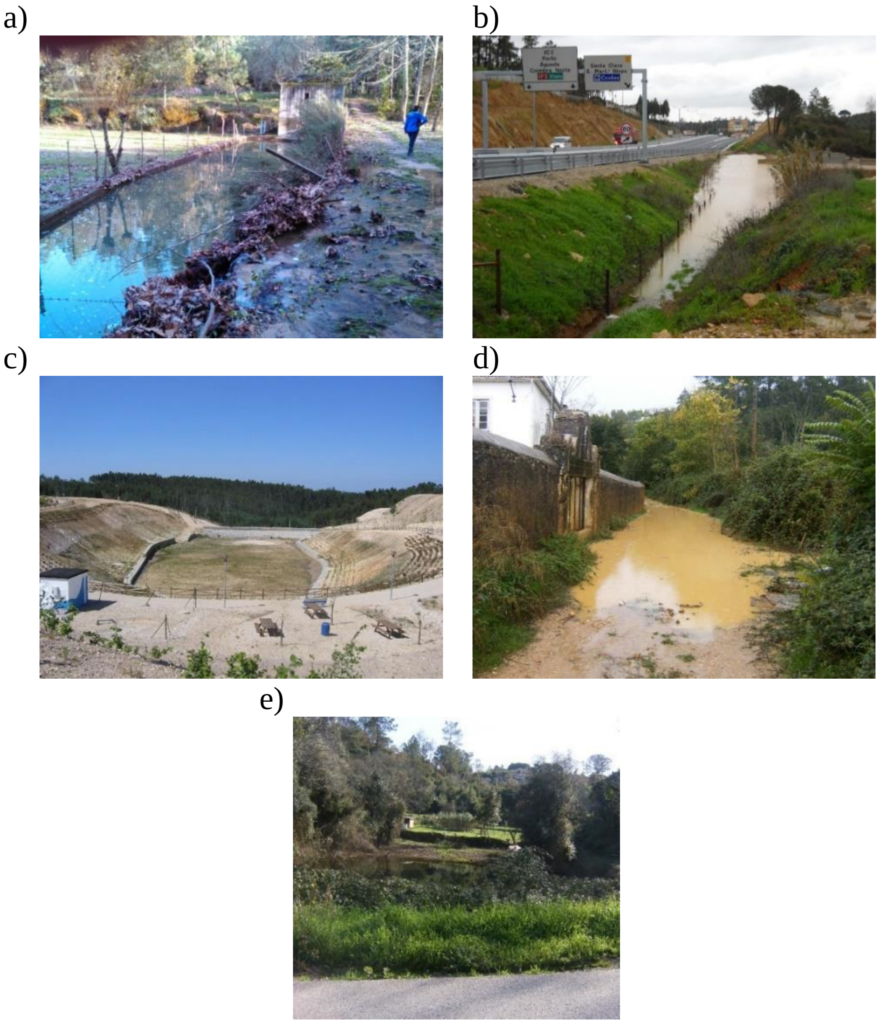


Figure 5.32 - Urbanization features that provide surface water retention: a) tank used for irrigation purposes (~700m^3), b) surface depression within a construction site (~1100m^3), c) detention basin, d) overland flow retention promoted by walls, and e) road embarkment.

Most of these urban features were located in *Porto Bordalo* and led to a lack of connectivity between sources of overland flow and the stream network. This surface water retention explains the lower increase of stream discharge during wettest conditions, when saturation was observed in some upslope sites. Also an increase of urban areas from 35 to 42% only increased impermeable surfaces by 2%. Most of the flow which reached *Porto Bordalo* gauging station represents overland flow diverted by the storm drainage system installed in downslope urban areas.

The area between *Porto Bordalo* and *Drabl* gauging stations, despite only representing 26% of *Drabl* drainage area, provided 51% of its stormflow. This was not only because of the lack of connectivity within *Porto Bordalo*, but also because the great connectivity within this highly urbanized area (encompasses nearly 80% of the *Drabl* urban area), promoted by the storm drainage system (Figures 5.32c and 5.32d). The greater flow connectivity provided by the storm drainage system within the urban areas was also observed in the downslope *ESAC* drainage area (below *Drabl* and *Ribeiro da Póvoa* gauging stations), covering 19% of the catchment area. This area was characterized by 50% urban land-use and was largely served by a storm drainage system (road runoff collection), leading to 15% contribution to the catchment storm flow. The downstream part of *Ribeiro da Póvoa* (21% of the drainage area), despite being ~35% urban, supplied only 20% of the gauging station stormflow. This lower contribution from the urban areas, may be a result of a lower storm drainage system coverage, such that part of the overland flow generated finds its way to downslope soils where it infiltrates and fails to reach the stream network.

Only a few studies have investigated the effect of urban areas and impermeable surfaces, and their spatial arrangement, on runoff volume, as well as the impact of storm drainage system. In a catchment in Indiana, USA, Tang et al. (2005) demonstrated the greater impact on runoff volume from urban growth dominated by commercial and high density residential uses, compared with the low density residential areas. Several researchers have found, through statistical analyses of field data, that some types of urbanization had no discernible effects on peak-flows or floods (Dudley et al., 2001). Despite an 161% increase in catchment imperviousness from 1.3 to 3.5% in a 34 km^2 catchment located in southern Maine, Dudley et al. (2001) found that there was no significant change in peak flows and hydrograph shape. Hammer (1972) also reported the small effect of impervious areas associated with detached houses, unless the gutters connect directly with storm sewers. Storm drainage systems result in little opportunity for infiltration. These impacts were also reported in the review of impacts of impervious surfaces on catchment hydrology (Shuster et al., 2014). Through modelling, Zhang and Shuster (2014) also demonstrated that increasing distance to the stream is associated with weaker connectivity, because of the infiltration opportunities downslope. Complex interplays between spatial distributions of soil, impervious area and catchment shape may result in considerable differences within catchments in the changes of runoff behaviour in response to urbanization.

Increasing imperviousness tends to enhance the depth and speed of overland flow by diminishing infiltration and leading to quicker response time (Zhang and Shuster, 2014). However, the location and the characteristics of the urban cores, particularly the presence or absence of storm drainage systems, also have an important impact on the response time. *Drabl* and *Espírito Santo*, with the largest percentage of urban areas, reached peak flows in less than 20 minutes (Figure 5.26). Nevertheless, *Drabl* drains a considerable larger area than *Espírito Santo*, but in *Drabl* the stream network receives water mostly from downslope urban areas, mainly via storm drainage system, whereas in *Espírito Santo* overland flow runs over the surface because of the absence of storm drainage system. A reduced response time during storm events was also found in *Porto Bordalo* and *Covões*. Despite draining smaller urban areas, the flow reaching the gauging stations was mostly supplied by the downslope impermeable surfaces and discharged by storm drainage systems a few metres above the gauging stations. In addition, the peak flows in *Porto*

Bordalo represented a considerable fraction of the *Drabl* peak flow. Peak flows in *Drabl* were reached, in median, only 5 minutes later than *Porto Bordalo* sub-catchment, located ~700 m upstream. The quick flow between these gauging stations was favoured by the artificial channelization of the stream (Figure 5.31e and 5.31f), which is used to carry excess water rapidly away (Baker et al., 2004). The downstream *Ribeiro da Póvoa* and *ESAC* gauge stations, draining larger areas partially covered by storm drainage systems, required in median 40-50 minutes to reach the peak flows. In natural catchments, larger streams are usually less flashy than small ones, due to hydrograph mixing accompanying flood routing through stream networks and other scale dependent runoff factors (Baker et al., 2004). In *Quinta*, longer response time (~50 minutes) was probably due to in part to the distance of the upslope urban cores from the stream network, as the overland flow from impermeable surfaces flowed into the downslope woodland soil and infiltrated before reachig the stream network, as refered on section 5.4.3.2.3.. Also in the recent enterprise park area, overland flow was diverted from the detention basin which delays the peak flow observed in *Quinta* gauging station. According with Baker et al. (2004), the construction of storm runoff holding basins is a water management practice that could shift flow regimes back toward a more natural condition.

An urbanization impact on the recession time of storm events was not perceived (Figure 5.27), possibly due to different sizes of the drainage areas (*ESAC* and *Ribeiro da Póvoa* with largest areas showed longer recession time), but also due to differences in the overland flow drainage systems. Previous studies reported reduced recession time in downslope areas of the catchment, in larger streams, as a result of the storm drainage systems on rapid transportation of runoff, which mask the effect of the natural drainage (Baker et al., 2004). A study performed by Hood et al. (2007) also reported increased lag times in areas with low impact development, associated with disconnected impervious areas, than traditional residential development.

Generally, the study of *Ribeira dos Covões* catchment showed that peri-urbanization, characterized by dispersed urban cores and low imperviousness, enhance the lack of flow connectivity within the landscape, favouring the maintenance of a more natural streamflow, associated with minor stormflows and larger recession time. On the other hand, urbanization styles favouring extensive impervious surface will enlarge streamflow during rainfall events, particularly if runoff is piped to the stream network. This type of urbanization, mostly associated with recent urban cores, can have detrimental impacts on flood hazard, particularly if downslope areas are occupied by urban land-uses. Few past flood events affected downslope urban areas located adjacent to the watercourse. The enlargement of impervious surface within urban areas, mainly located downslope and supplied by artificial drainage systems, can enlarge the flood risk within these areas.

5.5.4. Spatial pattern of urbanization and stormwater management: problems and future challenges

Actual landscape arrangement within *Ribeira dos Covões* comprises urban areas mainly along ridges and downslope catchment (Figure 5.8). Urbanization pattern over the last decades created distinctive urban settings characterized by different extension of impermeable and semi-permeable surfaces, with storm runoff routed to the stream network naturally (following the topography) or through artificial drainage systems. Discharge measurements performed in different sections of the stream network revealed generally low annual runoff coefficients. Streamflow increased with the urban land-use cover, but it was affected by the presence or absence of storm drainage systems, and the distance between the source or the storm discharge and the stream network. Urban features, such as houses, walls and road embankments, particularly in valley bottoms provided surface water retention, breaking the flow connectivity between the sources and the stream network. Analyses of storm events revealed greater flows under antecedent wettest conditions, demonstrating the increased surface and subsurface connectivity as soil moisture increases. The limited retention capacity provided by urban features may represent an additional flood hazard, since they may be exceeded by overland flow in major rainstorms.

On 25th October 2006 an extreme daily rainfall event of 102.1 mm led to floods. According to Brandão et al. (2001), in Coimbra, rainfall events of 93.6 mm day^{-1} and 112.2 mm day^{-1} have return periods of 10- and 50-years respectively. Flood damage included the collapse of walls and costs linked to the flooding of houses in topographic lows. The collapse and “dam failure” of urban features which usually retained storm runoff exacerbated the problem of downslope and downstream areas. It is unclear if the major flood driver was urbanization or extreme rainfall, but according to older local residents, other significant flood events were reported about 50 and 80 years ago.

The presence of the storm drainage systems and the partial channelization of the stream network leads to quicker runoff concentrations in downslope areas. Althoug the median response time of the catchment was 40 minutes, sub-catchment gauging stations with downslope urban areas (*Porto Bordalo*, *Drabl* and *Covões*), reached peak flows in less than 20 minutes. This flashy response of the catchment highlight the problem of the local authorities to activate timely warning and alert systems.

However, within *Ribeira dos Covões*, problems with storm management were not only observed in the downstream section of the catchment, where flow depths are usually greater. The lack of capacity of the stream network and/or hydraulic infrastructures located upslope also caused occasional inconvenience for local population. These problems were driven by the partial obstruction of culverted drains with sediments and/or plant material (Figure 5.33a), and the limited flow capacity of some stream sections (Figure 5.33b). These problems were identified mainly near *Quinta* gauging station, and are recognized by the local residents as an increasing problem after the construction activities in the upslope enterprise park. The deforestation of a considerable area increased the overland flow and although the retention basin stores most of this and releases it after a delay, the flow capacity of the downslope stream is not enough to carry all the additional runoff promoted by the urbanization process. Damages has been reported in the downslope agricultural fields, in terms of crop losses and soil erosion.

a) b)

Figure 5.33 - Problems with current storm drainage system: a) decreased flow capacity of drain pipes due to sediment deposition, and b) limited flow capacity by artificial bottleneck of the stream channel.

Projected urban changes indicate a substantial development within the catchment for the near future, mainly in the upper catchment, with the enlargement of the enterprise park area. This additional urbanization will enhance even more the runoff and reduce water infiltration opportunities, exacerbating the actual problems of stormwater management. To minimize these problems it would be necessary to enlarge the river bed, particularly downslope the enterprise park. However, this will bring social resistance since the stream flows through private properties, and expropriation processes or loss of private land is always difficult to accept, at least in Portugal. On the other hand, it is also important that responsible authorities provide adequate maintenance and cleaning of the river bed and hydraulic structures. But different authorities are responsible for the stormwater management across the catchment. For instance, local authorities are responsible for the stream bed, municipal water authority is responsible for the storm drainage system, whereas hydraulic structures associated with the major road construction belong to the national semi-private authority responsible for the national roads. The involvement of different legal authorities within the same catchment is not easy and represents a management challenge, particularly within a national scenario of economic crises.

An additional challenge is related to the stream network flowing mainly through private properties, some of them fenced without easy access, which makes intervention by the authorities difficult. Thus, landowners sometimes take actions which affect the streamflow. For example, in 2014, a landlord decided to install small branches and trunks in the stream channel, few metres upstream *Ribeiro da Póvoa* gauging station, within his property, in order to prevent bank erosion. However, this led to a local reduction of the flow capacity and flooding of the surrounding land. In the past, private owners were responsible for maintenance of the river bed, and they could be fined if inappropriate management was performed. The loss of this landowners' responsibility and restricted maintenance by the authorities has accentuated the state of degradation of many Portuguese rivers. Another problem resulting from rivers flowing through private properties is associated with illegal constructions close to the streams. For example, a private house under construction in the river bed, involved local stream diversion a few metres above *Espírito Santo* gauging station. Despite national legislation forbiden construction activities within 100 m of a river (Lei nº58/2005), cases like this do occur. The current houses and walls installed in valley bottoms of *Ribeira dos Covões* should be of increasing concern in a continuous urbanization process, not only because of the social expropriation problems already discussed, but also for the economic and social fragilities of these local residents.

Appropriate stormwater management is required to minimize the runoff increment provided by additional urbanization. This requires a complement to the actual and the above stated measures associated with the current storm drainage system. Additional measures may include dry detention ponds to store and delay runoff excess in the limestone areas, infiltration basins within sandstone areas (based on greater infiltration capacities of sandstone than limestone soils) and use of permeable pavements in the new urban cores. These structures and measures would diminish increases in peak discharge and runoff volume, as well as increases lag times and retention of smaller and more frequent rainfall events (Baker et al., 2004; Hood et al., 2007; Loperfido et al., 2014).

Structural measures, however, need to be complemented with non-structural measures, such as adequate land management and urban planning at the catchment level. The magnitude of the potential benefits of land-use planning based on water resource impacts, in particular on runoff processes and systems affected by runoff processes, is largely unknown. A few studies, however, have been demonstrating the potential of distributed hydrological models to investigate the hydrological impacts of new urban areas. Zheng and Baetz (1999) evaluated design alternatives for new urban cores and found that designs with smaller total development area can effectively reduce the increase of peak flows and total runoff volumes due to development, when compared with less efficient designs. Moglen et al. (2003) suggested a framework for quantifying smart growth in land development in which the runoff impact was reduced by minimizing the total area change in imperviousness. Both studies revealed that the impact of development can be reduced by limiting the total impervious area. Ravazzani et al. (2014) used a distributed hydrological model to evaluate the impacts of downstream detention basins, in order to investigate the best location within the urbanized catchment to install them. Nonetheless, the magnitude that runoff can be minimized depends on site specific land-use types, soil properties and the urbanization level of a catchment. Smart growth is being promoted as a progressive approach to development. One of the goals of smart growth is water resources protection, in particular minimizing the impact of urban sprawl on runoff and systems affected by runoff processes (Tang et al., 2005)

5.6. Conclusions

Land-use changes, particularly associated with peri-urbanization have affected the hydrological processes. In *Ribeira dos Covões* catchment, although urban surfaces cover near 40% of the catchment area annual runoff coefficient did not exceed 22%. This chapter highlighted the importance of distinct biophysical properties, such as weather, lithology and urban style and its distribution over a catchment on streamflow variation:

1. Runoff is mainly generated by infiltration-excess overland flow processes, dominant during dry conditions, and by saturation and subsurface lateral flow during wet weather. Through wet season, increasing surface and subsurface flow connectivity, promoted by soil moisture rise, led to highest storm runoff coefficients in late winter. However, in *Ribeiro da Póvoa* (mainly sandstone) and *Covões* (mostly limestone), storm runoff coefficients were higher in the summer, possibly due to infiltration-excess promoted by woodland hydrophobic soils.

2. Sandstone areas showed a perennial regime, with few days without flow even in driest periods, and with baseflow representing 30% to 40% of the annual flow. Streams in limestone areas were only active during rainfall events, except *Drabl* which is located downslope, showing a continuous trickle flow. Thus, baseflow delivered by the limestone areas represented ~2% of the annual catchment baseflow. During storm events, limestone areas provided a greater contribution to the peak flow at the catchment outlet than sandstone areas. Quicker response time in limestone than sandstone sub-catchments were found (<15 minutes vs. 15-50 minutes).

3. Considering the results from gauging stations installed in similar lithology, storm runoff coefficients over the study period increased with the urban cover and provided quicker peak flows. In sandstone areas storm runoff coefficients ranged from 9% in *Quinta*, with 9% urban area, and 21% in *Espírito Santo*, represented by 23% urban surface. Overlaying limestone, storm runoff coefficients ranged from 3% in *Covões*, with a 15% urban area, to 18% in *Drabl*, encompassing 47% urbanization.

4. Over the study period, the urbanization impact on streamflow at the catchment outlet and upstream gauging stations varied according with the type of urbanization, particularly if it was patchy and dispersed within the landscape or not, the distance to the stream network and the type of storm drainage system. An urban area increase of about 2% (from 15% to 17%), mainly located downslope and with storm runoff being piped to the stream led to a storm runoff increase from 3% to 9% in *Covões*. On the

other hand, an urban cover increase from 9% to 25% (*Quinta*), in upslope locations and with storm runoff coefficient being diverted to downslope urban and woodland soils, did not have a discernible impact on storm runoff coefficient (14%). The type of urbanization also plays an important impact on the storm reponse time, with downslope urban areas connected to artificial storm drainage system reaching the peak flow in 5 minutes (*Covões*), wereas in larger areas with upslope dispersed urban cores it takes 40 minutes (*Ribeiro da Póvoa* and *ESAC*). When storm runoff runs freely and/or is diverted into pervious soils it may be infiltrated. Furthermore, surface water retention, either provided by vegetated surfaces or urban infrastructures (e.g. embarkments and walls), may break flow connectivity and/or retard its downslope transfer, minimizing the impact of urbanization on streamflow.

The creation of local opportunities for water infiltration, provided by an appropriate urbanization pattern, associated with the size and position of urban developments on the landscape, the degree of sealing and the strategy for stormwater management (storm drainage system and the location where runoff is delivered within the landscape), should be considered in catchment management and urban planning. This is of utmost importance to break the flow connectivity and minimize flood hazard. However, identifying the best arrangement of urban patches whilst maximizing the use of land for urban development needs now to be a research priority.

CHAPTER 6

ASSESSING SPATIO-TEMPORAL VARIABILITY OF STREAMWATER CHEMISTRY WITHIN A PERI-URBAN MEDITERRANEAN CATCHMENT, IN RELATION TO RAINFALL EVENTS

ABSTRACT

Peri-urban areas are characterized by a complex land-use pattern which influences surface water quality. In this study, the impact of land-use pattern was investigated through surface water quality assessment in *Ribeira dos Covões*, a peri-urban catchment (615 ha) in central Portugal, with a 40% urban cover. Besides catchment outlet, surface water quality was monitored in three upstream locations, encompassing different drainage areas (56 – 150 ha). Two of the sub-catchments are of similar percentage urban cover (42% and 49%) but different lithologies (sandstone and limestone), whereas the third is of lower urban extent (25%) and includes a construction site covering 10% of its drainage area. Numerous surface water samples were collected during ten rainfall events (of different amount and intensity), between October 2011 and March 2013. Several chemical parameters, including nutrients, major cations and metals were analysed. The results were compared with Portuguese national water quality guidelines for environmental and irrigation uses, and the spatio-temporal variation of pollutant loads was assessed. The outcomes of the study highlight the complexity of spatio-temporal impact on surface water quality, particularly considering the variations of analytical parameters between sites. Generally, chemical loads per unit area increased in the study site with greater urban land-use extent. Parameters such as EC, COD, NO_2+NO_3, Ca, Mg and K on dissolved phase of surface water also increased with percentage impervious surface. The role of hydrological connectivity between pollutant sources and the stream network is discussed. COD, nutrients (Nk, NH_4, NO_2+NO_3 and TP) and Mn attained highest concentrations during the first rainfall events after the summer, as a result of lower dilution effect provided by the low discharge. Standards for minimum water quality and recommended guidelines for irrigation practices were occasionally exceeded, not only during low flow conditions, but also in wettest settings. Further monitoring is required for a fuller understanding of the spatio-temporal changes of water quality. The information gained, however, should guide sustainable landscape management and urban planning, in order to avoid conflicts between urban development and water quality degradation in peri-urban catchments.

Keywords: land-use, rainfall, connectivity, spatio-temporal variation, surface water quality

6.1. Introduction

The replacement of natural land surfaces, including woodland and agricultural areas, by impervious coverage, such as paved roads, car parks and roofs, leads to significant changes on both quantity and quality of the stormwater runoff, with deleterious impacts on stream ecosystems (e.g. Arnold and Gibbons, 1996; Brilly et al., 2006). Urban runoff has been considered a major non-point source of pollutants within catchments (Wahl et al., 1997; Schoonover and Lockaby, 2006; Yu et al., 2012). Research studies have identified high loads of heavy metals from industrial sources (Pitt and Maestre, 2005; Qin et al., 2013), roads and vehicular traffic (Ellis et al., 1986; Emmenegger et al., 2004; Gilbert and Clausen, 2006; Li et al., 2012) and material corrosion (Neff et al, 1987). Organic matter, nutrients and pathogenic microorganisms have been also found with greater concentrations within urban areas due to sewage contaminations, resulting from septic tanks (Gold et al., 1990; Steffy and Kilham, 2004), combined sewer systems (Gromaire et al., 2001; Soonthornnonda et al., 2008; Mannina and Viviani, 2009), sewage leaks (Le Pape et al., 2013) and discharge of wastewater treatment plants (Yu et al., 2014). In addition, high loads of nutrients and the presence of pesticides have also been identified in the runoff from pervious urban surfaces, such as lawns and golf courses, as a result of inappropriate management, linked to fertilization and irrigation activities (Steuer et al., 1997; Khai et al., 2007). Soil erosion also represent a significant source of suspended sediments, as well as nutrients and heavy metals in particulate forms (Line et al., 2002; Goonetilleke et al., 2005; Atasoy et al, 2006). These contaminants will have a detrimental impact upon water quality and aquatic organisms.

It is usually accepted that pollutant loads increase with the percentage of total impervious area (Arnold and Gibbons, 1996; Morse et al., 2003; Kuusisto-Hjort and Hjort, 2013). However, the impact of different urban cores configuration (e.g. isolated houses with gardens vs townhouses) and their location within catchments have been recognised as important parameters affecting pollutant transport and water quality impacts (e.g. Corbetts et al., 1997). Based on a study performed in Queensland, Australia, Goonetilleke et al. (2005) observed greater pollutant load from detached houses than multifamily dwelling units, due to a greater extent of road surface area and higher nitrogen concentrations resulting from gardens extension and fertilise use in detached housing areas comparing with high-density residential development. Main roads and industrial areas have been also associated with greater suspended sediments and heavy metals than residential, open spaces and commercial areas (Pitt and Maestre, 2005). In addition, the location within the landscape can play a significant role on streamwater quality impact. Urban areas located downslope may provide runoff flowing into the stream network, whereas runoff from upslope areas may be infiltrated and/or retained in downslope pervious areas (Groffman et al., 2004; Wilson and Weng, 2010; Carey et al., 2011), if the natural drainage is not replaced by artificial drainage systems.

The complex landscape of peri-urban areas, characterized by a mosaic of different land-uses and urban infrastructures, determines the potential sources and sinks of pollutants and the impacts on streamwater quality (Booth and Jackson, 1997; Brabec et al. 2002; Groffman et al., 2004). Despite the importance of knowing potential runoff and pollutant sources and understanding their connectivity with the stream network, it requires further investigation. Apart from land-use, runoff properties can vary significantly with rainfall characteristics, such as the amount and intensity (Memon et al., 2013; Yu et al., 2014). For example, Rodríguez-Blanco et al. (2013) observed that 68% of phosphorus transport ocurred in storm events. In a small catchment of Macau, chemical oxygen demand (COD) ranged between 41 and 464 mg L^{-1} during five rainfall events (Huang et al., 2007). Inter-storm variability observed in a typical urbanizing area of China also leaded to mean COD concentration with 5-folder difference (Qin et al., 2013). Furthermore, the length of Antecedent Dry Period (ADP) may greatly affect runoff discharge and its characteristics, due to pollutant accumulation, from atmospheric deposition (Sullivan et al., 1978; Valiela et al., 1997; Easton and Petrovic, 2004) from natural sources (e.g. pollen) and human activities, such as vehicular traffic (Bannerman et al., 1993; Li et al., 2012). During rainfall events, pollutants are totally or partially washed-off, depending on rainfall characteristics. Rainfall intensity determines the available energy to overcome surface resistance (Athayde et al., 1982), whereas rainfall volume affects the removal rates and pollutant dilution (Helsel, 1978). Higher pollutant concentration during dry seasons have been reported by several authors (Barbosa and Hvitved-Jacobsen, 1999; Zhang et al., 2007), but the influence of climate on temporal variability of pollutant load and its influence on streamwater quality is not fully understood.

The main aim of this part of the study is to investigate the impact of different land-uses and distinct urbanization patterns, typical of Portuguese peri-urban areas, on surface water quality during storm events. The specific objectives are to: 1) assess spatio-temporal variability of several physical-chemical parameters (including solids, nutrients, major cations and metals) of the streamwater, during different rainfall events; 2) explore the influence of rainfall pattern on chemical loads; 3) verify if the monitored parameters exceed Portuguese minimum surface water quality and irrigation water uses; and 4) discuss the influence of land-use pattern on streamwater quality.

Knowledge of spatio-temporal variability of potential runoff and pollutant sources and sinks are relevant to guide decision-makers and policy actors to implement the most suitable solutions to achieve good water quality and preserve aquatic ecosystems. However, understanding the relationship between land-uses and physical-chemical runoff properties, and how they change before reach the stream network, is essential for urban planning and catchment management, in order to prevent water quality degradation within peri-urban areas.

6.2. Study Area

The *Ribeira dos Covões* study area has been characterized by a fast urbanization process, linked to population increase from about 2500 to 8000 inhabitants between 1958 and 2011. Nowadays, the land-use is largely dominated by woodland areas (56%), with a significant urban cover (40%) and only minor sparse agricultural fields (4%). Urban land-use comprises mostly residential areas, including some leisure areas, commercial buildings (small supermarkets and pastry shops), educational and health services, including a central hospital, and few facilities (garage shops, sawmill and a pharmaceutic industry). An enterprise park, covering 5% of the catchment area, is under construction in the catchment headwaters. A network of roads extends across the catchment, covering 7% of its area, and includes a recent motorway. Residential areas comprise distinct urban cores with contrasting urbanization styles, marked by single-family houses, most of them surrounded by gardens, and apartment blocks (mostly in downslope catchment). These distinct residential areas are linked to contrasting population densities, ranging from <25 inhabitants km^{-2} to >9900 inhabitants km^{-2} (Tavares et al., 2012). Agricultural land-use is dominated by a few olive plantations, pasture areas with extensive cattle rearing and small family farms. Pasture areas are mostly concentrated along the stream network.

Within the urban areas, the artificial drainage network encompasses separated systems for stormwater and wastewater transport. Urban storm runoff is collected in culverts and gutters, covering the majority of the road network, and is routed/piped to the main river or into its tributaries. In urban settlements surrounded by agricultural and woodland soils, stormwater just dissipates in these areas. Runoff from the enterprise park is partially routed to a retention basin and then to a downslope tributary, with a delay during peak flows. Domestic effluent is piped to a wastewater treatment plant (WWTP), located outside the catchment. However, a small WWTP was installed about 30 years ago within *Ribeira dos Covões*, in an upslope area, in order to receive the wastewater from a small urban core. Despite being abandoned several years ago, only recently (~3 years) was it effectively disabled, with the wastewater being routed to the larger sewer network. During this period, sewage was piped to the WWTP infrastructure and released to the surface water network. The landowners of downslope agricultural fields reported several damages on crop production and irrigation systems during this period.

In this region, water supply for human consumption is provided by groundwater sources, whereas surface water is mostly used for irrigation purposes.

6.3. Methodology

6.3.1. Sampling strategy: spatial and temporal

Locations for surface water sampling were considered in order to assess the influence of different land-uses, particularly with distinct urban cores. Apart from the catchment outlet (*ESAC*), three additional sub-catchment sites were selected upstream: *Espírito Santo*, embracing an urban land-use associated with high imperviousness intensity; *Porto Bordalo*, with similar urban extent but sprawl imperviousness; and *Quinta*, encompassing a minor urban area but covering the enterprise park under construction (covering 10% of the drainage area) (Figure 6.1). However, the selected sub-catchments do not differ only in land-use, but also in the extent of drainage areas and lithology, as shown in Table 6.1. Flow regime of the selected drainage areas is also distinctive: *ESAC* has perennial flow, whereas the *Quinta* and *Espírito Santo* streams dry in summer, and *Porto Bordalo* flow is ephemeral.

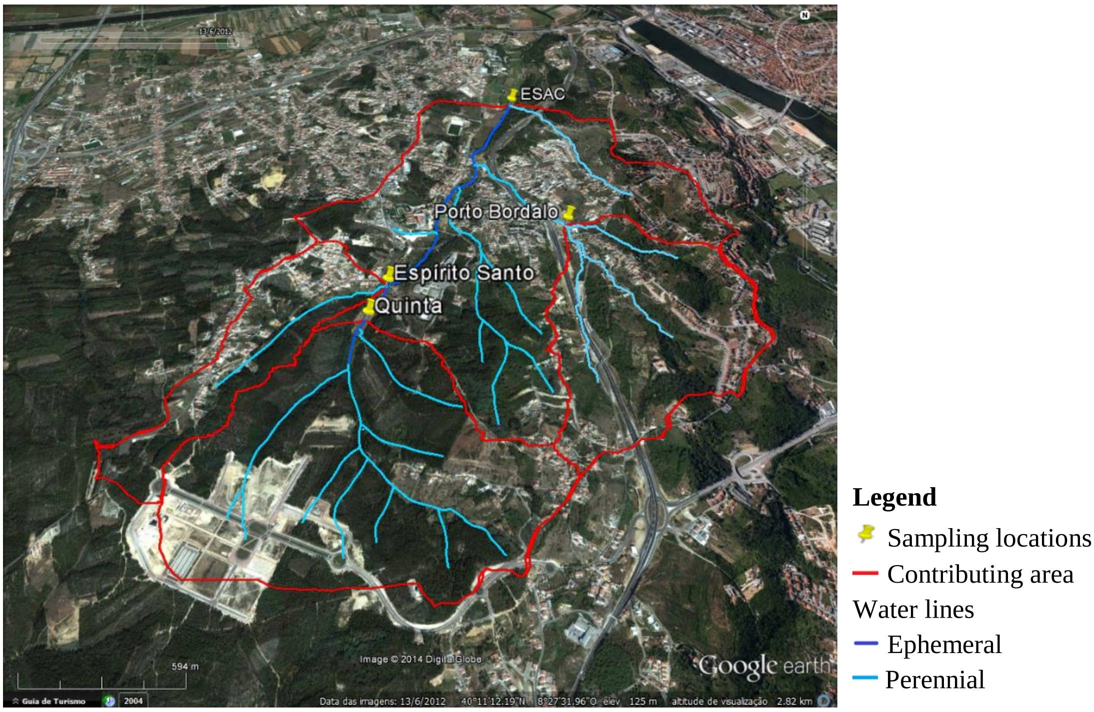


Figure 6.1 - *Ribeira dos Covões* catchment and location of the sampling sites (adapted from Google Earth, 2012).

Table 6.1 – Catchment and sub-catchment characteristics: land-use, mean slope and lithology (S.: sandstone, L.: limestone; A.: alluvial).

Sampling site	Area (ha)	Land-use / Land cover (%)						Mean slope (°)	Lithology (%)		
		Urban			Woodland	Agricultural	Open spaces		S.	L.	A.
		Impervious	Semi-pervious	Pervious							
ESAC (outlet)	615	20	9	10	54	4	3	10	56	41	3
Porto Bordalo	113	15	8	19	55	3	0	12	2	98	0
Espírito Santo	56	27	7	15	46	5	0	8	97	0	3
Quinta	150	5	17	3	67	5	3	4	100	0	0

NOTE: Land-use and land cover was based on Corine Land Cover 2007, and updated through Google Earth Imagery 13/06/2012 and field observations. Within the urban areas, impervious surfaces represent sealed soil, such as roads and buildings, semi-pervious consists of construction sites, parking zones, courtyards and sidewalks, and pervious surfaces encompasses gardens. Open spaces consists of clear-felled areas.

Surface water samples were collected during 10 rainfall events, observed between October 2011 and March 2013. Sampling dates were based on weather forecast, in order to assess rainfall events with different frequency, following dry and wet conditions. Prior to each rainfall event, whenever possible, one sample was taken from each monitored site, if stream was flowing, to provide the base water quality level. Additional samples were collected after the rainfall start, in order to assess hydrograph variation (raising limb, peak discharge and the falling limb). Samples were collected manually. Due to limited human resources, samples were taken at different times in each study site. Time differences ranged between 15 to 30 minutes for equivalent site samples, except in cases were no significant flow difference was observed when compared with the previous sample taken on that specific site. It was considered that rainfall event ended when no additional rainfall was observed during a period of 8 h (Asdak et al., 1998). Because of the different flow regimes between study sites, the number of water samples was dissimilar. In total, 76 samples were taken in *ESAC*, 75 in *Porto Bordalo*, 56 in *Espírito Santo* and 58 in *Quinta*. Each sample was analysed for a large number of water quality parameters.

Rainfall and discharge data were provided by the hydrological network in *Ribeira dos Covões*. Rainfall data were provided by weighted average values from 5 rainfall tipping-buckets (assumed for all the sub-catchments), and discharge data was provided by water level records, with a 5-minutes interval, at each stream gauging station.

6.3.2. Analytical procedures

Grab water samples were collected into different containers, according with the analytical parameters. Two-liter polyethylene bottles were used for chemical oxygen demand (COD), nitrogen, including kjeldahl nitrogen (Nk), ammonium (NH_4), and nitric oxide (NO_2+NO_3), major cations (such as sodium (Na), magnesium (Mg), calcium (Ca) and potassium (K)), and metals (such as iron (Fe), manganese (Mn), cupper (Cu), zinc (Zn) and cadmium (Cd)). Smaller polyethylene bottles (250 mL) were used for pH, electrical conductivity (EC), total dissolved solids as NaCl (TDS), turbidity and total solids (TS) analysis. Glass bottles (250 mL) were also used to collect samples for total phosphorus (TP) quantification. Some water quality parameters including pH, EC and TDS were measured on site, using a portable meter (Hach, Sension Portable case). The samples were transported to the laboratory in thermal boxes with ice (~4ºC) and stored.

In the laboratory, the 2-L water samples were filtered through a 0.45 μm nitrocellulose filter (Millipore filters), using a vacuum pump, in order to quantify the dissolved fraction of several chemical elements, as described in Standard Method 3030-E (APHA et al., 1998). Aliquots of filtered samples were then stored in smaller bottles. For major cations and metals, samples were acidified with nitric acid and frozen until analysis. Samples for COD, Nk, NH_4 and TP were acidified with sulphuric acid and subsequently frozen. Samples for nitric oxide were only frozen. Sample storage and preservation was performed in accordance with Standard Method 1060-C (APHA et al., 1998).

Turbidity was analysed in the original water samples, using a single beam spectrophotometer (Hach DR 2000) according with the HACH-8237 method, range 0-1000 NTU (HACH, 1999). Total solids (TS) were quantified through sample evaporation at 105ºC, until constant weight, following Standard Method 2540-B (APHA et al., 1998).

COD was quantified by using a low range (0 to 150 mg L^{-1}) kit test (HI 93754A-25, Hanna Instruments). The sample was measured (2 mL) into digestion vials and oxidized at 150ºC during 2h, in a reactor digester (HACH), under acidic conditions. The remaining dichromate ion concentration was determined through absorbance at 420 nm (Hach DR 2000 spectrophotometer). The method is in accordance with EPA 410.4 and ISO 15705:2002 standards. Total phosphorus was also analysed with a low range (0.00 to 3.50 mg L^{-1}) test kit (HI 93758A-50, Hanna Instruments). The method is based on acid persulfate digestion at 150ºC over 30 minutes (Hach reactor digester), followed by reaction with molybdate ascorbic acid and antimony potassium tartrate. Subsequent quantification was performed at 610 nm (single beam spectrophotometer, Hach DR 2000) (adapted from EPA 365.2 and 4500-P E Standard Methods).

Analytical procedure for Tk (including ammonia, organic and reduced nitrogen forms, excluding nitrate and nitrite) was based on Standard Method 4500-Norg B (APHA et al., 1998), with samples digestion performed at 400ºC, during 2h (J.P. Selecta reactor), with selenium catalyser. Digested samples were than distilled in a Kjeltec System 1026 Distilling Unit (Tecator), followed by titration with hydrochloric acid, performed in automatic burette.

Ammonium nitrogen was quantified according with the Skalar Method 155-316 (Skalar, 2004a), based on ISO 14255: 1998. This method focus on molecular absorption spectrophotometry, performed in a segmented flow auto-analyser (SAN^{++} system). It is based on a modified Berthelot reaction and subsequent quantification at 660 nm. Nitric oxide was also measured in the auto-analyser SAN^{++} system, using the Skalar Method 461-322 (Skalar, 2004b). This method was adjusted from ISO 14255: 1998 and is based on nitrate reduction within a cadmium-cupper column, coupling with N-1-napthylethylenediamine dihydrochloride and quantification at 540 nm.

Major cations and metals were quantified after digestion with nitric acid, in accordance with Standard Method 3030-E (APHA et al., 1998), through ebullition in hotplates. Individual chemical elements were than quantified by atomic absorption spectrophotometry (Perkin Elmer AA300 analyser), with direct air-acetylene flame method and corresponding hollow cathode lamp, in accordance with Standard Method 3111-B (APHA et al., 1998).

Water samples were defrozen at room temperature before analysis. Some samples required dilution, in order to fit the method range. Reagent blanks and duplicate samples were used for quality control purposes and mean concentration values (repeated analysis of same sample) were used in data analysis.

6.3.3. Data analysis

The hydrological regime of the ten sampled rainfall events was characterized in terms of rainfall and stream discharge. For each rainfall event, the amount, duration and intensity of the rainfall was calculated. Rainfall intensity was described in terms of the event mean value (Imed) and maxima in 15- and 60- minutes (I_{15} and I_{60}). Antecedent precipitation index values were calculated as the sums of the precipitation in 7 and 14 days prior to each rainfall event (API_7 and API_{14}). Streamflow parameters used included instantaneous flow (at the time of water sampling) and event flow description. Surface and baseflow components were also estimated for individual hydrographs, using a mathematical digital filter (Nathan and McMahon, 1990).

The results of surface water quality parameters were visualized by box- and whisker diagrams for the four study sites, over the ten rainfall events monitored. Statistical differences between the four study sites were investigated through the analysis of individual water qualiy parameters (based in all the sample results of each site), using the non-parametric Kruskal-Wallis test, since the criteria for normal distribution was not met. Surface water quality differences over the time were also explored for individual parameters, considering all the measurements performed in each rainfall events, based on the same statistical test. Whenever significant spatial and/or temporal water quality differences were identified, further investigation was carried out with post-hoc Fisher's Least Significant Difference test. All the statistical analysis were accomplished for a 95% confidence interval. The relationship between individual water quality parameters, and between water quality and the discharge properties at the sampling time (flow, surface and baseflow component at sampling time) were explored using Spearman's rank correlation coefficient (r).

Water quality parameters were compared with Portuguese guidelines, established for environmental goals of minimum surface water quality, as well as for irrigation uses (Ministry of Environment, 1998). As regards to irrigation purposes, the results were compared with the established maximum recommended values (MRV) and maximum admissible values (MAV) defined by the legislation. According with the Portuguese water irrigation standards, Sodium Adsorption Relation (SAR) parameter was calculated for individual water samples (equation 1):

$$\mathrm{SAR} = Na \,/\, [(Ca + Mg)\,/2]\ ½ \qquad (1)$$

where Na is the concentration of sodium; Ca is the concentration of calcium, and Mg represents the concentration of magnesium. All the concentrations are expressed in meq L^{-1}.

In order to assess the impact of different rainfall events on water quality, pollutant loads were calculated for the four study sites. Event load (EL) was estimated for all quantifiable parameters analysed, based on weighted mean concentration per rainfall event (EMC) (equation 2). EMC was calculated using equation 3, adapted from Qin et al. (2010) methodology, developed for discrete water samples.

$$\mathrm{EL} = \mathrm{EMC} \times \mathrm{Qt} \qquad (2)$$

where EL is the event load, EMC is the event weighted mean concentration, and Qt is the total streamflow during the event.

Total streamflow represents the cumulative flow during individual sampling events. The duration of the streamflow was defined by the time between the first and the last water sample collected in each monitoring date. This assumption does not consider the different flow regimes between study sites, displayed by dissimilar hydrograph shapes. However, this criterion was considered the most adequate for comparison purposes between study sites, since water samples were collected at different times and distinct stages of the hydrographs.

$$\mathrm{EMC} = \sum (\mathrm{Ci} \times \mathrm{Qi}) \,/ \sum \mathrm{Qi} \qquad (3)$$

where EMC is the event mean concentration, Ci is the concentration at time i, and Qi is the streamflow at time i.

Specific event loads (SEL) were calculated by dividing EL for the extent of the drainage area, in order to better assess the impact of different land-uses within the study sites. SEL represents the mass of the physical-chemical property washed off per unit area per rainfall event, and describes the area-averaged intensity of runoff property loads.

The impact of hydrological processes and catchment biophysical properties on spatio-temporal variation of EMCs and ELs, was explored through Spearman correlation analysis (r). The role of the rainfall characteristics (amount, duration, intensity – including Imed, I_{15} and I_{60}) on catchment physico-chemical parameters wash-of and their influence on stream water quality was considered, together with the possible effect of build-up parameters between rainfall events (through the correlation of EMCs and ELs with API_7 and API_{14}). The correlation of EMCs and ELs with sub-catchments total streamflow during montitored rainfall events was investigated, as well as the importance of storm flow on catchment physico-chemical properties wash-off. The baseflow contribution for potential dilution effect of storm flow physic-chemical properties and/or contribution with specific chemical properties were also investigated. The influence of distinct lithologies (percentage of sandstone and limestone) on different water chemical parameters was also assessed through the correlation with EMCs and ELs. The biophysical properties of the sub-catchments also included the land-use cover (percentage of woodland, agriculture and urban) and the extent of impervious surfaces (percentage of the drainage area). All statistical analyses were performed using IBM SPSS Statistics 22 software.

6.4. Results and analysis

6.4.1. Storm rainfall

Sampling performed in *Ribeira dos Covões* catchment was linked to different rainfall events, associated with dissimilar amount, duration and intensity, following different antecedent weather conditions, as summarized on Table 6.2 and shown on Figure 1 of Annex. Rainfall ranged from small (2.3 mm) to larger amounts (46.8 mm), falling within a few hours (2.3 h) or more than one day (93.3 h). The rainfall event of 02/11/2011 was different from all the other measurement dates ($p<0.05$), in terms of its greatest rainfall intensity (I_{15}=24.0 mm h^{-1}).

Table 6.2 – Rainfall and mean runoff characteristics of monitored rainfall events.

		Rainfall							Mean runoff (mm)				Peak runoff (mm h^{-1})			
Sampling	Sampling date	Depth (mm)	Duration (h)	I_{mean} (mm h^{-1})	I_{15} (mm h^{-1})	I_{60} (mm h^{-1})	API_7 (day)	API_{14} (day)	ESAC	Porto Bordalo	Espírito Santo	Quinta	ESAC	Porto Bordalo	Espírito Santo	Quinta
1	23-24/10/2011	7.9	13.0	0.6	6.4	3.1	0.0	0.1	0.20	0.32	0.00	0.00	0.14	0.26	0.22	0.11
2	26/10/2011	3.8	3.5	1.1	8.8	8.4	28.1	28.1	0.07	0.10	0.20	0.10	0.09	0.27	0.19	0.13
3	02/11/2011	24	2.3	10.7	24.0	15.9	22.7	50.8	0.51	0.66	1.51	0.16	0.84	2.85	0.40	0.83
4	14/11/2011	8.9	7.8	1.1	10.8	3.6	32.9	98.5	0.63	0.62	1.36	0.64	0.23	0.45	0.29	0.24
5	16/12/2011	3.6	4.5	0.8	4.4	1.6	33.6	43.2	0.15	0.09	0.24	0.14	0.07	0.14	0.10	0.04
6	04/05/2012	2.4	7.4	0.3	3.6	1.3	42.5	82.6	0.31	0.06	0.24	0.23	0.07	0.20	0.07	0.04
7	25-26/09/2012	14.3	22.1	0.6	7.2	4.1	14.3	14.3	1.11	1.79	3.26	1.00	0.32	0.83	0.32	0.17
8	08-10/01/2013	9.9	28.9	0.3	4.5	2.3	0.0	17.0	0.45	0.33	1.31	0.65	0.11	0.24	0.29	0.13
9	15-17/01/2013	20.2	24.6	0.8	6.0	5.4	25.4	25.4	1.36	0.97	2.80	1.63	0.43	0.83	0.32	0.22
10	25-29/03/2013	46.8	93.3	0.5	14.8	5.3	47.3	70.8	17.05	12.13	14.08	10.73	1.04	1.89	0.46	0.64

Mean storm streamflow increased with rainfall amount (Figure 6.2) (r=0.648 and 0.685 in *ESAC* and *Espírito Santo*, p<0.05), particularly in *Porto Bordalo* which exhibits a ephemeral flow regime (r=0.806, p<0.01). In *Quinta* sub-catchment, the largest woodland land-use cover (67%) and the presence of several springs, could have masked the significance of the correlation between mean runoff and rainfall depth (p>0.05). Only in *Porto Bordalo*, where part of the impervious surface runoff is piped directly to upstream gauging station, and *Espírito Santo*, with the largest impervious surface cover, was mean storm flow significantly correlated with maximum rainfall intensity measured in 15- (r=0.903 and 0.806, p<0.01, respectively) and 60-minutes (r=0.794 and 0.685, p<0.01). However, all the monitored sites showed peak flow increases with increasing rainfall depth (*ESAC*: 0.952, *Porto Bordalo*: 0.879, *Espírito Santo*: 0.994 and *Quinta*: 0.903, p<0.01) and rainfall intensity, with slightly stronger correlations with maximum 15 minutes than hourly intensities (*ESAC*: 0.745 vs 0.685, p<0.05; *Porto Bordalo*: 0.855 vs 0.830, p<0.01; *Espírito Santo*: 0.720 vs 0.665, p<0.05; and *Quinta*: 0.842 vs 0.733, p<0.01).

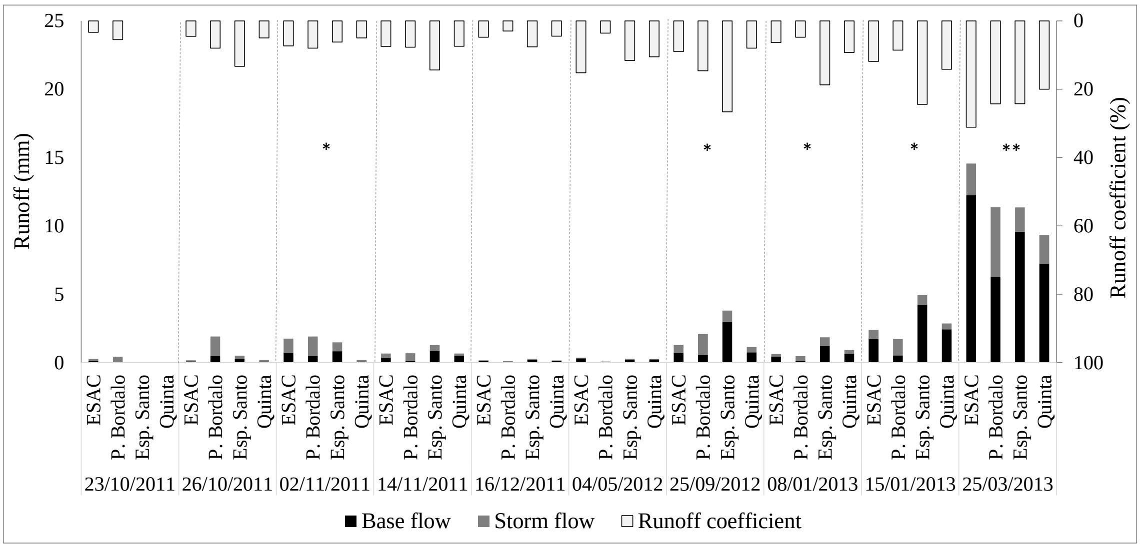


Figure 6.2 - Variation of runoff depth (base and storm component) and runoff coefficient at different monitoring sites, between sampling events (*larger event; **very large event).

During monitored rainfall events, *Espírito Santo*, which encompasses the largest impervious surface cover (27%), exhibited greatest median runoff coefficient (13.8%). However, *Quinta* with the smallest impervious cover (5% of the drainage area) exhibited a greater median runoff coefficient (8.0%) than *ESAC* (7.4% runoff coefficient and 20% imperviousness) and *Porto Bordalo* (6.6% runoff coefficient and 15% impervious cover). This is thought to be a consequence of the greatest baseflow component in *Quinta* (73%). Despite the median runoff coefficient in *ESAC* being lower than *Espírito Santo*, it reached 31% of the rainfall for the 25/03/2013, which may be linked to the greatest overland flow connectivity at the end of the wet season, given the similar baseflow contribution (84% of the streamflow in both gauging stations).

Generally, during monitoring rainfall events, streamflow within sandstone areas was dominated by baseflow, which represented, in median, 75% of *Quinta* flow, 69% of *Espírito Santo* and 62% of *ESAC* discharge (Figure 6.2). In *Porto Bordalo*, overlaying limestone, median baseflow did not surpass 24% of the streamflow during the storm events, highlighting the relevance of storm flow on stream discharge. Besides the low baseflow in the limestone area, the partial piping of the urban storm runoff to the *Porto Bordalo* stream may contribute to its greatest storm flow.

Baseflow amount follows a seasonal pattern (Figure 6.2), with lowest values observed after summer seasons (23/10/2011, 26/10/2011 and 25/09/2012) and greater values in the late wet season (15/01/2013 and 25/03/2013).

6.4.2. Surface water quality

6.4.2.1. Streamwater composition

Physical-chemical parameters

Water samples exhibited pH largely in the slightly acidic and lightly alkaline range (6.0-8.0), with few samples attaining stronger alkali characteristics (not surpassing 9.0). *Porto Bordalo* displayed the highest pH (median of 7.6), statistically different from the lower values observed in *ESAC* (median of 7.1, $p<0.05$). In *Espírito Santo* and *Quinta*, median pH were 7.3 and 7.4 (Figure 6.3). Over the study period, pH showed a tendency to decrease through the wet season.

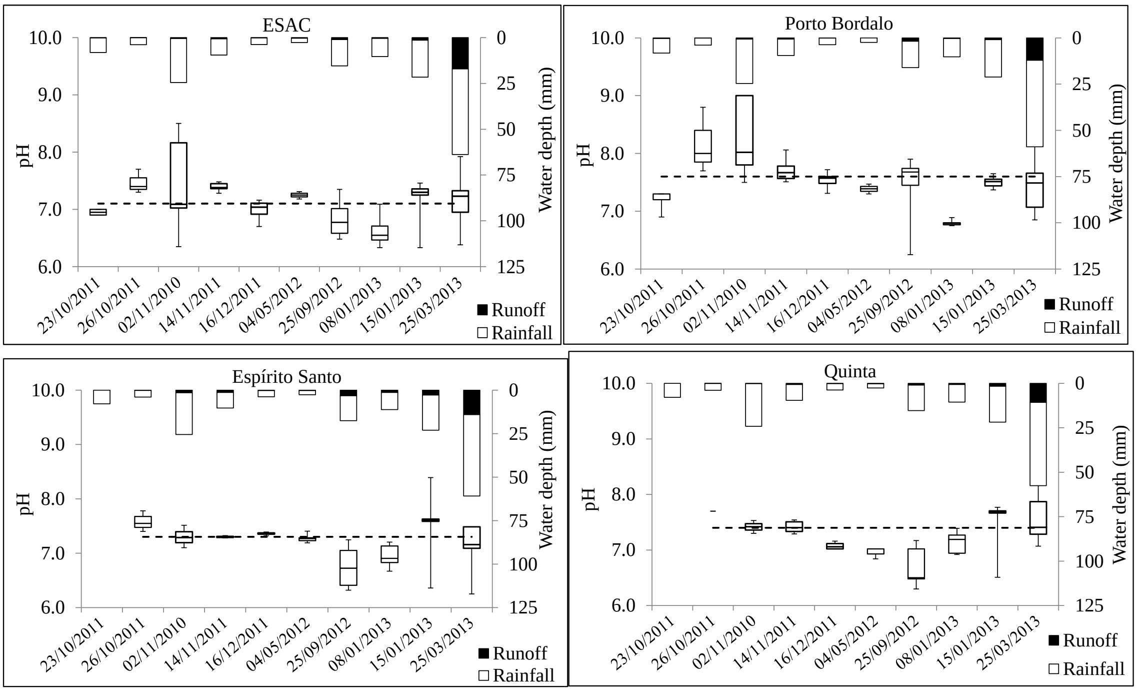


Figure 6.3 - Temporal variability of surface water pH between the four study sites. Dashed lines represent median values of all the results over the study period.

Electrical conductivity showed a wide range of values (32 – 991 µS cm^{-1}), associated with high heterogeneity between samples collected in same locations, particularly in autumn and spring rainfall events (Figure 6.4). Distinct distribution of EC values were found between the four study sites ($p<0.05$), however, only marginal median EC increase was observed from *Porto Bordalo* (160 µS cm^{-1}), to *Quinta* (182 µS cm^{-1}), *ESAC* (297 µS cm^{-1}) and *Espírito Santo* (318 µS cm^{-1}).

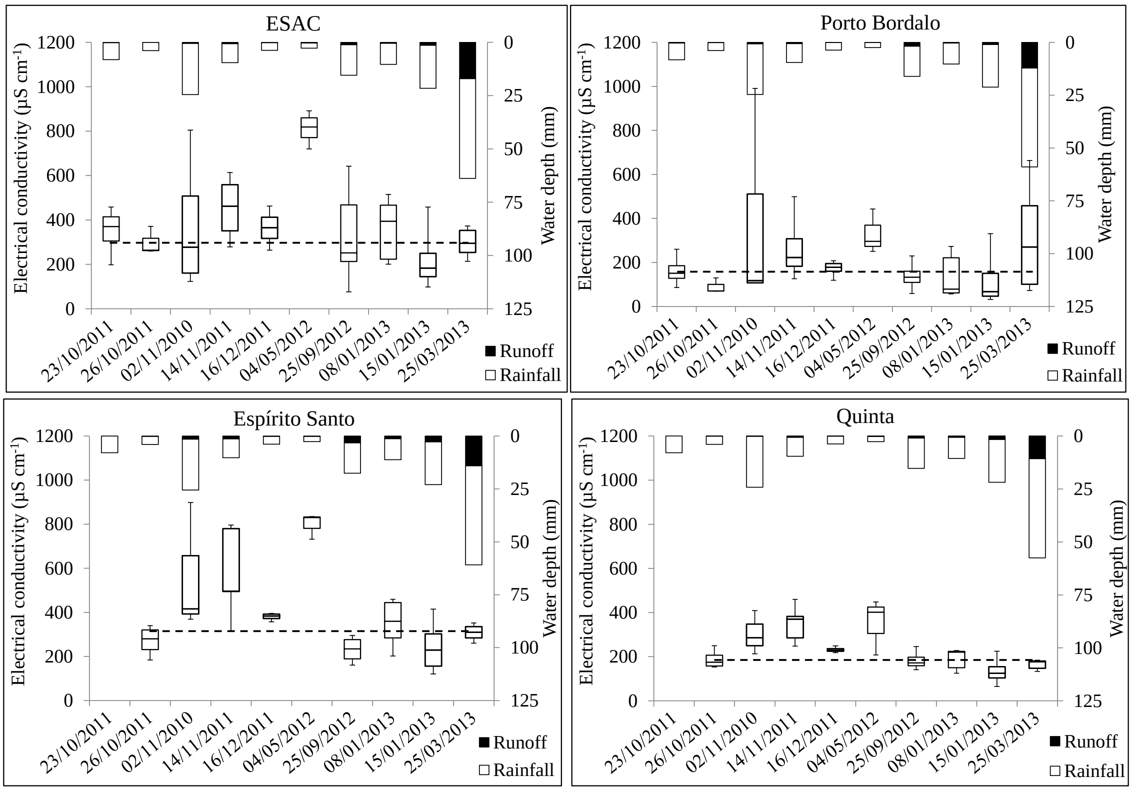


Figure 6.4 - Temporal variability of electrical conductivity between the four study sites. Dashed lines represent median values of all the results over the study period.

Temporal variability of EC was identified ($p<0.05$), with distinct results during 02/11/2011, 14/11/2011 and 04/05/2012 water sampling. During this measurments, median values between sites ranged from 117-416 µS cm^{-1} to 296-830 µS cm^{-1}. These rainfall events were characterized by a mix of greater rainfall intensity and antecedent precipitation in previous days (Table 6.2). Nevertheless, EC exhibited significant positive correlations particularly with TDS and TS ($r=0.816$, 0.397, $p<0.01$), as well as NO_2+NO_3, Na, Mg and Ca ($r=0.461$, 0.367, 0.639, 0.681, $p<0.01$) (Table 6.3).

Table 6.3 - Spearman's correlations between physical-chemical parameters of surface water and associated discharge characteristics, of all the surface water samples collected in *Ribeira dos Covões* during the study period (n=2623). Red color highlight strong (>0.4/-0.4) and significant correlations.

		pH	EC	TDS	Turbidity	TS	Pt	Nk	NH_4	NO_2+NO_3	COD	Na	Mg	Ca	K	Mn	Fe	Cu	Zn	Cd
pH	r	1.000	-.231**	-.152*	0.025	-.153*	-.230**	-.167**	-.218**	-.334**	-.128*	-.214**	-.250**	-.296**	-.204**	-.144*	.172**	0.020	-.167**	-0.009
	Sig. (2 tailes)		0.000	0.013	0.690	0.013	0.000	0.007	0.000	0.000	0.038	0.000	0.000	0.000	0.001	0.020	0.005	0.748	0.007	0.890
EC	r	-.231**	1.000	**.816****	-.138*	.397**	-.233**	-.194**	-0.107	.461**	0.016	.367**	.639**	.681**	.295**	.148*	0.026	-.128*	-.344**	-0.088
	Sig. (2 tailes)	0.000		0.000	0.025	0.000	0.000	0.002	0.087	0.000	0.795	0.000	0.000	0.000	0.000	0.016	0.678	0.038	0.000	0.155
TDS	r	-.152*	**.816****	1.000	-.163**	.357**	-.211**	-0.110	-0.093	.390**	0.008	.365**	.635**	.676**	.266**	.142*	.126*	-0.077	-.248**	0.062
	Sig. (2 tailes)	0.013	0.000		0.008	0.000	0.001	0.078	0.138	0.000	0.901	0.000	0.000	0.000	0.000	0.021	0.042	0.214	0.000	0.315
Turbidity	r	0.025	-.138*	-.163**	1.000	.573**	-.159*	-0.003	.212**	-.320**	-0.038	-.331**	-.308**	-0.114	-.198**	-0.061	.195**	0.105	-.125*	0.027
	Sig. (2 tailes)	0.690	0.025	0.008		0.000	0.011	0.963	0.001	0.000	0.540	0.000	0.000	0.066	0.001	0.327	0.002	0.089	0.043	0.665
TS	r	-.153*	.397**	.357**	.573**	1.000	-.170**	0.007	.164**	.145*	0.025	0.061	.291**	.384**	0.105	0.101	.148*	0.074	-0.093	0.012
	Sig. (2 tailes)	0.013	0.000	0.000	0.000		0.006	0.912	0.009	0.020	0.692	0.328	0.000	0.000	0.092	0.104	0.017	0.232	0.137	0.843
Pt	r	-.230**	-.233**	-.211**	-.159*	-.170**	1.000	.489**	.254**	0.114	.229**	0.033	-0.002	0.012	.206**	0.000	-.219**	.208**	.469**	-0.012
	Sig. (2 tailes)	0.000	0.000	0.001	0.011	0.006		0.000	0.000	0.069	0.000	0.596	0.977	0.844	0.001	0.994	0.000	0.001	0.000	0.851
Nk	r	-.167**	-.194**	-0.110	-0.003	0.007	.489**	1.000	.476**	.129*	.295**	0.015	-0.006	-0.036	0.090	-0.049	-0.014	.282**	.584**	0.064
	Sig. (2 tailes)	0.007	0.002	0.078	0.963	0.912	0.000		0.000	0.038	0.000	0.809	0.919	0.571	0.149	0.439	0.821	0.000	0.000	0.307
NH_4	r	-.218**	-0.107	-0.093	.212**	.164**	.254**	.476**	1.000	0.057	.280**	-.218**	-.207**	-0.100	-.144*	0.002	.216**	.130*	.274**	0.047
	Sig. (2 tailes)	0.000	0.087	0.138	0.001	0.009	0.000	0.000		0.359	0.000	0.000	0.001	0.110	0.021	0.970	0.001	0.038	0.000	0.451
NO_2+NO_3	r	-.334**	.461**	.390**	-.320**	.145*	0.114	.129*	0.057	1.000	.409**	.368**	.498**	.422**	.453**	0.020	-0.060	-0.056	-0.020	-0.040
	Sig. (2 tailes)	0.000	0.000	0.000	0.000	0.020	0.069	0.038	0.359		0.000	0.000	0.000	0.000	0.000	0.747	0.343	0.372	0.754	0.527
COD	r	-.128*	0.016	0.008	-0.038	0.025	.229**	.295**	.280**	.409**	1.000	.202**	.124*	0.097	.336**	0.021	0.013	0.022	.205**	-0.050
	Sig. (2 tailes)	0.038	0.795	0.901	0.540	0.692	0.000	0.000	0.000	0.000		0.001	0.044	0.116	0.000	0.734	0.831	0.725	0.001	0.415
Na	r	-.214**	.367**	.365**	-.331**	0.061	0.033	0.015	-.218**	.368**	.202**	1.000	.617**	.460**	.459**	.251**	-.240**	-0.065	0.088	-0.059
	Sig. (2 tailes)	0.000	0.000	0.000	0.000	0.328	0.596	0.809	0.000	0.000	0.001		0.000	0.000	0.000	0.000	0.000	0.291	0.157	0.341
Mg	r	-.250**	.639**	.635**	-.308**	.291**	-0.002	-0.006	-.207**	.498**	.124*	.617**	1.000	**.779****	.523**	.195**	-0.088	0.029	0.049	0.012
	Sig. (2 tailes)	0.000	0.000	0.000	0.000	0.000	0.977	0.919	0.001	0.000	0.044	0.000		0.000	0.000	0.001	0.156	0.640	0.426	0.844

Table 6.3 (cont.) – Spearman's correlations between physical-chemical parameters of surface water and associated discharge characteristics, of all the surface water samples collected in *Ribeira dos Covões* during the study period (n=2623). Red color highlight strong (>0.4/-0.4) and significant correlations.

		pH	EC	TDS	Turbidity	TS	Pt	Nk	NH_4	NO_2+NO_3	COD	Na	Mg	Ca	K	Mn	Fe	Cu	Zn	Cd
Ca	r	-.296**	.681**	.676**	-0.114	.384**	0.012	-0.036	-0.100	.422**	0.097	.460**	**.779****	1.000	.449**	.167**	0.026	0.020	-0.082	0.036
	Sig. (2 tailes)	0.000	0.000	0.000	0.066	0.000	0.844	0.571	0.110	0.000	0.116	0.000	0.000		0.000	0.007	0.673	0.749	0.185	0.557
K	r	-.204**	.295**	.266**	-.198**	0.105	.206**	0.090	-.144*	.453**	.336**	.459**	.523**	.449**	1.000	0.079	-.259**	-0.010	.184**	-0.043
	Sig. (2 tailes)	0.001	0.000	0.000	0.001	0.092	0.001	0.149	0.021	0.000	0.000	0.000	0.000	0.000		0.202	0.000	0.870	0.003	0.486
Mn	r	-.144*	.148*	.142*	-0.061	0.101	0.000	-0.049	0.002	0.020	0.021	.251**	.195**	.167**	0.079	1.000	-0.027	0.040	0.012	0.111
	Sig. (2 tailes)	0.020	0.016	0.021	0.327	0.104	0.994	0.439	0.970	0.747	0.734	0.000	0.001	0.007	0.202		0.659	0.518	0.841	0.073
Fe	r	.172**	0.026	.126*	.195**	.148*	-.219**	-0.014	.216**	-0.060	0.013	-.240**	-0.088	0.026	-.259**	-0.027	1.000	0.112	-0.046	0.063
	Sig. (2 tailes)	0.005	0.678	0.042	0.002	0.017	0.000	0.821	0.001	0.343	0.831	0.000	0.156	0.673	0.000	0.659		0.071	0.459	0.315
Cu	r	0.020	-.128*	-0.077	0.105	0.074	.208**	.282**	.130*	-0.056	0.022	-0.065	0.029	0.020	-0.010	0.040	0.112	1.000	.275**	-0.018
	Sig. (2 tailes)	0.748	0.038	0.214	0.089	0.232	0.001	0.000	0.038	0.372	0.725	0.291	0.640	0.749	0.870	0.518	0.071		0.000	0.775
Zn	r	-.167**	-.344**	-.248**	-.125*	-0.093	.469**	.584**	.274**	-0.020	.205**	0.088	0.049	-0.082	.184**	0.012	-0.046	.275**	1.000	0.089
	Sig. (2 tailes)	0.007	0.000	0.000	0.043	0.137	0.000	0.000	0.000	0.754	0.001	0.157	0.426	0.185	0.003	0.841	0.459	0.000		0.152
Cd	r	-0.009	-0.088	0.062	0.027	0.012	-0.012	0.064	0.047	-0.040	-0.050	-0.059	0.012	0.036	-0.043	0.111	0.063	-0.018	0.089	1.000
	Sig. (2 tailes)	0.890	0.155	0.315	0.665	0.843	0.851	0.307	0.451	0.527	0.415	0.341	0.844	0.557	0.486	0.073	0.315	0.775	0.152	
Total flow	r	0.048	-0.010	-0.045	.408**	.313**	-0.059	-0.059	0.000	-0.090	-0.106	-0.034	-0.063	-0.002	-.146*	0.016	0.062	0.085	-0.060	0.033
	Sig. (2 tailes)	0.439	0.866	0.465	0.000	0.000	0.343	0.346	0.996	0.148	0.086	0.585	0.310	0.973	0.018	0.796	0.321	0.171	0.332	0.599
Storm flow	r	0.099	-.192**	-.209**	.381**	.205**	0.003	0.031	0.073	-.132*	-0.017	-.220**	-.244**	-.168**	-.223**	-0.100	.135*	0.066	-0.003	0.059
	Sig. (2 tailes)	0.108	0.002	0.001	0.000	0.001	0.966	0.626	0.243	0.034	0.786	0.000	0.000	0.007	0.000	0.104	0.030	0.288	0.968	0.344
Base flow	r	-0.057	.168**	.148*	.342**	.383**	-0.096	-0.088	-0.034	-0.012	-.141*	.137*	.136*	.167**	-0.051	0.099	0.004	0.085	-0.075	0.028
	Sig. (2 tailes)	0.359	0.006	0.016	0.000	0.000	0.127	0.158	0.591	0.846	0.022	0.027	0.028	0.007	0.411	0.108	0.953	0.168	0.225	0.655

** Correlation significant at the level 0.01 (2 tailes).

* Correlation significant at the level 0.05 (2 tailes).

Total dissolved solids exhibited the same spatio-temporal pattern as EC ($r=0.829$, $p<0.01$), despite the slightly higher values in *ESAC* than *Espírito Santo*. Median values increased from *Porto Bordalo* (76.4 mg L^{-1}), to *Quinta*, (109.4 mg L^{-1}), *Espírito Santo* (163.6 mg L^{-1}) and *ESAC* (174.6 mg L^{-1}) (results not shown). Maximum values ranged between 401.0 mg L^{-1} and 758.0 mg L^{-1} within the four study sites.

Turbidity displayed a different spatial pattern than pH, EC and TDS, with greatest values in *Quinta* surface water ($p<0.05$). Over the study period, median turbidity values in *Quinta* (134 FTU), were almost twice higher than in *ESAC* (79 FTU), and about four times the amount found in *Espírito Santo* and *Porto Bordalo* (38 FTU and 33 FTU, correspondingly) (Figure 6.5). Surface water quality showed significant turbidity increases during 02/11/2011 and 14/11/2011 measurements ($p>0.05$). Nevertheless, during these rainfall events, differences in maximum turbidity were not so large between *Quinta* and *ESAC* (1548 FTU and 1127 FTU), but were clearly distinct from *Espírito Santo* and *Porto Bordalo* (313 FTU and 493 FTU).

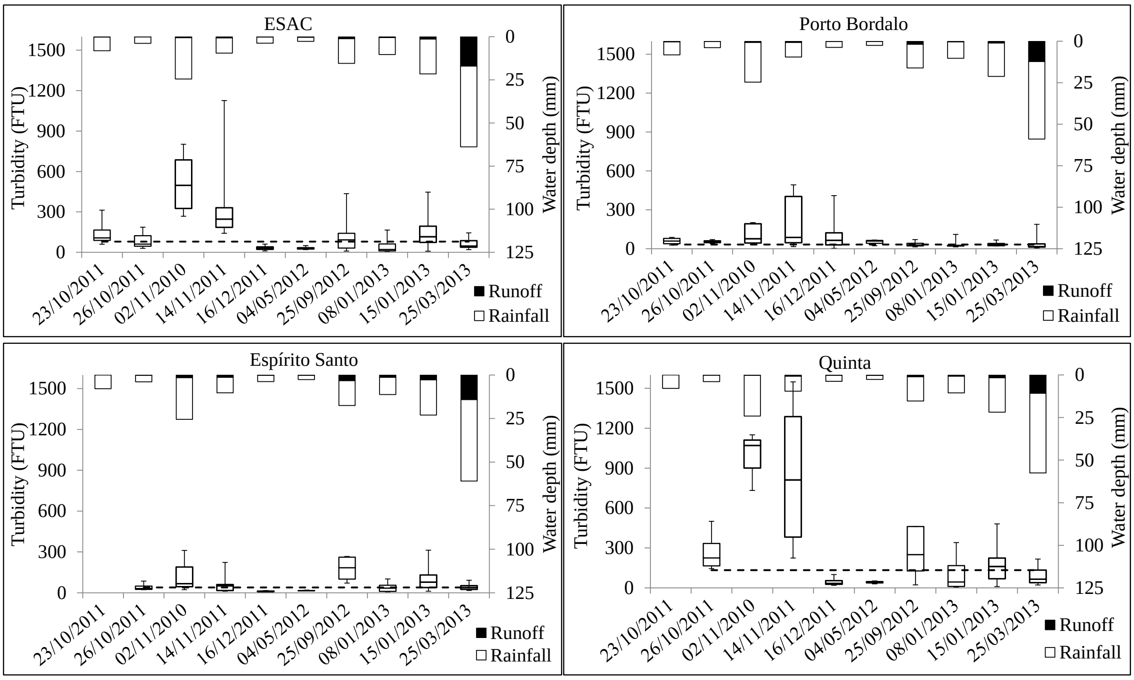


Figure 6.5 - Temporal variability of turbidity between the four study sites. Dashed lines represent median values of all the results over the study period.

Greater TS concentrations were observed in *ESAC* and *Quinta* surface water (75% of the samples ranged between 200-470 mg L^{-1} and 113-456 mg L^{-1}, respectively), opposing to *Espírito Santo* and *Porto Bordalo* (183-292 mg L^{-1} and 47-209 mg L^{-1}, $p<0.05$) (Figure 6.6). Although water samples from *ESAC* displayed generally higher TS concentrations during rainfall events, maximum values, associated with greater rainfall intensities and

ADP (02/11/2011 and 14/11/2011), were reached in *Quinta*, and exceed twice higher the maximum concentrations in *ESAC* (4320 mg L^{-1} vs 1656 mg L^{-1}). Nevertheless, even under these rainfall conditions, TS concentrations did not surpass 852 mg L^{-1} and 598 mg L^{-1} in *Espírito Santo* and *Porto Bordalo*, correspondingly.

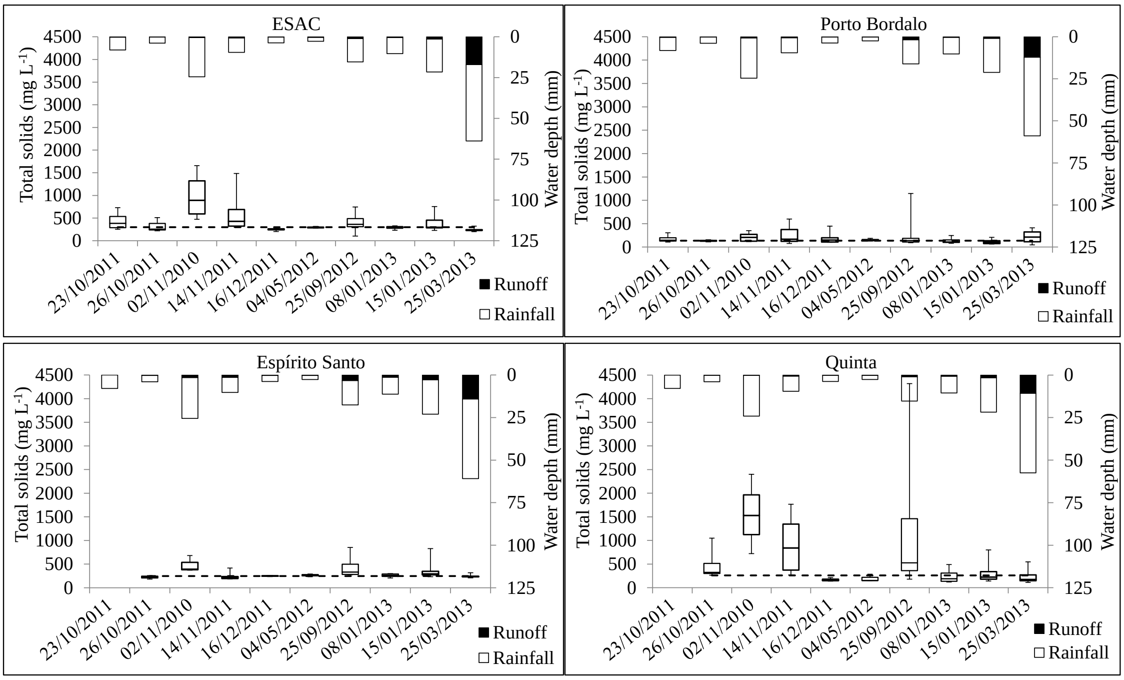


Figure 6.6 – Temporal variability of total solids between the four study sites. Dashed lines represent median values of all the results over the study period.

Total solids followed similar temporal pattern as observed for turbidity and both showed greater values with peak flows. However, general TS increases were also noticed in 25/09/2012, representing one of the first rainfall events after the dry summer. In fact, this rainfall event triggered the beginning of streamflow in *Espírito Santo* and *Quinta*, which exhibited some of the highest concentrations during this sampling event, measured at the beginning of the flow and not following discharge variation as generally observed. Within *Porto Bordalo*, despite the relatively constant TS over the study period, and contrary to the measurements performed in the other study sites, high concentrations were quantified during 14/11/2011. This is linked with urbanization works performed nearby the sampling site regarding to a dich opening on the soil surface.

Total solids concentration was significantly correlated with turbidity ($r=0.573$, $p<0.01$). Concentrations of TS and TDS increased with increasing stream discharge (total flow and storm component), despite the week correlations, particularly with TS (TS: $r=0.313$ and 0.205, TDS: $r=0.408$ and 0.381, for total flow and storm component, $p<0.01$) (Table 6.3).

Opposing to the previous physical-chemical parameters, COD in dissolved phase was greater in *Espírito Santo* (median values of 17.8 mg L^{-1}), followed by *ESAC* (13.0 mg L^{-1}) and *Porto Bordalo* (12.0 mg L^{-1}), with lowest concentrations in *Quinta* (9.5 mg L^{-1}, demonstrating significant differences to the other study sites, $p<0.05$) (Figure 6.7). Nevertheless, over the study period, the highest concentrations were attained in *ESAC* and *Porto Bordalo* (56.0 mg L^{-1} and 83.5 mg L^{-1}). Temporal pattern of COD displayed a lower surface water quality immediately after driest settings (23/10/2011 and 25/09/2013) ($p<0.05$) and decreasing concentrations through the wet periods. Generaly, highest concentrations were measured in baseflow during rainfall events after the summer, but with peak flow in winter storms. COD increased significantly with NO_2+NO_3 concentrations ($r=0.409$, $p<0.01$).

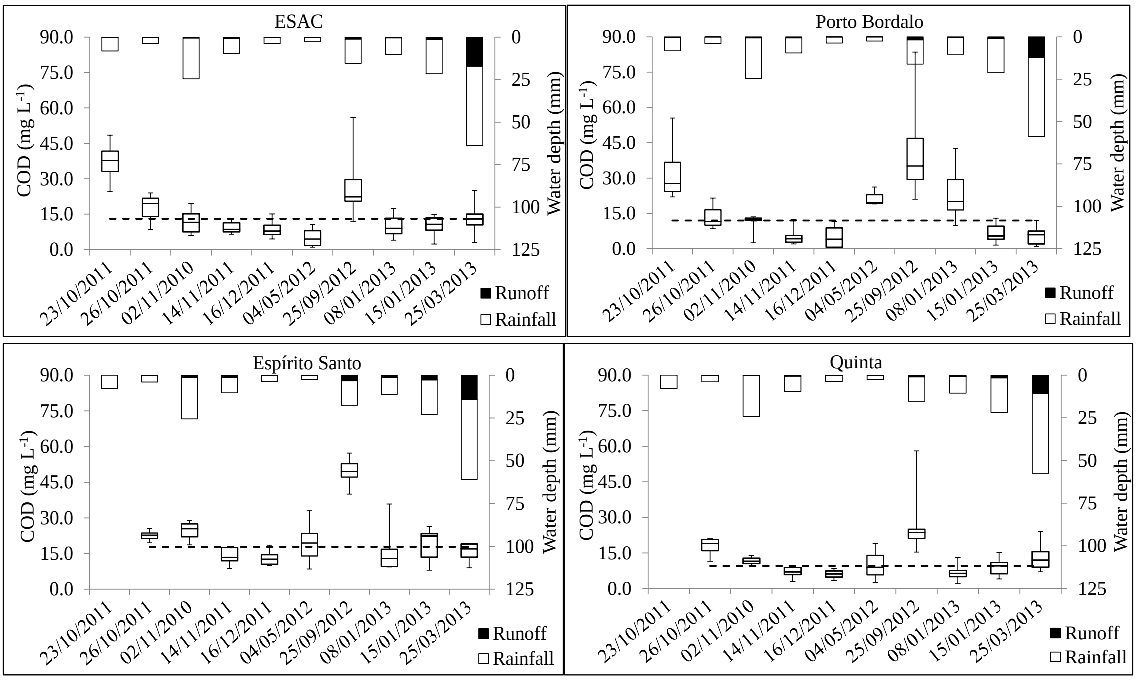


Figure 6.7 Temporal variability of chemical oxygen demand between the four study sites. Dashed lines represent median values of all the results over the study period.

Nutrients

Kjeldhal nitrogen in dissolved phase did not show significant differences between study sites ($p>0.05$), but a minor decrease in median concentrations from downstream to upstream monitoring locations was observed (1.34 mg L^{-1} in *ESAC*, 1.31 mg L^{-1} in *Porto Bordalo*, 1.22 mg L^{-1} in *Espírito Santo* and 1.20 mg L^{-1} in *Quinta*) (Figure 6.8). Similarly to Nk, NH_4 concentrations were slightly higher in *ESAC* (median values over the study period of 0.41 mg L^{-1}), but minor decreases were displayed from *Quinta* to *Porto Bordalo* and *Espírito Santo* (0.36 mg L^{-1}, 0.32 mg L^{-1} and 0.26 mg L^{-1}, respectively).

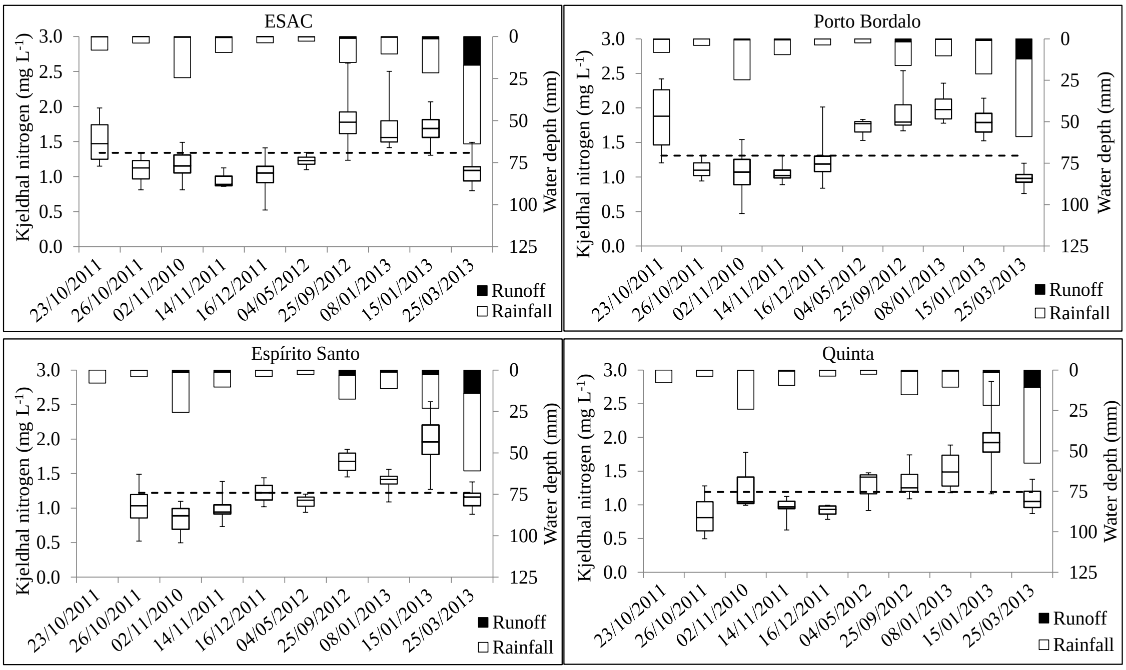


Figure 6.8 Temporal variability of Kjeldhal nitrogen between the four study sites. Dashed lines represent median values of all the results over the study period.

Both Nk and NH_4 compounds presented the same temporal pattern (only shown for Nk, Figure 6.8). In *ESAC* and *Porto Bordalo*, the temporal pattern was analogous to COD concentrations, with great concentrations in dry periods (in late summer – 25/09/2012, and in rainfall events after several days without rainfall - 23/10/2011 and 08/10/2013, both with API_7=0.0 mm), decreasing values through wet seasons (lowest values in 14/11/2011, with the largest API_{14}), and increasing in late spring (04/05/2012). On the other hand, *Espírito Santo* and *Quinta* seemed to show increasing Nk and NH_4 over the wet season, with the highest values measured in 15/01/2013 (2.5 mg L^{-1} and 2.8 mg L^{-1}, measured at the beginning of flow increase in *Espírito Santo* and immediately after peak flow in *Quinta*).

Generally, NH_4 represented a small fraction of the Nk: 31% in *ESAC*, 30% in *Quinta*, 25% in *Porto Bordalo* and 21% in *Espírito Santo* (Figure 6.9). Significant positive correlation was found between both nitrogen forms ($r=0.476$, $p<0.01$). Over the study period, nitrogen was mostly in organic form in *Quinta* surface water, based on lower NO_2+NO_3 than Nk concentrations, and considering the small percentage of NH_4. In *Porto Bordalo* and *ESAC*, median concentrations of NO_2+NO_3 were also lower than Nk, but with minor differences than observed in *Quinta*. Contrary to these sites, in *Espírito Santo* NO_2+NO_3 was the most dominant nitrogen form in surface water.

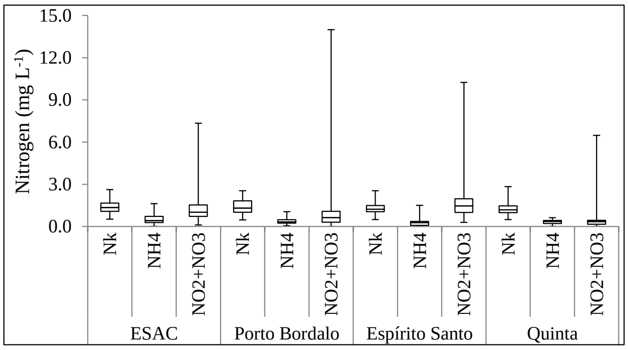


Figure 6.9 Variation of different nitrogen forms concentration (Kjeldhal, ammonium and nitrogen oxide) in the four study sites, considering all the stream values measured during the ten storm events monitored.

Generally low NO_2+NO_3 concentrations were found within the four study sites (Figure 6.10), but minor contribution of NO_2 is expected, given the usual oxidative conditions. Nitrates displayed the same spatial pattern as COD, with dissolved concentrations decreasing from *Espírito Santo* (1.46 mg L^{-1}), to *ESAC* (1.01 mg L^{-1}), *Porto Bordalo* (0.62 mg L^{-1}) and *Quinta* (0.35 mg L^{-1}) (Figure 6.10).

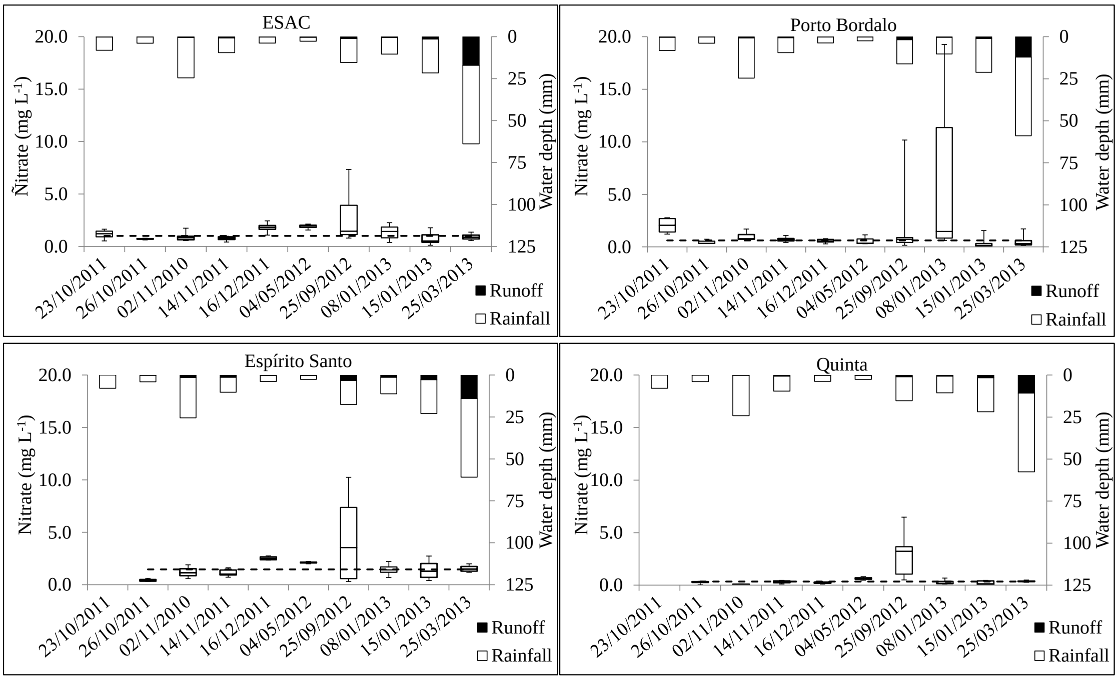


Figure 6.10 – Temporal variability of NO_2+NO_3 concentration between the four study sites. Dashed lines represent median values of all the results over the study period.

Higher concentrations of NO_2+NO_3 were observed in *ESAC*, *Espírito Santo* and *Quinta* after the summer, particularly during the 25/09/2012 rainfall event, where few samples reached 6-14 mg L^{-1} (immediately after the peak flow), but after few rainless days during the wet season in *Porto Bordalo* (08/01/2013, with API_7=0.0 mm), with peak concentrations attaining 19 mg L^{-1} with peak flow. In *Quinta* and *Porto Bordalo*, after the greatest NO_2+NO_3 concentrations were reached, a considerable decrease was observed in the subsequent rainfall events, demonstrating a distinct temporal pattern than Nk and NH_4. Nitrates concentration was positively correlated with COD ($r=0.409$, $p<0.01$). Generaly, COD and nitrogen compounds did not correlate significantly with streamflow parameters ($p>0.05$).

Total phosphorus in dissolved phase was mostly lower than 0.10 mg L^{-1}, with greater concentrations in *Porto Bordalo* and *ESAC* (median values of 0.07 mg L^{-1} in both sites) than in *Espírito Santo* and *Quinta* (0.06 mg L^{-1} and 0.05 mg L^{-1}) ($p<0.05$) (Figure 6.11). During the study period, peak concentrations of TP attained 0.39 mg L^{-1} in *ESAC*, 0.30 mg L^{-1} in *Porto Bordalo*, 0.17 mg L^{-1} in *Espírito Santo* and 0.14 mg L^{-1} in *Quinta*, mostly at peak flows. The highest concentrations were observed not only in driest settings (23/10/1011, 04/05/2012 and 25/09/2012), but also during wet seasons, after few days without rainfall (08/01/2013). The temporal variability of TP is similar to COD and alike Nk and NH_4. Nevertheless, significant correlation was only identified between TP and Nk ($r=489$, $p<0.01$).

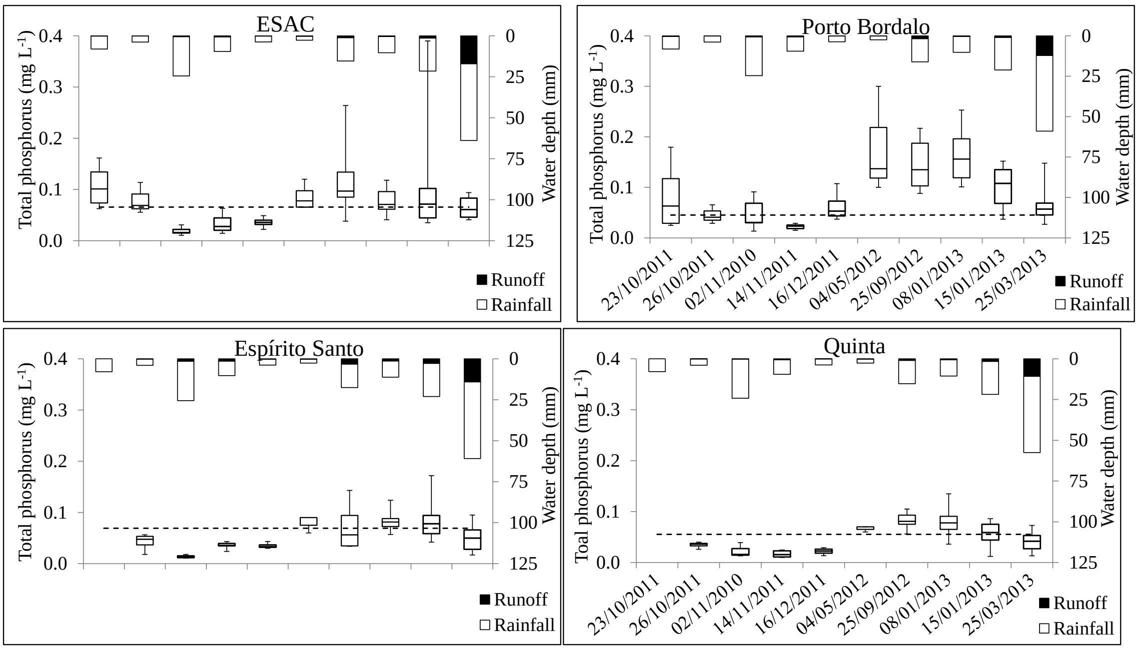


Figure 6.11 – Temporal variability of total phosphorus concentration between the four study sites. Dashed lines represent median values of all the results over the study period.

Major cations

Dissolved concentrations of Na, K, Ca and Mg exhibited significant differences between study catchment sites ($p<0.05$), but varying with the chemical element. Nevertheless, *Espírito Santo* surface water showed greater concentrations for all the cations.

Sodium displayed lowest concentrations in *Porto Bordalo* (median values of 5.7 mg L^{-1}) ($p<0.05$), less than half that recorded in *Espírito Santo* (18.6 mg L^{-1}) (Figure 6.12). *Quinta* only showed slightly lower Na concentrations comparing with *ESAC* (11.9 mg L^{-1} and 14.7 mg L^{-1}) ($p>0.05$). The temporal pattern of Na displayed a tendency for lower values in rainfall events after driest periods (23/10/2011 and 25/09/2012), and increasing concentrations through the wet season, particularly in *Espírito Santo* and *Quinta* (attained 34.7 mg L^{-1} in 04/05/2012 and 33.1 mg L^{-1} in 25/03/2013, immediately after the peak flow). This temporal pattern is opposite to the pattern observed for COD and nutrients concentrations. However, *Porto Bordalo* exibited the highest Na concentrations in 25/09/2012, different from the other study sites.

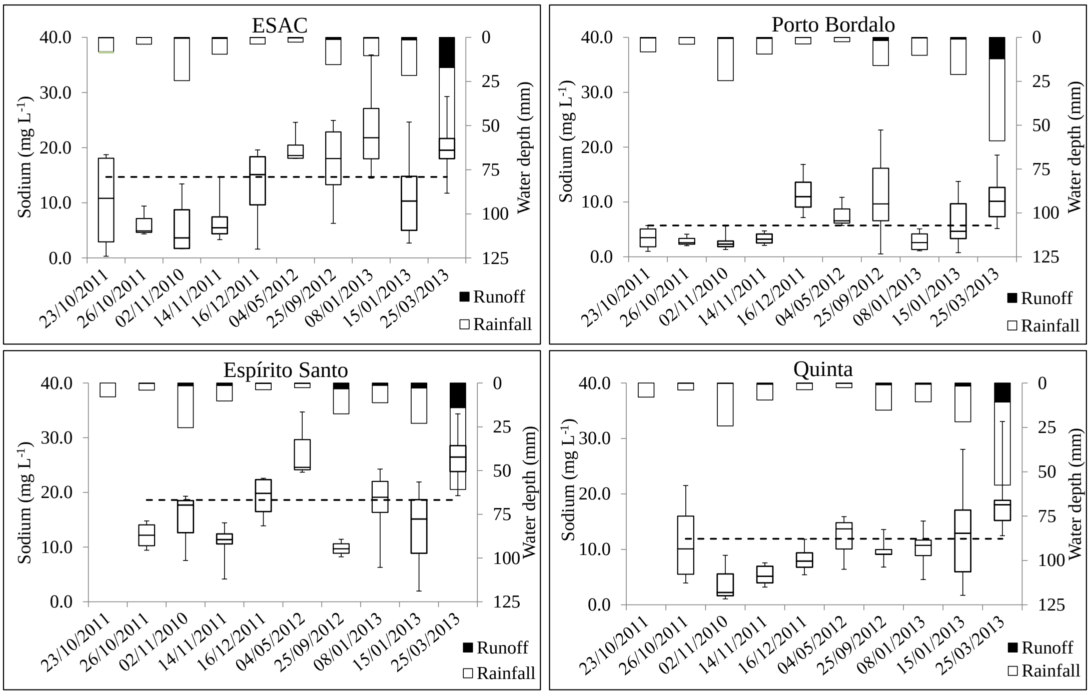


Figure 6.12 – Temporal variability of dissolved sodium concentrations between the four study sites. Dashed lines represent median values of all the results over the study period.

Surface water from *Porto Bordalo* displayed lowest Ca (median values of 19.8 mg L^{-1}), followed by *Quinta* study site (22.6 mg L^{-1}), similar to Na measurements (Figure 6.13). No significant difference was observed between Ca concentrations in *Espírito Santo* and *ESAC* ($p>0.05$), which showed the greatest median values within *Ribeira dos Covões*

(30.9 mg L^{-1} and 34.4 mg L^{-1}). Calcium did not exhibit significant variability between measurement dates ($p>0.05$), as observed with Mg (Figure 6.14). Furthermore, Mg in surface water displayed similar spatial pattern as Ca, despite the significant highest median concentration in *Espírito Santo* (10.4 mg L^{-1}) ($p<0.05$). The lowest Mg concentrations were also measured in *Porto Bordalo* surface water (2.3 mg L^{-1}).

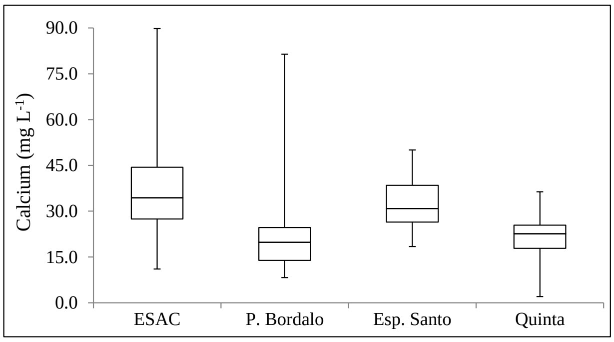


Figure 6.13 – Differences in calcium variability between the four study sites, measured between October 2011 and March 2013.

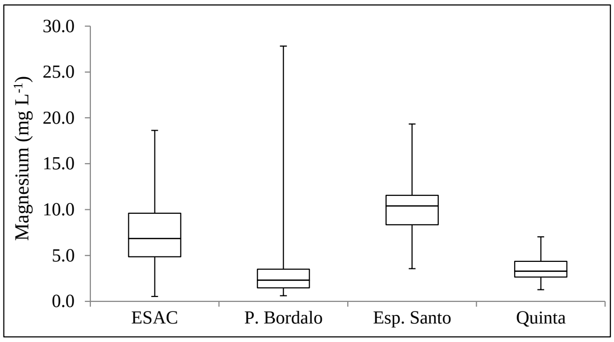


Figure 6.14 – Temporal variability of dissolved magnesium concentrations between the four study sites. Dashed lines represent median values of the ten measurement dates.

The spatial pattern of K was similar to Mg, with concentrations in surface water decreasing from *Espírito Santo* (6.1 mg L^{-1}) and *ESAC* (5.5 mg L^{-1}), but with slightly higher concentrations in *Porto Bordalo* (4.9 mg L^{-1}) than *Quinta* (3.1 mg L^{-1}) (Figure 6.15). The temporal pattern of K was analogous to the variation observed for Na, which demonstrated an increasing concentration tendency over the wet season, particularly in *ESAC* and *Porto Bordalo*. Generally, major cations attained the highest concentrations under baseflow conditions, but also under peak flows in later winter storms (results not shown).

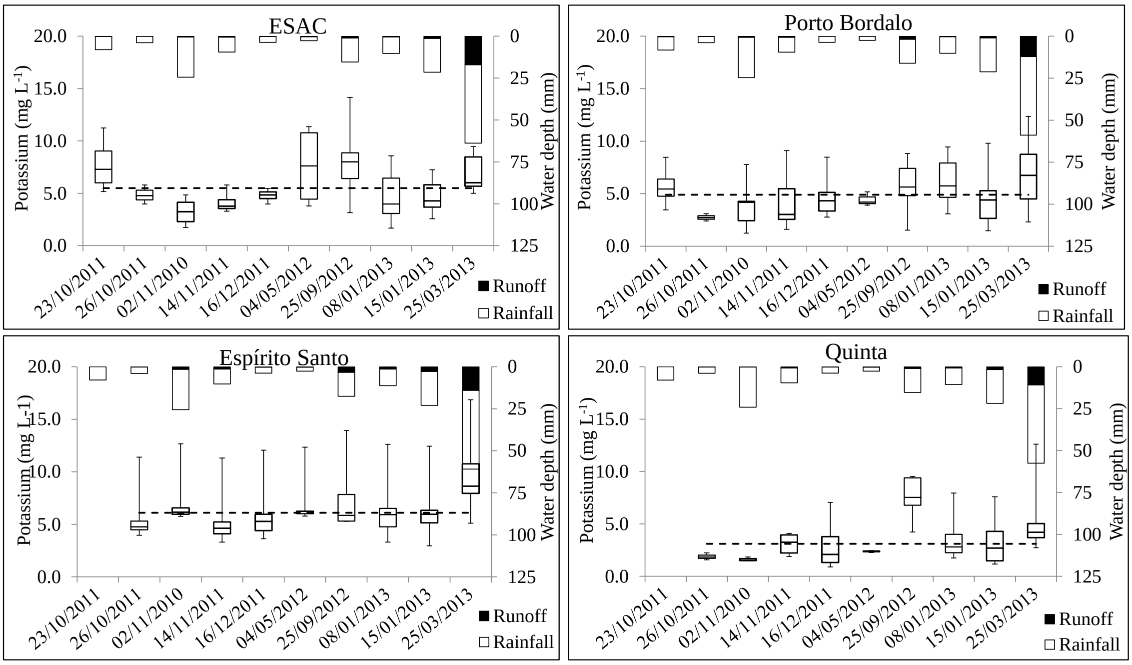


Figure 6.15 – Temporal variability of dissolved potassium concentrations between the four study sites. Dashed lines represent median values of all the results over the study period.

Surface water concentrations of Na, K, Ca and Mg were positively correlated between each other ($p<0.01$), but with stronger correlations among Ca and Mg ($r=0.779$). Streamflow regime did not show a great impact on major cations concentrations, given the very week negative correlations with storm flow component, although significant ($p<0.01$) (Table 6.3). Major cations established significant correlations with EC (r=-0.639, -0.681, -0.295 and -0.367, for Mg, Ca, K and Na, $p<0.01$).

Metals

Dissolved Fe showed a spatial and temporal pattern distinct from the other water quality parameters. Throughout the ten rainfall events, *Espírito Santo* exhibited the highest Fe concentrations (median values of 0.366 mg L^{-1}), whereas the lowest median value was observed in *ESAC* (0.302 mg L^{-1}) (Figure 6.16). *Quinta* surface water displayed distinct Fe concentrations comparing with the other study sites ($p<0.05$), marked by greatest heterogeneity within the same rainfall events and highest maximum concentrations (2.25 mg L^{-1}), largely noticed during the initial five water sampling dates. In general, surface water displayed decreasing Fe concentrations over the study period.

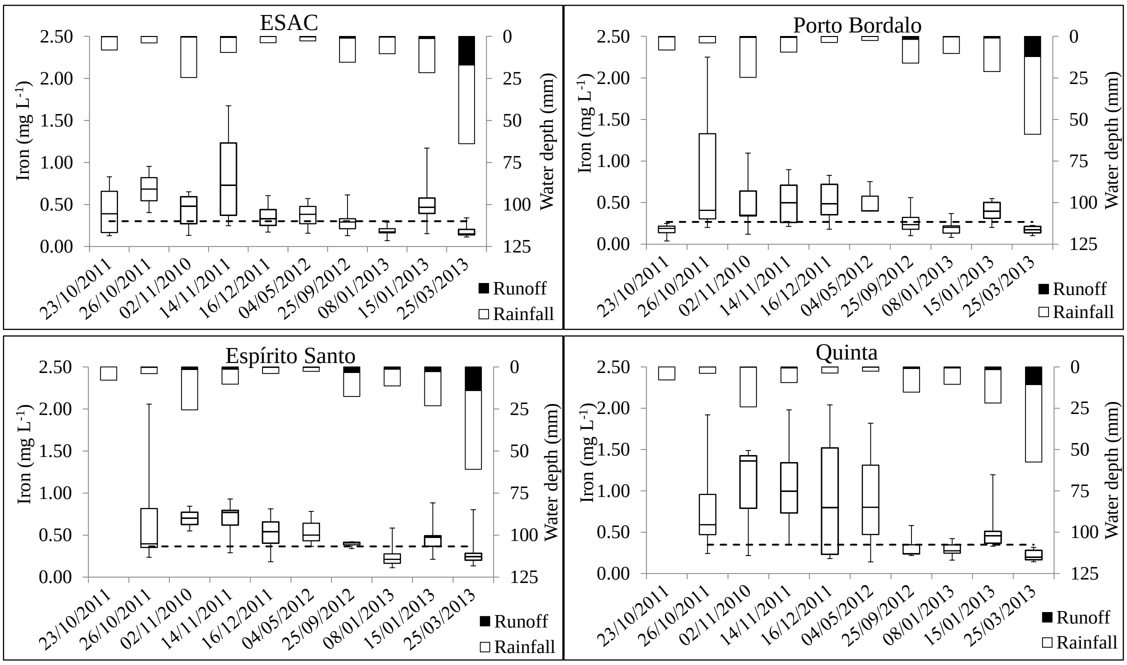


Figure 6.16 – Temporal variability of dissolved iron concentrations between the four study sites. Dashed lines represent median values of all the results over the study period.

Within *Ribeira dos Covões* surface water, median Zn concentrations were similarly low at all study sites ($p>0.05$), varying only from 0.118 mg L^{-1} in *Espírito Santo*, to 0.128 mg L^{-1} in *Quinta*, 0.157 mg L^{-1} in *Porto Bordalo* and 0.165 mg L^{-1} in *ESAC* (Figure 6.17). However, it was in *ESAC* that Zn reached the highest concentrations (0.91 mg L^{-1}). Zn varied in opposite fashion to Fe, with distinctively higher concentrations in rainfall events observed after the summer season (25/09/2013) and in late winter season (08/01/2013 and 15/01/2013) ($p<0.05$).

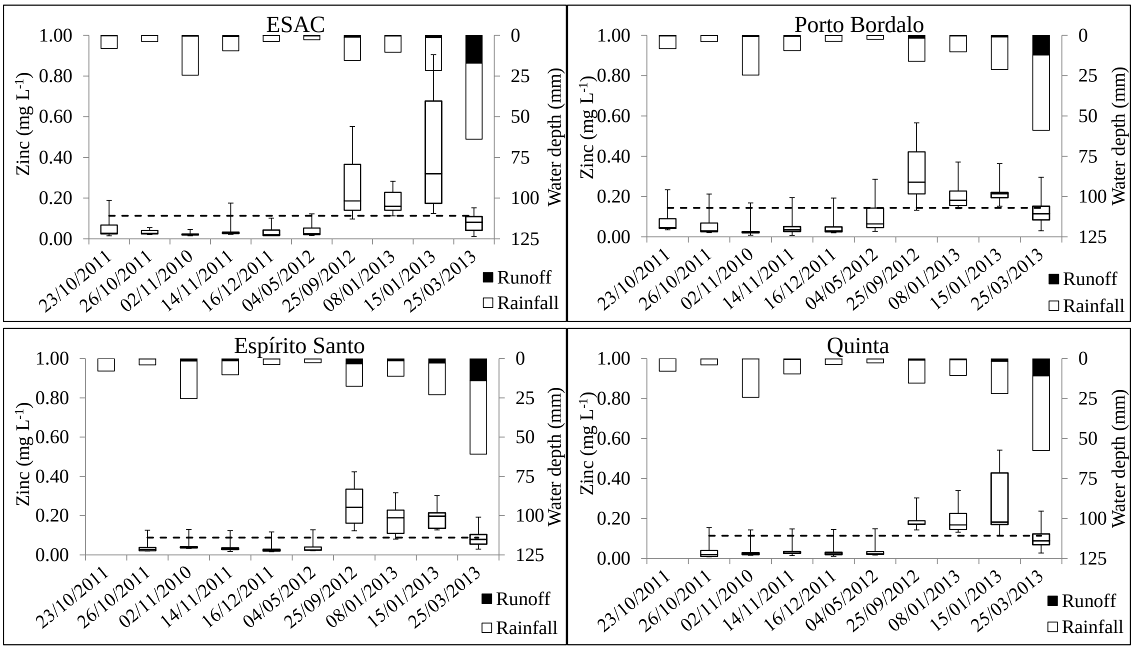


Figure 6.17 – Temporal variability of dissolved zinc concentrations at the four study sites. Dashed lines represent median values of all the results over the study period.

Most of the heavy metals investigated in the dissolved phase were below detection limits. Cadmium exceeded the detection limit (0.031 mg L^{-1}) on only one occasion at *ESAC*, which attained 0.050 mg L^{-1} during the hydrograph rising limb of 15/01/2013 (results not shown).

Cupper also rarely exceeded the detection limit (0.068 mg L^{-1}) at the study sites, representing 9% of *Espírito Santo* and *ESAC* water samples, 7% in *Porto Bordalo* and 5% in *Quinta* (results not shown). These quantifiable concentrations of Cu were largely observed during 15/01/2013 rainfall event, reaching 0.174 mg L^{-1} in *ESAC*, 0.102 mg L^{-1} in *Porto Bordalo*, 0.219 mg L^{-1} in *Espírito Santo* and 0.094 mg L^{-1} in *Quinta* (linked with greater discharges).

Manganese exceeded the detection limit (0.048 mg L^{-1}) more frequently than Cu: 33% of *ESAC* water samples, 31% in *Quinta*, 18% of *Espírito Santo* and 5% in *Porto Bordalo* (results not shown). The majority of these high values were attained during the rising limb of storms observed after the summer (26/10/2011 and 25/09/2012), but also at peak flows in late winter (especially during 15/01/2013 and 25/03/2013). Maximum Mn values were 0.867 mg L^{-1} in *ESAC*, 0.400 mg L^{-1} in *Porto Bordalo*, 0.150 mg L^{-1} in *Espírito Santo* and 0.148 mg L^{-1} in *Quinta*. Water samples collected at the four sites did not show significant differences ($p>0.05$).

6.4.2.2. Compliance with Portuguese water quality guidelines

According with the Portuguese guidelines (Environmental Ministry, 1998) for *minimum surface water quality*, pH (5.0-9.0) and total phosphorus (1 mg L^{-1}) did not represent problems for aquatic ecosystems within *Ribeira dos Covões*. However, nitrogen and a few heavy metals occasionally threatened surface water quality in all the study sites.

The minimum water quality threshold of Nk (2 mg L^{-1}) exceeded in 15% of the *Porto Bordalo* water samples, 9% in *Quinta* and 7% in *ESAC* and *Espírito Santo*. Problems linked to high concentrations of Nk were largely observed on 25/09/2012, 08/01/2013 and 15/01/2013 (Figure 6.10). Some of these high Nk concentrations found in *ESAC* and *Porto Bordalo*, were identified in baseflow samples, before rainfall start, but also during the falling limb of the hydrograph. Ammonium standards (1 mg L^{-1}) were surpassed in 8% of *ESAC* surface water samples, 3% in *Porto Bordalo* and 2% in *Espírito Santo*. The highest NH_4 concentrations were linked to Nk maxima.

Cadmium standard (0.01 mg L^{-1}) was surpassed in the only quantifiable sample over the study period, which was collected in *ESAC*, during the 15/01/2013 rainfall event (raising limb). At this time, *ESAC* also exceeded Cu water quality standards (0.1 mg L^{-1}) in two samples. Furthermore, Cu concentration also exceeded the threshold in 2% of the *Espírito Santo* samples, on 25/03/2013 (during peak flow). Dissolved Zn concentrations also surpassed minimum surface water quality guidelines (0.5 mg L^{-1}) in 11% of *ESAC* water samples and 3% in both *Porto Bordalo* and *Quinta*, not only on 25/09/2012 (rising limb) but also in the 15/01/2013 (peak flow and recession limb) storm events.

In the four study sites, recorded values always complied with recommended surface water quality guidelines for *irrigation purposes* for NO_3 (RMV=50 mg L^{-1}), Fe (RMV=5.0 mg L^{-1}), Zn (RMV=2.0 mg L^{-1} and MAV= 10.0 mg L^{-1}), and SAR parameter (RMV=8 meq L^{-1}). Maximum values of SAR attained 3 meq L^{-1} in *Quinta* and 2 meq L^{-1} in *ESAC*, *Porto Bordalo* and *Espírito Santo*, over the study period (results not shown). The MRV for TDS (640 mg L^{-1}) was exceeded on only one sample collected at *ESAC*, near the peak flow on late winter (15/01/2013).

Surface water quality displayed some limitations for irrigation purposes, associated with greatest Cu, Mn and pH values, above the recommended guidelines in some samples. Maximum recommended values of Cu (0.2 mg L^{-1}) were exceeded in 2% of *Espírito Santo* water samples, during 25/03/2013 (same samples which exceeded the minimum water quality standards). Manganese was surpassed in 4% and 1% of the *ESAC* and *Porto Bordalo* water samples (MRV=0.20 mg L^{-1}), due to great concentrations on 25/09/2012 (measured during the rising limb of the hydrographs). In *Porto Bordalo*, pH was at MRV (4.5-9.0) limit in 3% of the analyses (rising limb of 02/11/2010 rainfall event). Nevertheless, in all of these MRV exceedance, the maximum admissible standards (VMA) were always accomplished (Cu: 5.0 mg L^{-1}, Mn: 10 mg L^{-1} and pH: 4.5-9.0).

The high detection limit of the analytical method used for Cd quantification (0.031 mg L^{-1}), did not allow conclusions concerning to the water quality for irrigation practices (RMV=0.01 mg L^{-1} and MAV= 0.05 mg L^{-1}).

6.4.2.3. Variation of median concentrations and specific loads per event

Spatial and temporal differences in surface water quality were presented previously, in section 6.4.2.1., but event median concentrations are now summarized (Table 6.4). A wide range of differences were found according with the water quality parameter, as indicated by great standard deviation values. Marked differences were particularly observed in EC and turbidity, with standard deviation greater than mean values. On the other hand, major cations were the chemical elements analysed which displayed lower variability between rainfall events.

Table 6.4 – Summary of median concentration of surface water quality parameters in the four study sites, during the ten rainfall events monitored, as well as median and standard deviation off all the samples collected over the study period.

	23/10/2011	26/10/2011	02/11/2011	14/11/2011	16/12/2011	04/05/2012	25/09/2012	09/01/2013	15/01/2013	25/03/2013	*Median*	*Stand. dev.*
pH												
ESAC	7.0	7.4	7.1	7.4	7.0	7.3	6.8	6.6	7.3	7.2	*7.1*	*0.4*
P. Bordalo	7.3	8.0	8.0	7.7	7.6	7.4	7.7	6.8	7.5	7.5	*7.6*	*0.5*
Esp. Santo	-	7.6	7.3	7.3	7.4	7.3	6.7	6.9	7.6	7.2	*7.3*	*0.4*
Quinta	-	7.7	7.4	7.4	7.1	7.0	6.5	7.2	7.7	7.4	*7.4*	*0.4*
EC (µS cm^{-1})												
ESAC	370.5	264.0	277.9	462.5	365.5	819.0	252.0	394.5	183.7	295.0	*297.0*	*183.9*
P. Bordalo	151.3	70.7	117.4	222.5	178.0	296.0	133.0	79.1	67.3	270.0	*160.0*	*170.8*
Esp. Santo	-	280.5	416.0	496.0	384.0	830.0	234.2	360.0	229.0	310.0	*318.0*	*179.0*
Quinta	-	175.4	286.0	370.0	229.5	402.0	171.6	220.5	124.7	177.3	*181.8*	*87.8*
Turbidity (FTU)												
ESAC	107.0	61.0	497.5	246.5	29.3	27.8	92.5	20.8	116.3	46.0	*79.3*	*196.0*
P. Bordalo	59.3	52.5	77.0	87.0	64.8	59.0	28.0	23.5	28.8	16.5	*33.0*	*97.1*
Esp. Santo	-	30.7	66.0	51.0	9.3	14.5	184.0	34.3	78.5	38.0	*38.3*	*76.0*
Quinta	-	225.4	1070.0	811.5	34.0	43.5	250.0	44.8	160.8	65.0	*133.5*	*349.2*
TS (mg L^{-1})												
ESAC	383.5	255.0	893.0	427.5	254.5	291.5	364.5	294.5	297.0	239.0	*298.0*	*285.8*
P. Bordalo	148.0	133.0	209.0	167.5	151.0	139.0	139.0	109.5	103.0	215.0	*139.0*	*153.3*
Esp. Santo	-	228.0	392.0	225.0	248.0	268.0	334.0	263.5	295.0	236.0	*248.5*	*132.1*
Quinta	-	325.5	1529.0	840.5	160.5	154.0	525.0	190.0	227.0	175.0	*259.5*	*700.8*
TP (mg L^{-1})												
ESAC	0.101	0.069	0.016	0.028	0.036	0.078	0.097	0.071	0.072	0.061	*0.066*	*0.080*
P. Bordalo	0.063	0.041	0.031	0.024	0.053	0.137	0.135	0.156	0.108	0.057	*0.069*	*0.063*
Esp. Santo	-	0.048	0.013	0.036	0.034	0.090	0.057	0.082	0.078	0.050	*0.055*	*0.033*
Quinta	-	0.036	0.016	0.016	0.023	0.070	0.081	0.078	0.059	0.042	*0.044*	*0.029*
Nk (mg L^{-1})												
ESAC	1.47	1.12	1.16	0.89	1.05	1.23	1.78	1.56	1.69	1.09	*1.34*	*0.42*
P. Bordalo	1.88	1.10	1.07	1.02	1.19	1.77	1.80	1.98	1.79	0.98	*1.31*	*0.49*
Esp. Santo	-	1.03	0.89	0.94	1.22	1.11	1.68	1.42	1.96	1.16	*1.22*	*0.42*
Quinta	-	0.81	1.05	0.97	0.93	1.41	1.25	1.49	1.92	1.05	*1.19*	*0.47*
NH_4 (mg L^{-1})												
ESAC	0.41	0.40	0.42	0.37	0.05	0.33	0.89	0.70	0.46	0.11	*0.41*	*0.34*
P. Bordalo	0.78	0.29	0.28	0.28	0.36	0.84	0.37	0.55	0.40	0.11	*0.32*	*0.23*
Esp. Santo	-	0.34	0.37	0.35	0.04	0.26	0.51	0.16	0.36	0.05	*0.26*	*0.23*
Quinta	-	0.40	0.39	0.40	0.06	0.55	0.45	0.24	0.35	0.20	*0.36*	*0.15*
NO_2+NO_3 (mg L^{-1})												
ESAC	1.21	0.73	0.83	0.78	1.82	1.94	1.45	1.43	0.52	0.87	*1.01*	*1.22*
P. Bordalo	2.07	0.34	0.77	0.66	0.54	0.35	0.73	1.47	0.11	0.30	*0.62*	*3.05*
Esp. Santo	-	0.40	1.15	1.01	2.51	2.11	3.55	1.41	1.30	1.50	*1.46*	*1.49*
Quinta	-	0.33	0.07	0.31	0.25	0.63	3.23	0.20	0.13	0.37	*0.35*	*1.00*

Table 6.4 (cont.) – Median concentration of surface water quality parameters in the four study sites, during the ten rainfall events monitored, as well as median and standard deviation off all the samples collected over the study period.

	23/10/ 2011	26/10/ 2011	02/11/ 2011	14/11/2 011	16/12/ 2011	04/05/ 2012	25/09/ 2012	09/01/ 2013	15/01/ 2013	25/03/ 2013	*Median*	*Stand. dev.*
COD (mg L^{-1})												
ESAC	37.8	19.5	11.5	8.5	7.8	4.5	22.4	9.0	10.7	13.0	*13.0*	*11.1*
P. Bordalo	27.8	11.5	12.5	4.3	4.0	19.6	35.2	20.1	5.4	6.0	*11.5*	*17.2*
Esp. Santo	-	22.8	25.5	13.3	12.6	19.5	49.5	13.0	22.4	17.0	*18.0*	*10.9*
Quinta	-	18.9	11.5	7.0	6.2	9.0	23.6	6.4	9.6	12.0	*9.5*	*8.4*
Na (mg L^{-1})												
ESAC	10.84	4.91	3.64	5.47	15.13	18.59	18.03	21.83	10.34	19.54	*14.67*	*8.06*
P. Bordalo	3.48	2.57	2.31	3.21	10.96	6.58	9.64	2.60	4.64	10.11	*5.70*	*5.48*
Esp. Santo	-	12.17	17.71	11.37	19.82	24.60	9.70	19.13	15.15	26.48	*18.58*	*7.94*
Quinta	-	10.10	2.22	5.15	7.90	13.71	9.15	10.73	12.92	18.06	*11.87*	*6.68*
Mg (mg L^{-1})												
ESAC	6.39	6.09	4.49	4.93	7.57	8.66	8.13	10.90	5.55	7.20	*6.86*	*4.02*
P. Bordalo	1.49	1.15	1.50	2.13	2.77	1.72	2.95	1.92	2.03	10.83	*2.27*	*5.75*
Esp. Santo	-	6.98	11.54	11.03	9.77	11.01	6.17	13.22	10.73	10.27	*10.40*	*3.23*
Quinta	-	2.52	1.77	2.63	4.38	3.80	3.60	4.48	3.78	3.22	*3.28*	*1.34*
Ca (mg L^{-1})												
ESAC	51.42	35.07	20.36	32.48	48.69	47.23	37.52	33.67	29.77	34.38	*34.38*	*16.34*
P. Bordalo	19.68	18.62	18.61	17.51	21.59	21.80	19.32	21.63	15.02	39.92	*19.84*	*15.37*
Esp. Santo	-	32.48	43.29	29.65	36.16	41.87	22.90	40.72	31.32	30.65	*30.86*	*8.33*
Quinta	-	23.18	19.45	31.20	24.92	28.58	24.60	23.73	24.03	17.22	*22.60*	6.33
K (mg L^{-1})												
ESAC	7.29	4.78	3.24	3.78	4.86	7.62	8.01	3.98	4.28	6.01	*5.51*	*2.45*
P. Bordalo	5.45	2.73	4.20	3.02	4.33	4.21	5.64	5.75	4.40	6.74	*4.89*	*2.49*
Esp. Santo	-	4.76	6.16	4.63	5.28	6.24	5.85	5.93	5.96	8.64	*6.14*	*2.90*
Quinta	-	1.85	1.52	3.25	2.08	2.41	7.53	2.80	2.70	4.20	*3.10*	*2.46*
Fe (mg L^{-1})												
ESAC	0.390	0.684	0.481	0.731	0.332	0.384	0.292	0.175	0.467	0.150	*0.302*	*0.303*
P. Bordalo	0.189	0.408	0.348	0.498	0.486	0.402	0.236	0.203	0.397	0.175	*0.316*	*0.342*
Esp. Santo	-	0.398	0.702	0.771	0.542	0.501	0.408	0.213	0.475	0.244	*0.366*	*0.316*
Quinta	-	0.591	1.362	0.996	0.798	0.802	0.240	0.275	0.457	0.198	*0.435*	*0.557*
Zn (mg L^{-1})												
ESAC	0.027	0.027	0.022	0.028	0.020	0.025	0.187	0.160	0.321	0.081	*0.113*	*0.193*
P. Bordalo	0.045	0.030	0.024	0.035	0.029	0.064	0.272	0.182	0.215	0.115	*0.140*	*0.134*
Esp. Santo	-	0.028	0.038	0.028	0.023	0.026	0.243	0.189	0.197	0.079	*0.088*	*0.101*
Quinta	-	0.019	0.023	0.026	0.023	0.023	0.172	0.168	0.182	0.088	*0.114*	*0.123*

Generally, based in all the rainfall events sampled, water quality at the catchment outlet (*ESAC*) demonstrated higher event median concentration of TS (marginally higher than in *Quinta*) and Ca (slightly greater than in *Espírito Santo*), as well as a bit higher concentrations of Nk and NH_4 (Table 6.4). *Porto Bordalo*, overlying limestone, displayed greater median values of pH and TP (both slightly higher than *ESAC*), and somewhat greater concentrations of Zn, but lowest results of Na. In turn, with similar land-use but overlaying sandstone, *Espírito Santo* exhibited greatest median concentrations of EC, COD, NO_2+NO_3, Na, Mg, K and Fe. On the other hand, within the sandstone drainage area, partially under construction, *Quinta* demonstrated the highest median concentrations of turbidity and Fe, but the lowest concentrations of COD.

The spatial differences on surface water quality can be partially explained by the biophysical characteristics of the study sites. Lithology displayed significant correlations, with median TS (increased on sandstone, but decreased with limestone, $p<0.05$) and Mg median concentrations (decreased with limestone, $p<0.05$), despite de very week correlation with the latter (Table 6.5). Land-use seems to play an important role on surface water quality, with percentage woodland significantly correlated with lower medians of EC, NO_2+NO_3 and major cations (Na, Mg, Ca and K) (at least at $p<0.05$) (Table 6.6). Despite the smaller agricultural fields (including sandstone and limestone), this land-use demonstrated positive significant correlations with TS ($p<0.05$), although rather week coefficient. Within urban areas, decreases in TS were significantly correlated with increasing % pervious surfaces, such as gardens ($p<0.01$). On the other hand, percentage impervious surfaces, linked to roads and buildings cover, was positively correlated with EC ($p<0.05$), NO_2+NO_3 as well as major cations (Na, Mg, Ca and K) ($p<0.01$).

Table 6.5 - Spearman's correlations between median concentrations of the ten sampling events, for the quantifiable water quality parameters with rainfall, discharge and drainage area characteristics (n=38). Red colour highlight strong correlations (r≥0.4/-0.4).

		pH	EC	Turbidity	TS	Pt	Nk	NH_4	NO_2+NO_3	COD	Na	Mg	Ca	K	Fe	Zn
Drainage area	r	-0.309	0.131	0.279	.344*	0.045	0.014	0.236	-0.032	-0.210	0.011	-0.041	0.213	-0.058	-0.037	-0.146
	Sig. (2 t.)	0.067	0.433	0.090	0.035	0.788	0.934	0.153	0.848	0.205	0.949	0.808	0.200	0.730	0.828	0.382
Rainfall depth	r	-0.077	-.327*	-0.068	-0.037	0.201	0.141	-0.060	-0.120	0.063	0.023	0.110	-0.075	0.081	-.381*	.374*
	Sig. (2 t.)	0.655	0.045	0.684	0.827	0.226	0.400	0.721	0.472	0.707	0.891	0.511	0.653	0.627	0.018	0.021
Rainfall duration	r	-.383*	0.041	-0.050	0.071	.578**	.505**	0.270	0.196	0.165	.337*	0.300	0.243	0.317	-0.195	.649**
	Sig. (2 t.)	0.021	0.808	0.764	0.671	0.000	0.001	0.101	0.238	0.323	0.038	0.067	0.141	0.053	0.240	0.000
Imean	r	.334*	-0.317	0.192	0.003	-.462**	-.505**	-0.243	-0.278	-0.094	-.347*	-0.199	-0.309	-0.280	0.044	-0.254
	Sig. (2 t.)	0.047	0.052	0.247	0.987	0.004	0.001	0.141	0.090	0.574	0.033	0.231	0.059	0.089	0.791	0.124
I_{15}	r	0.280	-.330*	0.025	-0.069	-0.248	-0.316	-0.302	-0.276	0.012	-0.179	-0.050	-0.160	-0.104	-0.229	-0.041
	Sig. (2 t.)	0.098	0.043	0.880	0.680	0.133	0.053	0.065	0.094	0.944	0.282	0.764	0.338	0.534	0.166	0.808
I_{60}	r	0.143	-.489**	-0.073	-0.164	-0.083	-0.134	-0.261	-0.260	-0.015	-0.229	-0.116	-0.257	-0.061	-.351*	0.083
	Sig. (2 t.)	0.405	0.002	0.662	0.326	0.619	0.422	0.113	0.116	0.928	0.166	0.488	0.119	0.714	0.031	0.619
API_7	r	.402*	0.183	0.069	0.094	-0.224	-0.300	-.430**	-0.237	-.343*	0.133	0.147	0.168	-0.017	0.165	-0.096
	Sig. (2 t.)	0.015	0.271	0.682	0.574	0.175	0.067	0.007	0.152	0.035	0.427	0.378	0.314	0.920	0.322	0.567
API_{14}	r	.463**	0.183	0.169	0.161	-.467**	-.495**	-.328*	-0.251	-0.320	-0.029	0.019	0.041	-0.210	0.254	-0.283
	Sig. (2 t.)	0.004	0.272	0.310	0.335	0.003	0.002	0.044	0.129	0.050	0.863	0.911	0.805	0.205	0.124	0.085
Total flow	r	-0.271	-0.041	0.020	0.263	0.275	0.181	0.021	0.056	-0.059	0.193	0.283	0.244	0.206	-.356*	.321*
	Sig. (2 t.)	0.110	0.806	0.907	0.111	0.095	0.276	0.900	0.740	0.723	0.247	0.085	0.139	0.214	0.028	0.050
Storm flow	r	-0.126	-0.217	0.033	0.048	0.289	0.241	0.121	-0.031	-0.019	-0.014	0.087	0.023	0.127	-.370*	.366*
	Sig. (2 t.)	0.464	0.190	0.846	0.775	0.078	0.145	0.468	0.854	0.910	0.935	0.604	0.889	0.448	0.022	0.024
Base flow	r	-.384*	0.109	0.039	.394*	0.220	0.099	0.003	0.051	-0.068	0.296	.387*	.372*	0.172	-0.236	0.213
	Sig. (2 t.)	0.021	0.517	0.814	0.014	0.185	0.553	0.985	0.763	0.686	0.071	0.016	0.021	0.302	0.153	0.199
Event peak discharge	r	0.017	-0.272	0.064	0.000	0.207	0.130	0.104	-0.115	-0.116	-0.146	-0.095	-0.031	0.037	-.403*	0.186
	Sig. (2 t.)	0.920	0.098	0.705	0.999	0.213	0.438	0.535	0.490	0.489	0.382	0.570	0.853	0.827	0.012	0.264

Table 6.5 (cont.) - Spearman's correlations between median concentrations of the ten sampling events, for the quantifiable water quality parameters with rainfall, discharge and drainage area characteristics (n=38). Red colour highlight strong correlations (r≥0.4/-0.4).

		pH	EC	Turbidity	TS	Pt	Nk	NH_4	NO_2+NO_3	COD	Na	Mg	Ca	K	Fe	Zn
Runof	r	-0.106	0.071	-0.210	0.101	0.114	0.026	-0.279	0.115	-0.028	.323*	.371*	0.208	0.275	-0.192	0.308
coeficient	Sig. (2 t.)	0.538	0.670	0.206	0.548	0.495	0.876	0.089	0.490	0.869	0.048	0.022	0.209	0.094	0.247	0.060
Woodland	r	0.139	-.373*	0.162	-0.217	-0.051	-0.057	0.080	-.440**	-0.288	-.404*	-.587**	-.457**	-.373*	0.018	-0.118
	Sig. (2 t.)	0.418	0.021	0.332	0.191	0.763	0.735	0.632	0.006	0.080	0.012	0.000	0.004	0.021	0.916	0.480
Agriculture	r	-0.319	0.320	0.028	.371*	-.322*	-.341*	-0.268	0.035	0.082	0.311	.328*	0.236	-0.079	0.281	-0.275
	Sig. (2 t.)	0.058	0.050	0.868	0.022	0.048	0.036	0.103	0.835	0.623	0.057	0.044	0.153	0.636	0.087	0.095
Urban	r	0.236	0.027	-0.284	-0.217	0.100	0.130	-0.116	0.261	0.276	0.126	0.259	0.048	0.276	-0.074	0.249
	Sig. (2 t.)	0.166	0.872	0.084	0.191	0.549	0.436	0.486	0.113	0.093	0.449	0.117	0.776	0.094	0.658	0.131
Urban:	r	-0.139	.373*	-0.162	0.217	0.051	0.057	-0.080	.440**	0.288	.404*	.587**	.457**	.373*	-0.018	0.118
impervious	Sig. (2 t.)	0.418	0.021	0.332	0.191	0.763	0.735	0.632	0.006	0.080	0.012	0.000	0.004	0.021	0.916	0.480
Urban:	r	-0.236	-0.027	0.284	0.217	-0.100	-0.130	0.116	-0.261	-0.276	-0.126	-0.259	-0.048	-0.276	0.074	-0.249
semi-	Sig. (2 t.)	0.166	0.872	0.084	0.191	0.549	0.436	0.486	0.113	0.093	0.449	0.117	0.776	0.094	0.658	0.131
Urban:	r	.429**	-0.264	-0.245	-.481**	0.238	0.276	0.039	0.088	0.137	-0.170	-0.110	-0.234	0.183	-0.204	.344*
pervious	Sig. (2 t.)	0.009	0.109	0.139	0.002	0.150	0.094	0.818	0.599	0.411	0.309	0.513	0.157	0.273	0.219	0.035
Sandstone	r	-0.321	0.244	0.096	.354*	-.332*	-.356*	-0.226	-0.075	-0.009	0.216	0.183	0.148	-0.177	0.283	-0.320
	Sig. (2 t.)	0.056	0.140	0.567	0.029	0.042	0.028	0.172	0.653	0.958	0.194	0.272	0.376	0.289	0.085	0.050
Limestone	r	0.319	-0.320	-0.028	-.371*	.322*	.341*	0.268	-0.035	-0.082	-0.311	-.328*	-0.236	0.079	-0.281	0.275
	Sig. (2 t.)	0.058	0.050	0.868	0.022	0.048	0.036	0.103	0.835	0.623	0.057	0.044	0.153	0.636	0.087	0.095

** Correlation significant at the level 0.01 (2 tailes).

* Correlation significant at the level 0.05 (2 tailes).

Median concentrations per rainfall event were significantly affected by rainfall and streamflow patterns (Table 6.5). Increasing rainfall depth lead to significant increases of Zn ($p<0.05$), but decreases in Fe ($p<0.05$). Rainfall duration showed positive correlations with TP, Nk and Zn ($p<0.01$), but also negative correlations with pH ($p<0.05$). Furthermore, greater mean rainfall intensity reduced TP and Nk ($p<0.01$). Nonetheless, greater maximum rainfall intensity (I_{60}) lessened median EC ($p<0.01$) and Fe values ($p<0.05$). Antecedent rainfall also demonstrated some influence on surface water quality during rainfall events, displayed by the positive correlations between API_7 and pH ($p<0.05$) and negative correlations with median concentrations of NH_4 ($p<0.01$). Apart from pH, API_{14} was also negatively correlated with Nk and TP ($p<0.01$).

Cumulative values of streamflow per storm event also influenced median concentration values. Iron decreased significantly with increasing total flow, cumulative storm flow and peak flow ($p<0.05$). But increasing storm flow favoured median Zn concentrations ($p<0.05$). However, when all the water samples were considered together with the instantaneous discharge, total and storm flow only led to turbidity increases, as presented on section 6.4.2.1.. Furthermore, cumulative baseflow per storm event provided significant increases in median Mg and Ca concentrations ($p<0.05$), but decreases on pH ($p<0.05$) (Table 6.5).

Since ESAC represents the largest drainage area, including the upstream sub-catchments, it showed the greatest loads (Table 6.6), but not the highest specific loads (Table 6.7). Generally, over the study period, Espírito Santo, with smaller drainage area and larger urban land-use, demonstrated the higher specific loads of all the parameters quantified, except TS, which was greater in Quinta sub-catchment, encompassing the enterprise park construction site. Quinta also displayed the second larger mean of NH4 and Fe loads, whereas for all the other water chemical parameters (except NO2+NO3 and Mg) the second higher specific loads were found in ESAC. The lowest loads per unit area were perceived in Quinta (TP, NO2+NO3, Mg, Ca, K and Zn) and Porto Bordalo (TS, Nk, NH4, COD, Na and Fe). These spatial variation of specific loads between study sites did not follow the same order as observed for median concentrations, previously reported on section 6.4.2.1..

Table 6.6 - Event load of quantifiable water quality parameters analysed in the four study sites, during the ten rainfall events monitored, including mean and standard deviation per study site.

	23/10/2011	26/10/2011	02/11/2011	14/11/2011	16/12/2011	04/05/2012	25/09/2012	09/01/2013	15/01/2013	25/03/2013	*Mean*	*Stand. dev.*
TS (kg)												
ESAC	990	422	10624	3083	260	658	3742	1084	6852	21726	*4944*	*6780*
P. Bordalo	68	28	718	218	41	13	347	54	217	3081	*479*	*940*
Esp. Santo	0	62	449	183	38	40	725	291	1132	1551	*447*	*531*
Quinta	0	215	5915	939	41	76	1233	376	1199	3037	*1303*	*1864*
TP (g)												
ESAC	139	78	130	129	37	186	1284	306	1486	5825	*960*	*1788*
P. Bordalo	15	12	125	19	8	10	306	84	161	733	*147*	*227*
Esp. Santo	0	12	10	26	6	13	166	88	259	251	*83*	*104*
Quinta	0	10	91	15	5	24	131	98	249	563	*119*	*174*
Nk (g)												
ESAC	2880	1222	9936	3885	1058	2761	12556	5837	24675	97938	*16275*	*29582*
P. Bordalo	621	253	2497	832	163	174	3388	1125	3182	12205	*2444*	*3645*
Esp. Santo	0	306	763	697	188	173	3659	1438	5514	7003	*1974*	*2520*
Quinta	0	261	3252	874	217	477	2266	2210	9149	15426	*3413*	*5021*
NH_4 (g)												
ESAC	761	416	4997	1681	46	734	6219	2654	7274	8425	*3321*	*3135*
P. Bordalo	279	77	637	228	32	76	651	299	705	1625	*461*	*480*
Esp. Santo	0	100	309	254	9	44	1100	164	1181	449	*361*	*435*
Quinta	0	129	1117	400	17	204	806	311	1738	2641	*736*	*868*
NO_2+NO_3 (g)												
ESAC	2222	710	6529	2772	1796	4191	16716	3635	9927	84172	*13267*	*25370*
P. Bordalo	624	117	1589	411	70	31	8947	2931	192	11559	*2647*	*4154*
Esp. Santo	0	116	771	780	396	326	9124	1230	3116	10391	*2625*	*3873*
Quinta	0	89	147	296	52	238	3751	316	913	5234	*1104*	*1838*
COD (g)												
ESAC	57864	22346	83578	34556	8672	11645	178713	49830	159307	1224773	*183129*	*370697*
P. Bordalo	11232	2574	9479	2258	797	1913	84108	10727	11204	68930	*20322*	*30126*
Esp. Santo	0	6288	19316	9741	1832	3234	108754	12702	56074	107374	*32532*	*42948*
Quinta	0	5501	34260	5960	1404	4075	38240	8203	39354	178150	*31515*	*53895*
Na (g)												
ESAC	23172	6533	25734	23133	15055	44068	110022	74516	131567	1838592	*229239*	*567042*
P. Bordalo	1112	534	3035	1826	1815	564	11614	952	10521	149307	*18128*	*46273*
Esp. Santo	0	3525	10656	7295	3117	4561	21555	14301	28702	166910	*26062*	*50298*
Quinta	0	4627	8109	5102	2059	4511	16493	11203	45918	272660	*37068*	*83830*
Mg (g)												
ESAC	11470	5622	26674	17322	7320	18006	47929	25671	97802	701774	*95959*	*214600*
P. Bordalo	423	205	2002	1281	350	180	5110	659	5435	190011	*20565*	*59570*
Esp. Santo	0	1687	6835	8709	1432	1708	13915	11247	27650	64338	*13752*	*19616*
Quinta	0	729	4349	2228	1000	1385	6831	4427	14507	47824	*8328*	*14520*
Ca (g)												
ESAC	75065	35116	147975	117834	46482	97837	252844	125188	504622	3155275	*455824*	*958392*
P. Bordalo	7648	3889	20309	11018	2618	1882	41286	10409	30559	599564	*72918*	*185493*
Esp. Santo	0	8274	28166	22343	5274	6512	51213	36646	87933	185808	*43217*	*56742*
Quinta	0	6844	56190	28012	4213	10711	31953	31403	100354	233049	*50273*	*70897*

Table 6.6 (cont.) – Event load of quantifiable water quality parameters analysed in the four study sites, during the ten rainfall events monitored, including mean and standard deviation per study site.

	23/10/2011	26/10/2011	02/11/2011	14/11/2011	16/12/2011	04/05/2012	25/09/2012	09/01/2013	15/01/2013	25/03/2013	*Mean*	*Stand. dev.*
K (g)												
ESAC	12153	4866	23064	16780	5026	16865	61478	13633	77960	622214	*85404*	*190190*
P. Bordalo	1788	735	3168	1815	652	381	10336	3848	12862	80169	*11576*	*24477*
Esp. Santo	0	1351	5312	3392	776	940	12841	6403	16400	58004	*10542*	*17547*
Quinta	0	543	5044	2805	771	901	12620	3923	12062	72083	*11075*	*21920*
Fe (g)												
ESAC	1081	778	4148	2820	396	521	2676	715	7131	13897	*3416*	*4246*
P. Bordalo	119	399	350	377	81	69	812	134	874	2075	*529*	*615*
Esp. Santo	0	315	557	457	93	93	835	255	1008	1736	*535*	*534*
Quinta	0	387	3659	1165	212	353	460	443	2560	2872	*1211*	*1317*
Zn (g)												
ESAC	48	36	179	253	45	91	2396	635	5917	7491	*1709*	*2752*
P. Bordalo	19	11	24	34	9	3	786	201	411	1512	*301*	*495*
Esp. Santo	0	9	31	53	4	5	592	144	459	518	*181*	*241*
Quinta	0	15	71	32	6	11	303	248	1287	1511	*348*	*566*

Table 6.7 – Specific load of quantifiable water quality parameters analysed in the four study sites, during the ten rainfall events monitored, including mean and standard deviation values per study site.

	23/10/2011	26/10/2011	02/11/2011	14/11/2011	16/12/2011	04/05/2012	25/09/2012	09/01/2013	15/01/2013	25/03/2013	*Mean*	*Stand. dev.*
TS (kg km^{-2})												
ESAC	161	69	1728	501	42	107	609	176	1114	3533	*804*	*1102*
P. Bordalo	60	25	635	193	36	12	307	48	192	2727	*424*	*831*
Esp. Santo	-	116	847	344	71	76	1367	549	2136	2927	*937*	*1016*
Quinta	-	144	3943	626	27	51	822	251	799	2025	*965*	*1277*
TP (g km^{-2})												
ESAC	23	13	21	21	6	30	209	50	242	947	*156*	*291*
P. Bordalo	14	11	110	16	7	9	270	74	143	649	*130*	*201*
Esp. Santo	-	24	20	48	11	24	314	166	489	474	*174*	*200*
Quinta	-	7	61	10	3	16	87	65	166	375	*88*	*120*
Nk (g km^{-2})												
ESAC	468	199	1616	632	172	449	2042	949	4012	15925	*2646*	*4810*
P. Bordalo	550	224	2209	736	144	154	2998	995	2816	10801	*2163*	*3225*
Esp. Santo	-	577	1439	1315	355	326	6905	2713	10404	13213	*4139*	*4849*
Quinta	-	174	2168	583	144	318	1511	1473	6099	10284	*2528*	*3447*
NH_4 (g km^{-2})												
ESAC	124	68	812	273	7	119	1011	432	1183	1370	*540*	*510*
P. Bordalo	247	69	564	202	28	68	576	265	623	1438	*408*	*425*
Esp. Santo	-	190	582	478	18	83	2076	309	2228	846	*757*	*832*
Quinta	-	86	745	267	11	136	538	207	1158	1761	*545*	*586*

Table 6.7 (cont.) – Specific load of quantifiable water quality parameters analysed in the four study sites, during the ten rainfall events monitored, including mean and standard deviation values per study site.

	23/10/ 2011	26/10/ 2011	02/11/ 2011	14/11/ 2011	16/12/ 2011	04/05/ 2012	25/09/ 2012	09/01/ 2013	15/01/ 2013	25/03/ 2013	*Mean*	*Stand. dev.*
NO_2+NO_3 (g km^{-2})												
ESAC	361	115	1062	451	292	681	2718	591	1614	13687	*2157*	*4125*
P. Bordalo	552	104	1406	363	62	27	7918	2594	170	10229	*2343*	*3676*
Esp. Santo	-	219	1456	1471	746	614	17215	2320	5879	19606	*5503*	*7529*
Quinta	-	59	98	198	35	159	2501	211	608	3489	*817*	*1270*
COD (kg km^{-2})												
ESAC	9	4	14	6	1	2	29	8	26	199	*30*	*60*
P. Bordalo	10	2	8	2	1	2	74	9	10	61	*18*	*27*
Esp. Santo	-	12	36	18	3	6	205	24	106	203	*68*	*83*
Quinta	-	4	23	4	1	3	25	5	26	119	*23*	*37*
Na (kg km^{-2})												
ESAC	4	1	4	4	2	7	18	12	21	299	*37*	*92*
P. Bordalo	1	0	3	2	2	0	10	1	9	132	*16*	*41*
Esp. Santo	-	7	20	14	6	9	41	27	54	315	*55*	*99*
Quinta	-	3	5	3	1	3	11	7	31	182	*27*	*59*
Mg (kg km^{-2})												
ESAC	2	1	4	3	1	3	8	4	16	114	*16*	*35*
P. Bordalo	0	0	2	1	0	0	5	1	5	168	*18*	*53*
Esp. Santo	-	3	13	16	3	3	26	21	52	121	*29*	*38*
Quinta	-	0	3	1	1	1	5	3	10	32	*6*	*10*
Ca (kg km^{-2})												
ESAC	12	6	24	19	8	16	41	20	82	513	*74*	*156*
P. Bordalo	7	3	18	10	2	2	37	9	27	531	*65*	*164*
Esp. Santo	-	16	53	42	10	12	97	69	166	351	*91*	*109*
Quinta	-	5	37	19	3	7	21	21	67	155	*37*	*49*
K (kg km^{-2})												
ESAC	2	1	4	3	1	3	10	2	13	101	*14*	*31*
P. Bordalo	2	1	3	2	1	0	9	3	11	71	*10*	*22*
Esp. Santo	-	3	10	6	1	2	24	12	31	109	*22*	*34*
Quinta	-	0	3	2	1	1	8	3	8	48	*8*	*15*
Fe (g km^{-2})												
ESAC	176	127	675	459	64	85	435	116	1159	2260	*556*	*690*
P. Bordalo	105	354	309	333	71	61	718	118	773	1837	*468*	*544*
Esp. Santo	-	595	1051	863	175	176	1576	481	1902	3276	*1122*	*1000*
Quinta	-	258	2439	777	141	236	307	295	1706	1914	*897*	*881*
Zn (g km^{-2})												
ESAC	8	6	29	41	7	15	390	103	962	1218	*278*	*447*
P. Bordalo	17	10	22	30	8	3	696	178	364	1338	*266*	*438*
Esp. Santo	-	16	58	101	7	9	1116	272	865	977	*380*	*466*
Quinta	-	10	47	22	4	7	202	165	858	1007	*258*	*391*

Specific loads per rainfall event did not show the same correlations with the biophysical characteristics of the study sites as observed with median concentrations, particularly regarding to major cations. In terms of correlations with land-use, SEL of NO_2+NO_3 and Mg decreased with % woodland ($p<0.01$), but increased with % urban areas, particularly impervious surface extent ($p<0.01$) (Table 6.8). Within urban land-use, pervious areas did not show correlations with surface water quality. As regards to lithology, SEL of Na increased significantly with higher % sandstone ($p<0.05$), despite the week correlation, but decreased with % limestone ($p<0.01$).

Hydrological data demonstrated to be a major parameter influencing specific loads of surface water quality parameters (Table 6.8). During storm events, rainfall pattern, particularly rainfall amount and duration, showed strong correlations with all specific loads ($p<0.01$). Increasing I_{15} and I_{60} also leaded to higher SEL, except for NO_2+NO_3 and Na. However, API did not seem to influence specific loads of water quality parameters. Discharge properties (total flow, including storm and baseflow components, as well as runoff coefficients per event) significantly correlate with all specific loads ($p<0.01$). Peak discharge revealed lower correlation coefficients than total discharge properties, and it did not seem to influence NO_2+NO_3, COD, Na, Mg and Fe specific loads ($p>0.05$).

A positive linear correlation between event streamflow and SELs (Figure 6.18) highlight the relevance of stream discharge. *ESAC* no longer showed higher specific loads, but contrary, displayed the smallest SELs within *Ribeira dos Covões*, linked to the lowest regression lines (Figure 6.18). Despite the generally higher SELs in *Espírito Santo*, *Porto Bordalo* showed greatest increases with discharge as regards to TP, Mg, K and Zn loads. In turn, *Quinta* displayed the highest regression line of NH_4.

Table 6.8 – Spearman's correlation between specific loads of the ten sampling events, for the quantifiable water quality parameters with rainfall, discharge and drainage area characteristics (n=38).

		TS	Pt	Nk	NH_4	NO_2+NO_3	COD	Na	Mg	Ca	K	Fe	Zn
Rainfall	r	**.877****	**.799****	**.907****	**.897****	.639**	**.825****	.656**	.734**	**.831****	**.853****	**.805****	**.854****
depth	Sig. (2 t.)	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
Rainfall	r	.373*	.706**	.637**	.534**	.590**	.534**	.625**	.572**	.581**	.628**	.354*	.734**
duration	Sig. (2 t.)	.021	.000	.000	.001	.000	.001	.000	.000	.000	.000	.029	.000
Imean	r	.236	-.195	.006	.102	-.206	.004	-.167	-.044	.027	-.047	.306	-.075
	Sig. (2 t.)	.153	.240	.971	.543	.215	.982	.316	.794	.872	.780	.061	.655
I_{15}	r	.661**	.318	.480**	.532**	.294	.504**	.249	.370*	.467**	.432**	.657**	.406*
	Sig. (2 t.)	.000	.052	.002	.001	.073	.001	.131	.022	.003	.007	.000	.011
I_{60}	r	.561**	.337*	.467**	.541**	.164	.499**	.236	.329*	.413**	.410*	.621**	.391*
	Sig. (2 t.)	.000	.039	.003	.000	.326	.001	.154	.044	.010	.011	.000	.015
API_7	r	-.050	-.138	-.148	-.164	-.082	-.210	.059	.030	-.039	-.109	.071	-.178
	Sig. (2 t.)	.768	.408	.376	.324	.623	.206	.724	.857	.818	.516	.670	.285
API_{14}	r	.050	-.210	-.149	-.123	-.161	-.272	-.068	-.022	-.028	-.141	.119	-.224
	Sig. (2 t.)	.764	.206	.372	.464	.335	.099	.686	.895	.868	.400	.475	.177
Total flow	r	**.791****	**.782****	**.796****	**.812****	.606**	.679**	.667**	.728**	**.796****	**.766****	.630**	**.756****
	Sig. (2 t.)	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
Storm flow	r	.675**	.693**	.723**	.725**	.528**	.608**	.457**	.560**	.640**	.666**	.515**	.686**
	Sig. (2 t.)	.000	.000	.000	.000	.001	.000	.004	.000	.000	.000	.001	.000
Base flow	r	**.789****	.742**	.747**	**.760****	.590**	.656**	.736**	**.777****	**.814****	.749**	.623**	.717**
	Sig. (2 t.)	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
Peak discharge	r	.461**	.413*	.451**	.483**	.250	.300	.149	.256	.371*	.390*	.309	.401*
	Sig. (2 t.)	.004	.010	.005	.002	.129	.067	.372	.121	.022	.016	.059	.013
Runof	r	.667**	**.812****	**.779****	.707**	.697**	.705**	**.821****	**.804****	**.806****	**.771****	.710**	.744**
coeficient	Sig. (2 t.)	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
Woodland	r	-.130	-.181	-.134	-.098	-.437**	-.269	-.354*	-.424**	-.296	-.293	-.095	-.086
	Sig. (2 t.)	.436	.277	.421	.558	.006	.103	.029	.008	.071	.074	.569	.607
Agriculture	r	.311	.049	.107	.121	.079	.246	.422**	.337*	.287	.142	.330*	.078
	Sig. (2 t.)	.057	.770	.523	.468	.636	.136	.008	.038	.081	.394	.043	.640
Urban	r	-.019	.147	.128	.046	.363*	.210	.164	.225	.143	.218	.082	.091
	Sig. (2 t.)	.910	.379	.445	.783	.025	.206	.325	.174	.393	.188	.626	.588
Urban:	r	.130	.181	.134	.098	.437**	.269	.354*	.424**	.296	.293	.095	.086
impervious	Sig. (2 t.)	.436	.277	.421	.558	.006	.103	.029	.008	.071	.074	.569	.607
Urban:	r	.019	-.147	-.128	-.046	-.363*	-.210	-.164	-.225	-.143	-.218	-.082	-.091
semi-	Sig. (2 t.)	.910	.379	.445	.783	.025	.206	.325	.174	.393	.188	.626	.588
Urban:	r	-.217	.060	.030	-.047	.172	-.002	-.165	-.088	-.101	.047	-.109	.024
pervious	Sig. (2 t.)	.191	.720	.858	.778	.302	.990	.321	.599	.547	.778	.513	.888
Sandstone	r	.281	-.004	.061	.094	-.048	.161	.324*	.222	.206	.057	.288	.048
	Sig. (2 t.)	.088	.982	.714	.575	.774	.333	.047	.180	.214	.735	.079	.777
Limestone	r	-.311	-.049	-.107	-.121	-.079	-.246	-.422**	-.337*	-.287	-.142	-.330*	-.078
	Sig. (2 t.)	.057	.770	.523	.468	.636	.136	.008	.038	.081	.394	.043	.640

** Correlation significant at the level 0.01 (2 tailes).

* Correlation significant at the level 0.05 (2 tailes).

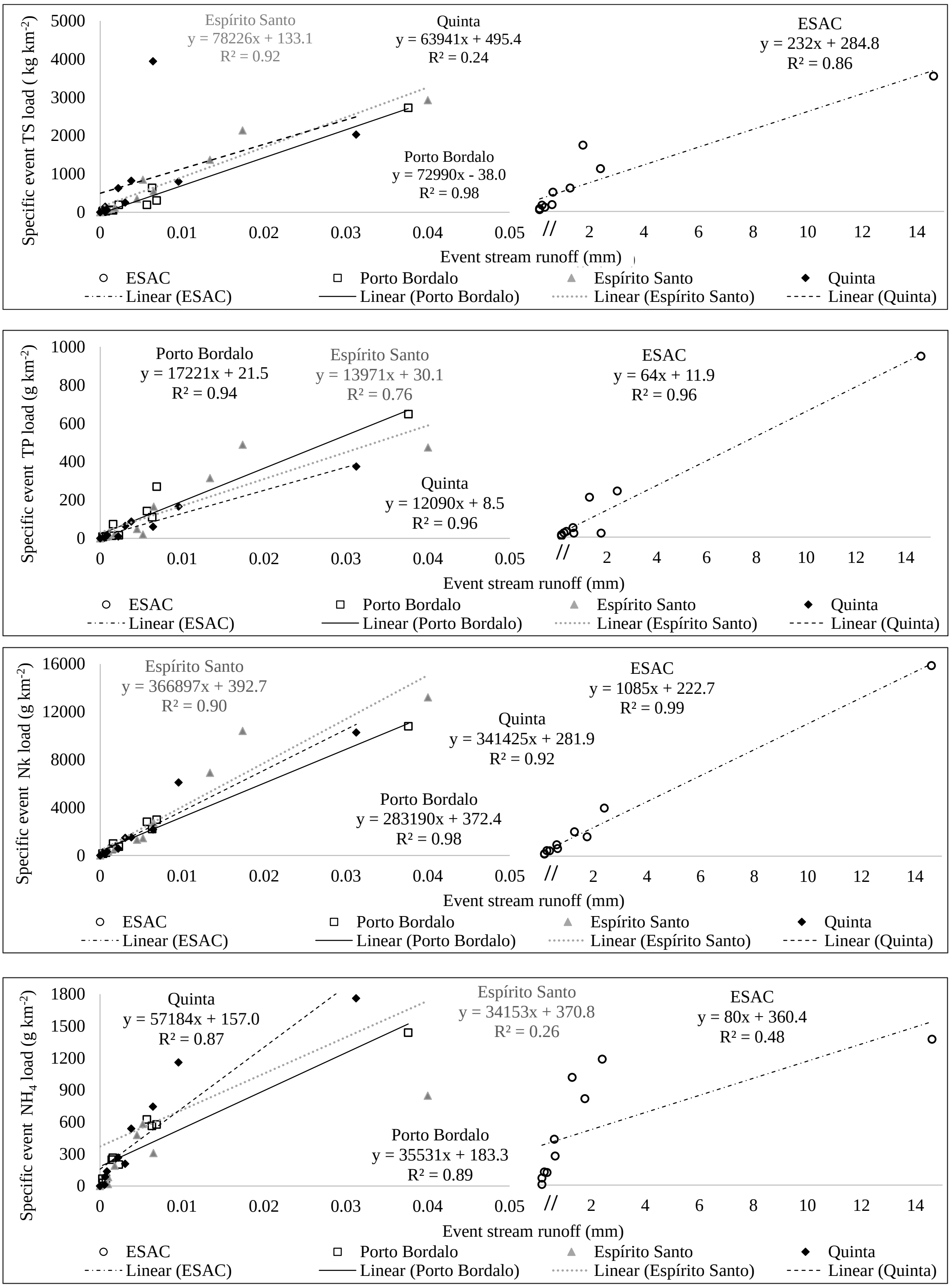


Figure 6.18 - Specific event load and event stream runoff for the four study sites, over the ten sampling periods, for individual quantifiable water quality parameters.

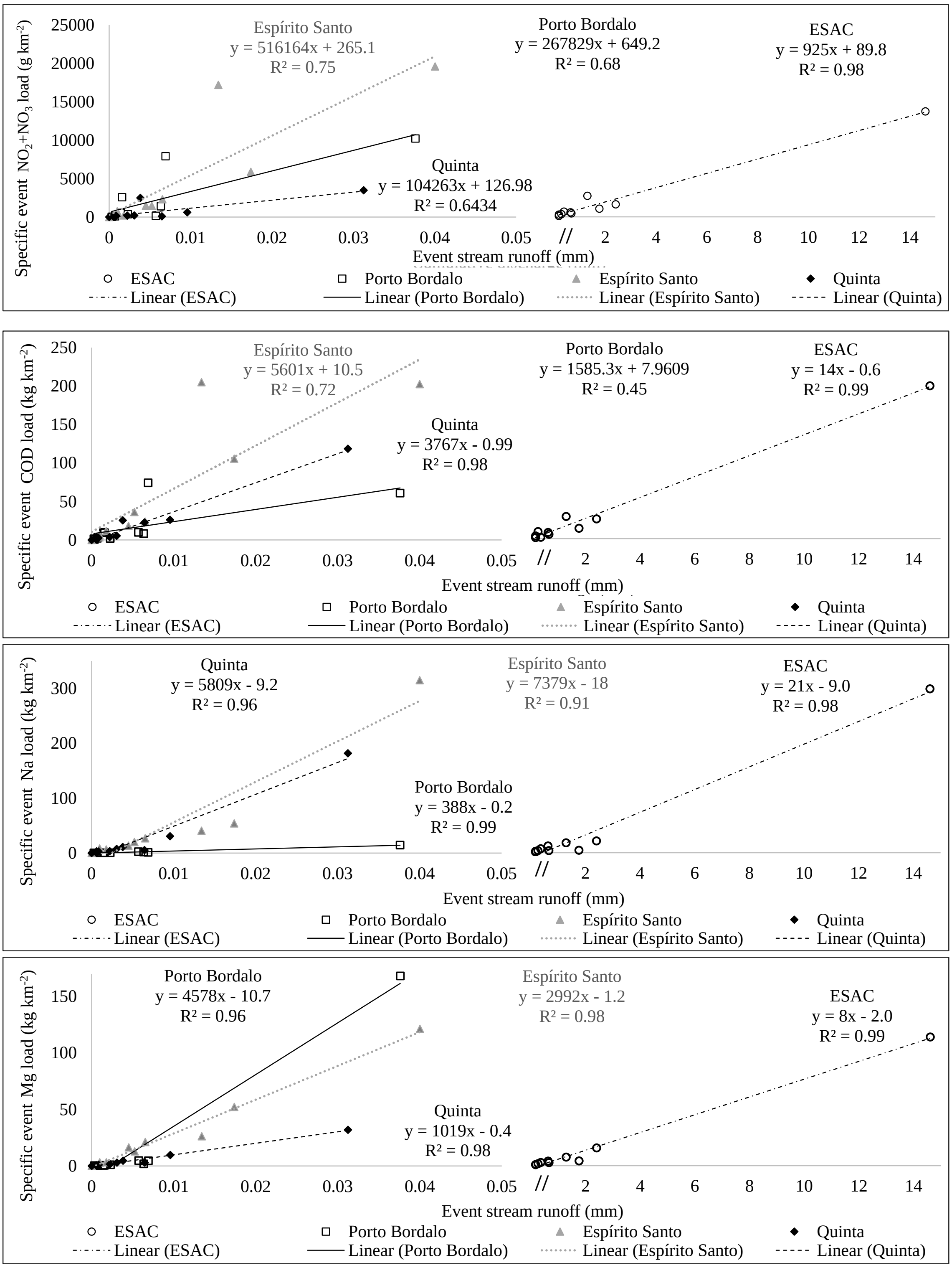


Figure 6.18 (cont.) - Specific event load and event stream runoff for the four study sites, over the ten sampling periods, for individual quantifiable water quality parameters.

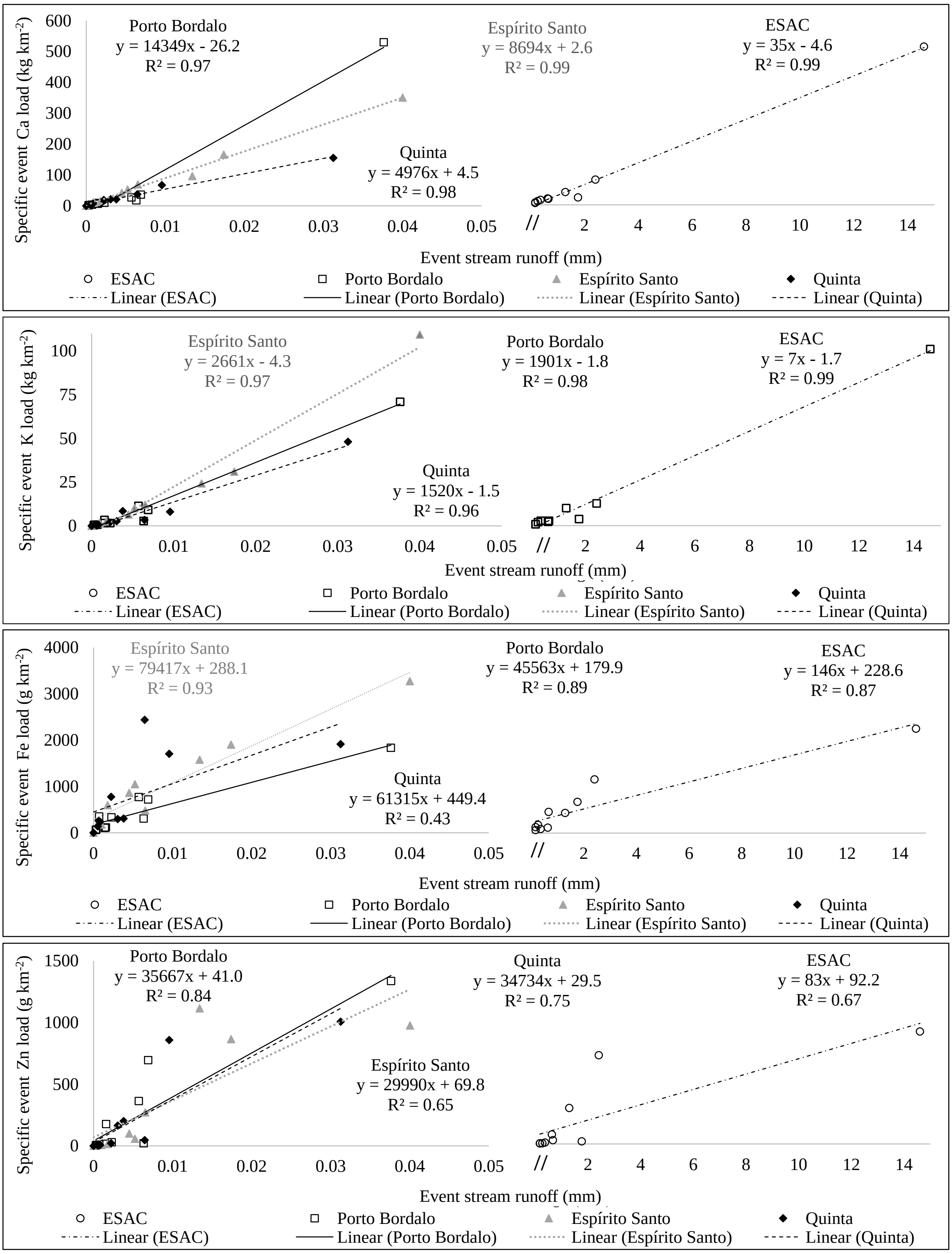


Figure 6.18 (cont.) - Specific event load and event stream runoff for the four study sites, over the ten sampling periods, for individual quantifiable water quality parameters.

6.5. Discussion

6.5.1. Spatial variation of surface water quality

6.5.1.1. Land-use impacts

The four study sites, characterized by different land-uses, revealed dissimilar surface water quality, although some chemical elements, such as EC, Nk, NO_2+NO_3 and heavy metals, did not show significant spatial variations. Despite the general acceptable water quality across *Ribeira dos Covões*, ocassional pollutant levels were achieved in all the measured sites, as regards to nitrogen and few heavy metals. Kjeldhal nitrogen achieved pollutant levels in few samples of all the study sites (maximum concentrations over the study period reached 2.5 mg L^{-1} in *Espírito Santo* and *Porto Bordalo*, 2.6 mg L^{-1} in *ESAC* and 2.8 mg L^{-1} in *Quinta*, when the standard is 2.0 mg L^{-1}). Pollutant levels of NH_4 (>1.0 mg L^{-1}) were also attained in few samples of *ESAC* and *Espírito Santo* (maximum values of 1.6 mg L^{-1} and 1.5 mg L^{-1}), with slightly exceedance of the quality standards in *Porto Bordalo* (1.1 mg L^{-1}). Few measurements of Zn revealed marginal pollutant concentrations (0.5 mg L^{-1}) in *ESAC* (maximum of 0.8 mg L^{-1}), as well as *Quinta* and *Porto Bordalo* (maximum of 0.6 mg L^{-1} in both sites). In *Espírito Santo*, there was one sample showing Cu concentrations twice higher than the minimum water quality standard (maximum of 0.2 mg L^{-1}), but in *ESAC*, Cd concentration exceeded five times the pollutant levels in one occasion (0.05 mg L^{-1}).

Within urban land-uses, impervious surfaces are usually associated with decreasing surface water quality. Considering the water quality of the four study sites, median event loads of EC, COD, NO_2+NO_3, Mg, Ca and K displayed a linear association with increasing TIA (Figure 6.19), despite the correlations were only statistical significant as regards to NO_2+NO_3 and Mg. Sodium also showed this tendency if results from *Quinta* are not considered, possibly due to partial disturbance caused by construction works in 10% of the contributing area.

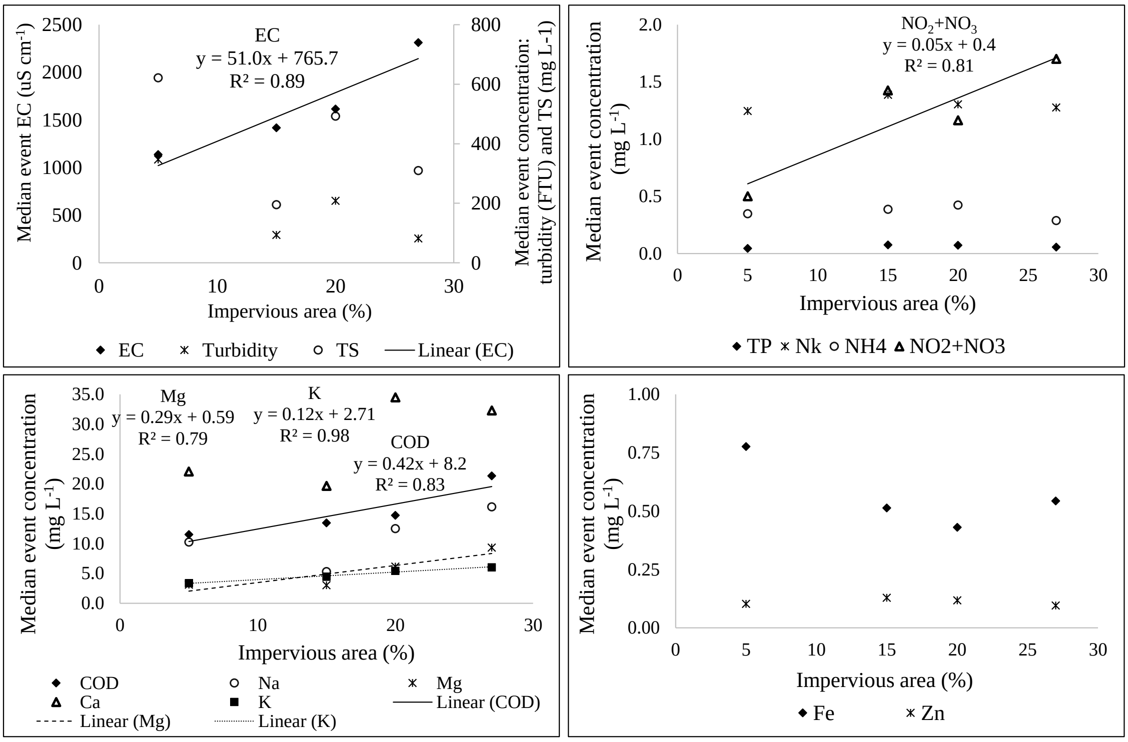


Figure 6.19 - Relationship between mean event load and total impervious area for the four study sites within *Ribeira dos Covões*.

Numerous studies have reported the impact of urban land-use on surface water quality degradation (Vander Laan et al., 2013; Yu et al., 2014). However, in Shanghai, China, Wang et al. (2008) demonstrated that despite there being a direct relationship between urbanization level and the degree of water degradation, this relationship takes the form of an inverted U-shaped curve, steeper in urban than suburban areas, linked with the economic development. After urbanization establishment, environmental concerns start to rise in economically developed cities, leading to increasing investment in pollution prevention, particularly, water quality protection.

Despite pollutant concentrations are of utmost importance for ecosystems status, they are highly variable during inter- and intra-storm events, representing environmental risk during short periods of time (in few samples), according with *Ribeira dos Covões* results. Because of the highly variable concentrations of water quality parameters, pollutant loads can be an interesting parameter to consider the longer term impacts on ecossystems. There can be high concentrations of pollutants, but if the discharge is low, there would only be a small quantity of pollutant transported, thus having minor environmental impact comparing with lower concentrations associated with higher flows. Considering the significant increases of most water quality parameters with increasing drainage area, normalized pollutant loads were considered the most appropriate to assess differences between the study sites.

In *Ribeira dos Covões*, despite the general increase of specific loads with urban extent, except for TS, linear relationships were only observed for TP, NO_2+NO_3, Ca and Mg (Figure 6.20).

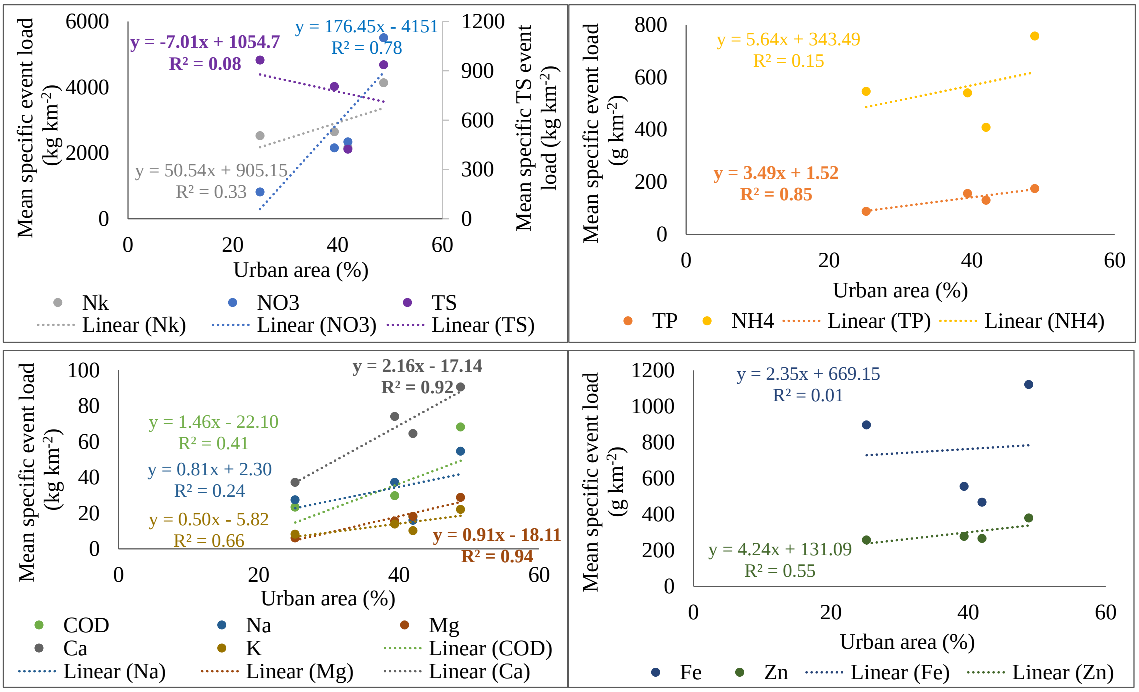


Figure 6.20 – Mean specific event load over the ten sampling periods and percentage urban area, for quantifiable water quality parameters.

Espírito Santo, with the largest urban land-use (49% of the drainage area and 27% impervious surface cover), displayed the highest specific event loads of COD, Nk, NO_2+NO_3, Na, K, Fe and Cu. *Porto Bordalo*, with minor urban areas and imperviousness (42% and 15%, respectively) recorded higher event loads of TP, Mg, Ca and Zn. *Quinta*, with the lowest urban extent (25% of the area and 5% impervious surfaces), but with 10% of the drainage area under construction phase, displayed greatest loads of TS and NH_4. *ESAC*, representing the entire *Ribeira dos Covões* catchment, with 40% urban extent and 20% urban impervious surface, showed the lowest specific pollutant loads.

Organic and nutrient pollutants

Chemical oxygen demand displayed significant lower concentrations within *Quinta* drainage area (median and maximum of all the samples: 9.5 mg L^{-1} and 58.0 mg L^{-1}), compared with the other sub-catchments, and highest values in *Espírito Santo* (median and maximum values of 18.0 mg L^{-1} and 62.5 mg L^{-1}), with the largest urban land-use. This study site, also revealed high concentrations (median of 1.2 mg L^{-1} and maximum of 2.5 mg L^{-1}) and highest specific loads of Nk (4 kg km^{-2}). Increasing COD and nitrogen loads from urban areas were also reported by previous authors (e.g. Wilbers et al., 2014). However, according to Shields et al. (2008), urbanized catchments export more nitrogen at higher but less frequent flows than catchment dominated by woodland, agricultural and low-density suburban areas. In fact, in *Ribeira dos Covões*, highest nutrients concentration were measured with peak flow in winter storms, but also under summer baseflow conditions due to lower dilution effect.

In a previous study performed to assess surface water quality in *Ribeira dos Covões*, between 2004 and 2006, the relation BOD/COD in different stream channels was about 0.1 (Ferreira, 2009). Assuming this relationship was constant over the time, despite the nearly 10% increase in the urban land-use, based on COD measurements, median BOD estimations per site (*ESAC*: 1.3 mg L^{-1}; *Porto Bordalo*: 1.1 mg L^{-1}; *Espírito Santo*: 1.8 mg L^{-1}; and *Quinta*: 1.0 mg L^{-1}) did not indicate organic contamination. However, during great rainfall events observed in late summer (25/09/2012), BOD concentrations could have exceeded water quality standards (5 mg L^{-1}, Environmental Ministry, 1998) in all the study sites (in 2% of *Espírito Santo* and *Quinta* samples, 3% and 8% of *ESAC* and *Porto Bordalo*, with maximum values of 6.3 mg L^{-1}, 5.8 mg L^{-1}, 5.6 mg L^{-1} and 6.2 mg L^{-1}).

In the urban land-uses, wastewater has been considered an important source of surface water contamination with COD and nutrients (Kaushal et al., 2011; Wilbers et al., 2014). In *Ribeira dos Covões*, contamination of surface water with untreated domestic wastewater was identified during field trips (through colour, aspect, and smell), possibly resulting from small leakages in the drainage system, but also large pipe ruptures. Such contamination was observed close to the catchment outlet, but also within *Porto Bordalo*, and can be related to the highest COD concentrations and higher median Nk concentrations observed in *ESAC* and *Porto Bordalo* water samples.

Nevertheless, after *Espírito Santo*, the greatest COD and Nk loads considering event streamflow were recorded for the *Quinta* sub-catchment (Figure 6.18). Considering the smaller urban land-use and the existence of sewer drainage system, these results may indicate past soil contamination from an inactive wastewater treatment plant, which received domestic wastewater from upslope urban cores and spread it downstream without treatment. Possible leaching of contaminants can explain the increasing concentrations through the wet season, contrary to the observations at the other study sites, which exhibited greatest concentrations after the summer. However, high COD and Nk loads within *Quinta* could be also a consequence of extensive cattle rearing in the upslope agricultural fields, adjacent to the water channel and close to the sampling location. Surface water contamination by organic compounds in *Quinta*, was also indicated by relatively high median concentrations (0.36 mg L^{-1}) and specific loads of NH_4 (545 g km^{-2}). In USA, manure management problems regarding to agricultural practices have been considered a major problem for water quality, particularly during rainfall events, due to runoff impact on stream network (EPA, 2001).

Despite the high NH_4 loads recorded in *Quinta*, concentrations occasionally exceeded the water quality standards (1.0 mg L^{-1}) at the other three catchment sites, with larger % urban land-use. High concentrations of NH_4 can be toxic to aquatic organisms (Lin et al., 2014).

As regards TP, higher concentrations were found in *Porto Bordalo* and *ESAC* (median values of 0.07 mg L^{-1} for both sites) than in *Espírito Santo* and *Quinta* (0.06 mg L^{-1} and 0.04 mg L^{-1}), and greates specific loads in *Porto Bordalo* (174 g km^{-2}). Phosphorus in urban areas is usually associated with household sources, such as laundry and dishwasher detergents, as well as organic matter biodegradation in domestic wastewater (Mendes and Oliveira, 2004; Carey et al., 2013). In *Porto Bordalo*, pavement and car washes also may be linked with the higher TP loads. Nevertheless, greater TP concentrations in *Porto Bordalo* and *ESAC*, can be also related in part perhaps to the higher clay content of the limestone soils. The high loads of TS can partially involve suspended sediments from clay nature, since *Porto Bordalo* and *ESAC* overlay fully and partially limestone. The contribution of phosphorus in suspended sediments with clay nature was reported by Lin et al. (2014), as a result of adsorptive properties. Furthermore, the downslope location of *ESAC* can favour high TS loads and sediment deposition, based on field observations. According with Mendes and Oliveira (2004), higher concentration of TP are usually found in surface water of sedimentary areas, usually at lower altitude (Mendes and Oliveira, 2004).

Within urban land-use, green areas, such as lawns and gardens, have been also recognised as an important source of nutrients, resulting from fertilization practices (Law et al., 2004; Carey et al., 2013). In *Ribeira dos Covões*, the higher NO_2+NO_3 concentrations were generally observed after the summer (23/10/2011 and 25/09/2012), possibly associated with lawns and gardens fertilization, mostly performed in spring and late summer. However, limited overland flow is usually generated in these pervious surfaces, leading to minor nutrient loads. The highest median NO_2+NO_3 concentrations in Espírito Santo (1.5 mg L^{-1}) could be due to agricultural fertilizers. Although *Espírito Santo* has a small percentage agricultural land-use (5%), some of the fields are adjacent to the stream channel, and may establish a direct contribution of nutrients, particularly nitrate, into the surface water. However, both in agricultural fields and green surfaces of urban areas, impacts on surface water quality will depend on fertilizer management practices, such its timing, recycling grass clippings without adjusting fertilizer rates, irrigation practices, species variability and soil characteristics (e.g. Carey et al., 2013; Wilbers et al., 2014). Furthermore, specific loads of NO_2+NO_3 increased with % urban area (Figure 6.20), which may result from atmospheric deposition, given the greater values recorded after the summer.

In *Ribeira dos Covões*, NO_3 did not represent a constraints for irrigation use, since the recommended guidelines were not exceeded (Environmental Ministry, 1998). Similarly, TP at all the study sites fulfilled the standards for minimum surface water quality.

Phosphorus seems to be the limiting nutrient of aquatic ecosystems in the study catchment. Higher nutrient loads in surface water usually trigger eutrophication problems.

Streamwater from woodland is usually associated with lower runoff and pollutant loads (Yu et al., 2014), which can explain the negative correlation between % of this land-use and median concentrations of EC and NO_2+NO_3. Furthermore, the negative correlation between % woodland and major cations concentrations (Na, Mg, Ca and K) may be due to greater infiltration and weathering (Table 6.5).

Impervious surfaces and other potential sources of metals

Automobile-related sources (e.g. fluids from parking lots, service stations, automobile exhaust, etc.) are important pollutant sources to runoff (Bannerman et al., 1993). Road runoff has been considered an important pollutant source within urban areas, partially due to greater runoff volumes, compared with other land-uses, and thus, increased pollutant loads (Ellis et al., 1986; Bannerman et al., 1993; Crabtree et al., 2006). Typical pollutants in highway runoff include TS, metals (As, Cd, Cu, Cr, Fe, Pb Hg, Ni and Zn), nutrients (NH_4, NO_3, Nk and TP), organic compounds (ex., polycyclic aromatic hydrocarbons, oil and grease), oxygen demand (COD and BOD) and conventional parameters, such as pH, turbidity and conductivity hardness (Herrera, 2007). Road runoff therefore may also have contributed to greater COD and nutrient specif loads in *Espírito Santo* (68 kg COD km^{-2}, 4 kg Nk km^{-2}, 1 kg NH_4 km^{-2} and 6 kg NO_2+NO_3 km^{-2}). Also the significant positive correlations between % impervious surfaces and SELs of Mg, Na and NO_2+NO_3 in *Ribeira dos Covões* may be linked to cement composition, which is largely represented by calcium oxide and silicon dioxide, with minor composition of aluminium and magnesium oxides, and several alkalis, such as sodium oxide and potassium oxide (Hellebois et al., 2013).

Vehicular traffic is an important factor affecting pollutant loads, particularly heavy metals (Zhao et al., 2010; Soares, 2014; Yu et al., 2014). Most pollutants associated with vehicles originate from engine parts (Cu, Cr, Mn), lubricants (Zn and Ni), rusting (Fe), tire wear (Zn, Pb) and tire breaks (Cd) (Herrera, 2007). In the characterization of runoff highway performed by Ellis et al. (1986), decrease metal loadings were observed in the order Fe > Mn > Pb > Zn > Cu > Cd which reflects the expected availability of these metals.

In *Ribeira dos Covões* metal concentrations were not present at pollutant levels, but Zn, Cu and Cd occasionaly exceeded the minimum environmental guidelines, mostly at recession limb of later winter storms. Harmful concentrations of Zn were attained in *ESAC*, *Porto Bordalo* and *Quinta*, possibly due to contributions from road traffic separators, particularly placed nearby *Porto Bordalo* stream and downslope *ESAC*, covering a greater road extension than within the other sites. Possible Zn contaminations could also result from industrial activities, namely wood conservation in sawmill companies and pharmaceutic industry, found in the study catchment. Industrial activities have been also considered has a source of metals by previous authors (e.g. Naeemullah et al., 2014).

Cupper concentration guidelines were exceeded in few samples of all the sites, whereas Cd was only measured in *ESAC*. Cupper exceeded the MRV guideline for irrigation purpose in *Espírito Santo*, whereas VRM of Mn were exceeded in few water samples of *ESAC* and *Porto Bordalo*. High concentrations of heavy metals in surface water may provide toxic effects when used for animals and cultures irrigation (Environment Ministry, 1986). Generally, there is not an apparent relation between heavy metals concentration and the urban extent, but the relatively high detection limit of the analytical methods used may be masking the metal loads and the urban impact of surface water quality.

According with other authors (Yuan et al., 2013; Wilbers et al., 2014), the presence of heavy metals in urban environments were also associated with urban and industrial wastewater, particularly as a results of metal pipes corrosion. However, Sansalone et al. (2005) found that loadings of Zn, Cu, Pb and Cd were higher in urban stormwater than in untreated municipal wastewater in a city with a population of 800000. Cupper, Zn and Cd have been associated with farm lands as a result of animal manure and sewage sludge applications (Antonious et al., 2008). Few heavy metals such as Cu and Zn for instance, are also used as components of insecticides and fungicides (Mendes and Oliveira, 2004; Yu et al., 2014), leading to potential sources of surface water contamination, not only from agricultural fields, but also from the urban areas, due to lawns and gardens maintenance. Vander Laan et al. (2013) identified agriculture and urbanization as most likely sources of metal contaminations, and that they are one of the stressors of aquatic ecosystems degradation. Metals may be also provided by natural sources, since metallic agents that are made available and mobile via reduced conditions (Mendes and Oliveira, 2014; Wilbers et al., 2014). Iron and Mn are present naturally in soil-derived sediments (Ellis et al., 1986).

Bare soil

Despite the catchment outlet (*ESAC*) displayed the highest TS concentrations (median values of 298 mg L^{-1}), *Quinta* drainage area demonstrated slightly higher specific TS loads than *Espírito Santo* and *ESAC* (965 kg km^{-2}, 937 kg km^{-2} and 804 kg km^{-2}, respectively). The higher TS load and turbidity values in *Quinta* are mostly because of the enterprise construction site, which covers 10% of the drainage area, and encompasses a major area of bare soil, resulting from deforestation and initial construction phase. Runoff erosion within the construction site was active during field visits, with widespread rills and visible accumulation of sediments in the retention basin which received the overland flow from this area (Figure 6.21). Nevertheless, within *Quinta* drainage area, there were additional bare soil sites associated with clear-felled woodland in upslope areas, which displayed signs of erosion. However, these sites do not seem to have a considerable impact on surface water TS or turbudity, since the overland flow from these areas tended to dissipate in downslope woodland areas, before reaching the stream network. On the other hand, overland flow from the enterprise park is routed to the retention basin, which then discharges to the stream channel, providing fewer opportunities for sediments to settle down, and thus, represents a major contribution to the *Quinta* TS load.

a) b)

Figure 6.21 – (a) Rill erosion in the enterprise construction site and (b) sediment accumulation within the retention basin.

In contrast, woodland clear-felled seemed to enhance TS loads in *Espírito Santo*, particularly in the last event (Table 6.6). Also afforestation of fields nearby the stream channel led to substantial runoff erosion confirmed by field observations. Since the overland flow from these areas was generated near the stream channel, it could represent an important sediment load contribution, in contrast to upslope *Quinta* clear-felled areas.

The impact of soil disturbance close to the stream network was also noted in *Porto Bordalo* during the 14/11/2011 rainfall event. At this time, there were roadworks (open ditch) a few metres above the sampling site, and despite the smaller area affected, its impact on surface water TS was very obvious and led to high TS concentrations, particularly at the beginning of rainfall event. This explains the higher median TS concentrations, as well as greater heterogeneity in the sampling records (Figure 6.6).

Within urban land-uses, despite semi-pervious surfaces, such as unpaved parking sites, did not correlate with TS, other authors refer to them as potential sources of sediments due to great overland flow generation, since they behave like impermeable surfaces (Carey et al., 2013). Opposing, pervious surfaces within urban land-use over the catchment, associated with minor or even absent overland flow, showed significant negative correlations with TS concentrations, as well as turbidity (Table 6.5).

In *Ribeira dos Covões*, TS can influence surface water quality, since it includes suspended sediment (SS) fraction, which can play an important role on environmental impacts due to its high adsorptive capacity and mobilization of pollutants, such as nutrients, particularly phosphorus (Atasoy et al, 2006; Carey et al., 2013) and heavy metals (Yu et al., 2014). Research has shown that due to their physical-chemical characteristics, the finer particulates are more efficient in the adsorption of pollutants and hence will carry a relatively higher pollutant concentration (Andral, 1999). Although much pollution is moving in dissolved form, increasing SS concentrations may lead to increasing pollutant loads (Goonetilleke et al., 2005). Furthermore, the presence of sediments in surface water increases turbidity and reduces the amount of light penetration, retarding photosynthesis and, as a consequence, decreasing the food supply available to aquatic life (Mendes and Oliveira, 2004).

The relationship between TS and SS in *Ribeira dos Covões* streamwater was measured in a previous project, based on samples collected over two years (under baseflow conditions) in five sampling locations (Ferreira, 2009). Median values of SS/TS were 0.7 for *Quinta* streamwater and 0.1 in the other streams. Assuming this relationship was kept constant over the time, despite the urbanization and during storm events, median SS concentrations over the ten storm events monitored increased form *Porto Bordalo* to *Espírito Santo*, *ESAC* and *Quinta*: 14 mg L^{-1}, 25 mg L^{-1}, 30 mg L^{-1} and 180 mg L^{-1}. In addition, maximum SS per storm event would range from 16-115 mg L^{-1} in *Porto Bordalo*, 25-85 mg L^{-1} in *Espírito Santo*, 29-166 mg L^{-1} in *ESAC* and 151-1680 mg L^{-1} in *Quinta*. These high concentrations within *Quinta* demonstrate the impact of construction site on surface water quality.

Despite Portuguese legislation do not establish an environmental standard for suspended sediments, it considers a MRV of 60 mg L^{-1} for irrigation uses. Based on the SS estimations presented on previous paragraph, this guideline is largely exceeded in *Quinta*, as well as in the other study sites in few samples collected during greater storm events, as denoted by the significant positive correlation between turbidity and streamflow at the sampling time. High concentrations of SS in irrigation waters may lead to clogging of soil and siltation of irrigation networks, particularly blockage of irrigation drop by drop and sprinkler systems (Environment Ministry, 1998).

6.5.1.2. Differences with lithology

Some differences in surface water properties between study sites can be linked to lithology. Major cations vary with bedrock material and soil. Generally, Ca is more abundant in limestone than sandstone (380 g kg^{-1} vs 13 g kg^{-1}), whereas the other major cations tend to be more profuse in sandstone than limestone (Mg: 7 g kg^{-1} vs 4 g kg^{-1}, Na: 17 g kg^{-1} vs 6 g kg^{-1}, K: 11 g kg^{-1} vs 3 g kg^{-1}) (Reimann and Caritat, 1998).

The *Porto Bordalo* sub-catchment, underlain by limestone, displayed low specific loads of Na and K (16 kg km^{-2} and 10 kg km^{-2}), but high Ca and Mg loads (65 kg km^{-2} and 18 kg km^{-2}), despite not always distinctively different from sandstone-dominated *Espírito Santo* and *Quinta* sub-catchments, possibly due to different hydrological regimes. Nevertheless, a characterization study performed within *Ribeira dos Covões*, identified Ca and Mg concentrations at the soil surface (0-20 cm) over 13- and 2- times higher in limestone than sandstone (Pato, 2007). There was also a significant positive correlation between specific Mg loads and impervious surface within urban land-use, which can be linked with *Porto Bordalo* results. As mentioned before, although this catchment does not have the largest impervious cover, surface runoff reaching the stream channel is largely provided by the urban drainage system, which collects and pipes overland flow from urban areas (mostly roads but also roof runoff routed to the roads) close to the sampling site.

Porto Bordalo displayed higher pH than in sandstone surface water. Previous studies in *Ribeira dos Covões*, also reported limestone soils exhibiting greater pH (~7.6) than sandstone (4.5-5.2) soils (Pato, 2007). *Porto Bordalo* surface water showed significant higher pH than *ESAC*, which is only partially overlying limestone (41%). This is possible due to the lower streamflow contribution from *Porto Bordalo* to the catchment outlet (23%) (Chapter 5). Nevertheless, surface water pH within *Ribeira dos Covões* was largely within neutral classification, and did not menace the environmental quality standards for surface water. However, the higher values measured in *Porto Bordalo* (during the recession limb of the small storm event of 26/10/2011 and the initial samples of 02/11/2011), surpassed the recommended guidelines for irrigation uses. These slightly alkaline properties could have been associated with greatest Fe concentrations, indicative of older water mobilization, which had greater contact time with soil and that was not mobilized during storm events observed immediately after the long summer. However, Fe abundance in limestone is typically lower than sandstone soils (5 g kg^{-1} vs 10 g kg^{-1}) (Reimann and Caritat, 1998).

Occasionally, Zn attained pollutant concentrations (slightly higher than 0.5 mg L^{-1}, Ministry of Environment, 1998) in *Porto Bordalo* and *ESAC*, fully or partially overlaying limestone, and in *Quinta* construction site. These highest concentrations of Zn were measured mainly under the falling limb of hydrograph (not shown), mostly in storm events after the summer, in the limestone dominated areas (25/09/2013). This high Zn concentrations could result from soil water accumulated during the summer which was easily mobilized with the first rainfall events after the dry period, since the presence of Zn in surface water may result from soil and rock leachate. Sandstone bedrock is usually associated with lower Zn proportions than limestone (20 mg kg^{-1} vs 40 mg kg^{-1}). However, in *Quinta*, pollutant concentration levels were observed in late winter (15/01/2013) and could result from materials being used under the constructions site.

Manganese concentrations were always very low within *Ribeira dos Covões* (<0.1 mg L^{-1}), but showed slightly higher values in *Porto Bordalo*, followed by *ESAC* (maximum values of 0.4 mg L^{-1} and 0.2 mg L^{-1}), which may indicate possible leachate from limestone areas. Limestone areas usually display higher Mn in its composition than sandstone (700 mg kg^{-1} vs 100 mg kg^{-1}) (Reimann and Caritat, 1998). Nevertheless, these differences between sandstone and limestone could be rather a result of anthropogenic sources, namely road runoff, as mentioned in section 6.5.1.1.

Total solids concentration significantly increased in sandstone but decreased in limestone areas. This is related to soil aggregation properties, which are lower under sandstone, and thus easily eroded, despite the higher infiltration capacity than in limestone. Stronger cohesion between limestone soil particles enhances the resistance to soil erosion.

6.5.2. Temporal variation of surface water quality

Surface water quality ranged over the study period, demonstrating opposing seasonal trends between some physical-chemical parameters (apart from Ca and Mg which did not reveal significant temporal differences between samplings). Many research studies have reported the influence of climate and hydrological variation, particularly of rainfall and flow discharge, on water quality (Meixner and Fenn, 2004; Brilly et al., 2006; Wilbers et al., 2014).

Rainfall events monitored after the summer (23/10/2011 and 25/09/2012), recorded greater concentrations of COD, nutrients (Nk, NH_4, NO_2+NO_3 and TP) and Mn, with general decreasing tendencies through the wet season. Some Nk and NH_4 concentrations found during these rainfall events surpassed the minimum surface water quality standards. First rainfall events sampled after the summer also leaded to great TS concentrations, or at least higher standard deviations. The impact on TS concentrations was particularly noticed in *Quinta* and *Espírito Santo*, especially in 25/09/2012 since it represents the beginning of streamflow (first runoff) after the dry season.

Generally, nutrients in *Ribeira dos Covões* (phosphorous and nitrogen forms) reached high concentrations during winter storm flows, near the peak discharge. In a vegetated catchment in southern England, May et al. (2001) reported greater phosphorus uptake during the growing season of plants (from spring to early autumn), leading to greater nutrient loads in the river system during the winter. In addition, authors also reported the greater phosphorus uptake by macrophytes and algae at low flow than higher winter flow. Nevertheless, in *Ribeira dos Covões* study green areas may not be the main TP source within the study catchment.

In a mainly agricultural region of Vietnam, highest concentrations of NO_3 and NH_4 were observed during the dry season, but in different regions of the country highest concentrations of NO_3 were found during the wet season, but no temporal variation in NH_4 concentrations were reported (Wilbers et al., 2014). These findings suggest that nutrient concentrations vary with location and over the time. In a set of catchments located in the San Bernardino Mountains, California, Meixner and Fenn (2004) found a positive relationship between nitrate and discharge, suggesting that nitrate may accumulate in the soil zone during dry periods. In an urban fringe catchment of Los Angeles, Barco et al. (2008) also exhibited highest NO_3 during the first runoff event after an extended dry period (flushing effect), and lower concentration in the spring. This hydrological enhanced behaviour was explained by NO_3 accumulation during dry periods in soils and groundwater from mineralization and nitrification processes, as well as high atmospheric deposition. Ocampo et al. (2006) also found that the antecedent moisture conditions of the catchment at seasonal and interannual times-scales had a major impact on the nitrate flushing response.

Atmospheric deposition may contribute with several pollutants, as a result of human activities emission, particularly industrial and vehicular traffic, but also natural sources, such as pollens. Fossil fuel combustion produces nitrogen oxides (NOx) which are converted to nitric acid and nitrate aerosols. Catalytic converters in vehicles also release gases enriched with nitrogen, which may deposit along major roads (Carey et al., 2013). Stolzenbach et al. (2001), using a regional air quality model, estimated that dry atmospheric deposition in Los Angeles region can contribute as much as 13–99% of the total mass loading of metals to Santa Monica Bay. In China, local air pollution with metal-enriched dust was considered an important source of Cu and Zn concentrations, leading to exceeding surface water quality standards (Yu et al., 2014).

In *Ribeira dos Covões*, pollutant accumulation during dry periods and subsequent wash-off process during the first rainfall events, may explain in part the higher concentrations of COD, nutrients and Mn. However, except with EC and Na, the negative or absent correlations between EMC parameters and API (7 and/or 14 days before the rainfall event), did not seem to support the pollutant accumulation theory. Higher concentration after the summer can, thus, be a consequence of the lower dilution effect resulting from lower streamflow. The small dilution effect was also considered by Wilbers et al. (2014), to explain the higher COD and Mn concentrations during dry season. Whitehead et al. (2009) stressed the relationship between decreased flow velocities and less mixing of water with higher concentrations of organic pollutants.

In the study catchment, higher SELs resulted from major rainfall events observed during wet season. Thus, SELs were significantly positively correlated with rainfall amount, rainfall duration and streamflow (Table 6.5). It has been argued elsewhere that the strong correlation of wash-off loadings with total runoff and event duration determines the flow volume required to overcome surface roughness and retention thresholds on the surface, leading to runoff and pollutants transfer downslope (Ellis et al., 1986). Wilbers et al (2014) also reported the impact of increasing rainfall events on run-off from urban and agricultural lands to enhance water pollutants contamination. Yu et al. (2014) reported positive correlations between rainfall amount and loadings of Zn, Pb, Cd and Cr in a rapidly developing mixed land-use catchment of China.

Peak discharge and SELs of all the quantifiable parameters analysed, except NO_2+NO_3, COD, Na, Mg and Fe, are positively correlated. An investigation into the quality of surface water from a motorway catchment stressed that it is peak flow intensity rather than volume which is of significance in runoff terms (Pope et al., 1978). Athayde et al. (1982) have suggested that runoff volume is the most significant predictive loading factor with preceding dry period and peak rainfall intensity as the most important regulators of pollutant concentrations.

Rainfall intensity was also an important parameter influencing temporal variation of surface water quality. Maximum rainfall intensity in 15- and 60-minutes displayed significant positive correlations with specific loads of all the quantifiable parameters, except NO_2+NO_3 and Na. Previous authors also showed pollutant removal and loss through overland flow to be dependent on rainfall intensity, due to increased erosivity of rain splash and greater depth of interaction between rainfall and soil (Thompson et al., 2012). The impact of rainfall intensity was particularly noticed in the greatest TS concentrations measured at the four sites in 02/11/2010 (I_{15}= 15.9 mm), but also in 14/11/2011 (I_{15}= 2.7 mm, observed after largest antecedent rainfall period, demonstrated by API_{14}= 98.5 mm). Impacts of rainfall intensity were particularly important for bare soil. Due to enterprise park construction, *Quinta* showed the highest TS concentrations and turbidity, greater than in *ESAC* surface water, which represents the catchment outlet. The increasing flow from other cleaner tributaries and baseflow dilutes the *Quinta* flow, minimizing the potential impact of upslope pollutant sources particularly on turbidity.

Through the wet season, increasing baseflow contribution as well as inputs of water retained in the soil during previous rainfall events may also have a positive impact of few chemical parameters. The longer contact between water and soil matrix may provide higher loads of soil leachate elements into the stream network. This could explain the high Nk concentrations exhibited in some surface water samples collected in late winter, the higher Na and K concentrations through the wet season, as well as the significant positive correlations observed between baseflow and major cations concentration in surface water (Na, Mg and Ca).

Since groundwater is usually associated with lower organic contamination (Carey et al., 2013), except when septic tanks are present (which is not the case in *Ribeira dos Covões*), baseflow increases could have led to significant COD decreases (significant correlation found between the variables), associated with a possible dilution effect on streamflow in storm episodes.

Higher heavy metal concentrations were also observed during wet settings (associated with stormflow), particularly Zn, Cu and Cd, which occasionally surpassed environmental and/or irrigation uses guidelines. These higher concentrations may be due to possible sewer contaminations, as discusses in section 6.5.1.. Iron and Zn concentrations exhibited a particular temporal variation over the study period. Iron displayed greater concentration during the first half sampling campaigns and greater dilution in later storm events, whereas Zn showed an opposite trend. This temporal variability of Fe and Zn could have been affected by human sources. However, since there were not an apparent change on car/local industry/sewage sources in the *Ribeira dos Covões*, a possible explanation may be linked with atmospheric contributions from a metallurgical industry, located 3 km from the north boundary of the catchment, and potential changes in the production chain. In fact, some of the Zn concentrations exceedance as regards to minimum surface water quality standards were observed in late summer (25/09/2012), after a longer potential period of accumulation. Nevertheless, further investigation is required to understand the temporal pattern of Fe and Zn within *Ribeira dos Covões*.

6.5.3. Water quality at the catchment scale

Surface water quality within *Ribeira dos Covões* revealed spatial variation, resulting from land-use and land-cover, as observed in other research studies (Basnyat et al., 1999; Carrey et al., 2011). Urban land-use, and particularly impervious surfaces, represented an important source of pollutants (Figure 6.19). The relation between major cations and TIA can be a result of cement composition, mainly under oxide forms of the cations (e.g. CaO, MgO, Na_2O and K_2O) (Hellebois et al., 2013; Yuan et al., 2013). Despite the increase of EC, COD, NO_2+NO_3 and major cations with imperviousness, these parameters do not seem to represent a direct threat for aquatic ecosystems, since they are not regulated by the Portuguese environmental standards for surface water quality (Environmental Ministry, 1998). Thus, the results of the study do not allow to identify a threshold of impervious cover leading to aquatic ecosystems degradation. Nevertheless, there is no doubt that increasing organic matter (included on COD) and nitrogen loads, namely under NO_2+NO_3 forms, may cause surface water degradation, including eutrophication, depending on phosphorous availability.

Total impervious area have been considered by other authors as an indicator of aquatic ecosystems conservation status (e.g. Arnold and Gibbons, 1996; Morse et al., 2003; Kuusisto-Hjort and Hjort, 2013). In previous research studies, several TIA values were recognised to degrade specific water quality parameters. TIA thresholds include 30-50% for several chemical measures and 5-50% for physical variables (Brabec et al., 2002). More specifically, TIA includes 42% for nutrients degradation (Griffin et al., 1980) and 45% for phosphorus (May et al., 1997). Considering metal degradation, 50% of TIA was identified, as well as 40% in the case of Zn (Horner et al., 1997). Although this TIA limits are specific for individual parameters, aquatic ecosystems behave as a whole and one parameter may trigger impacts which affect all the system. TIA thresholds for general water quality include different ranges recognized by distinct authors. For example, Schiff and Benoit (2007) reported that 5-10% TIA may weaken water quality, whereas Exum et al. (2005) recognised modest impacts for this TIA percentage. Other authors assumed a minimum of 10% TIA threshold for minimum degradation start (Schueler, 1994; Arnold and Gibbons, 1996; Exum et al., 2005), 20% TIA for successful remediation efforts (Exum et al., 2005) and a maximum of 30% threshold for unavoidable impacts (Arnold and Gibbons, 1996). Differences in TIA thresholds between authors may stress the importance of pollutant sources.

In *Ribeira dos Covões*, several water quality parameters did not show a relationship between mean event loads and TIA, including turbidity, TS, COD, Nk, NH_4, Zn, TP, Fe and Zn. Major sources of these pollutants may include bare surfaces as regards to TS loads, sewage contaminations (COD, TP, NH_4, Fe and Zn), manure (NH_4), industrial pollution and lithology (Fe and Zn).

Chemical loads were directly affected by hydrologic regime. Generally, streamflow increases during the wet season, not only as a direct consequence of rainfall events, but also antecedent rainfall and increasing baseflow, as a result of water table rise. Antecedent rainfall affects soil moisture content, which is an important parameter determining infiltration and, thus, overland flow processes (Grayson et al., 1997; Hardie et al., 2011). This leads to temporal variations in overland flow generation and transfer over the landscape. Differences in hydrological connectivity will have impacts on stream discharge, but also on water quality. Increasing flow connectivity within a catchment will involve a larger number of pollutant sources, enhancing the loads for the stream network. This can explain the generally high concentrations of COD, nutrients, major cations and heavy metals in later winter storms. The location of pollutant sources within a catchment and the connectivity with stream network may be crucial for water quality impacts (Brabec et al. 2002; Groffman et al., 2004).

Despite the greatest absolute chemical loads were observed at the catchment outlet (*ESAC*), this drainage area exhibited the lowest specific loads of the four study catchments. Lower cathments produce less loads per unit area than the monitored upstream tributary catchments. In extensive areas, higher infiltration opportunities may decrease flow connectivity between the sources of pollutants and the stream network, which can explain lowest specific loads at the catchment outlet. Ellis et al. (1986) stated that catchment loadings are controlled predominantly by transport limited hydrodynamic conditions rather than by source availability. According to Horner et al. (1997), runoff infiltration or retention in surface depressions is the key to reduce pollutant loads reaching the stream network.

The relevance of connectivity between pollutant sources and the stream network was highlighted with TS results. Solid contributions from clear-felled areas located upslope

Quinta were negligible, because overland flow had to overpass woodland land-use before reach the channel. On the other hand, clear-felled areas in *Espírito Santo* displayed a great impact in TS due to its proximity to the stream. Furthermore, fertilization and manure in agricultural fields nearby the stream channels also exhibited greater nitrogen impacts on surface water.

In addition, natural overland flow connectivity can be changed over a catchment through human interventions. Particularly in the urban land-uses, drainage systems are constructed in order to collect and pipe overland flow to downslope areas. In *Ribeira dos Covões*, storm runoff is usually piped into the stream network or nearby soils, where overland flow dissipates. Piping overland flow from impervious surfaces directly to the stream channels enhances not only the streamflow response, but also pollutant loads. The impact of induced drainage system connectivity on streamwater quality was more evident in *Porto Bordalo*, where partial urban runoff was discharged above the sampling site.

The hydrological connectivity provided by the urban drainage system may be particularly important under drier conditions. Despite the lower pollutant loads, some of highest concentrations where measured during the first rainfall events after the summer, leading to surpassed minimum water quality standards, particularly as regards to Nk and NH_4. Water quality degradation during drier periods was enhanced by the lack of dilution effect, resulting from lower streamflow. In contrast, natural pathways for overland flow or its discharge in downslope permeable soils, such as woodland and agricultural fields, would enhance the opportunity for overland flow infiltration and, thus, reducing pollutant loads. The placement of impervious surfaces and the location of urban systems discharge influence the possible absorption by pervious surfaces, and represent an important issue regarding stream quality (Horner et al., 1997; Barbec et al., 2002).

Several studies have investigated the role of green areas, such as woodland land-uses, riparian zones and turfgrass, to improve water quality in urban catchments (Wickham et al., 2002; Matteo et al., 2006). Vegetated areas are effective in overland flow infiltration and, particularly, at reducing nutrient exports because these areas function as active nutrient transformation zones or sinks (Basnyat et al., 1999; Groffman et al., 2009). Matteo et al. (2006) also indicated that the selection and placement of green areas cover can influence sediment and pollutant loadings.

Developing strategies to reduce overall pollutant exports within a catchment require an assessment of relative contribution sources and pollutant transport mechanisms (Carey et al., 2013). In addition, flow connectivity across the landscape and its seasonal variability as well as its impact on surface water quality represents important information for landscape planning. Stein and Ackerman (2007) also noted that management strategies to protect water quality should consider the seasonal importance of dry weather runoff. Prevent water quality damage under catchment management planning stage will be more cost effective than later implementation of structural measures, which should be specific for target pollutants (Goonetilleke et al., 2005).

Considering the relatively low storm events monitored and the huge land-use heterogeneity across the *Ribeira dos Covões* catchment, pollutant sources were not clearly identified. However, the results highlighted the potential environmental problems resultant from higher TS concentrations, particularly during the first rainfall events after the summer. Construction sites represent major sediment sources, and *in situ* measurements, such as surface cover with geotextile of areas temporarily unmanaged, should be implemented to minimize erosion. Fertilizer and manure application, particularly in agricultural fields adjacent to the stream channel should be appropriately managed, particularly as regards to the time and amount of application, in order to avoid pollutant levels of nitrogen, not only after the summer but also during winter storms. Higher concentrations of nutrients (nitrogen and phosphorus) and COD were also associated with urban areas, possibly due to domestic wastewater leakages. Periodic maintenance of sewer systems should be performed in order to avoid environmental problems. Sources of heavy metals within the study sites were possibly associated with road runoff, but further investigation should be performed in order to better understand if road runoff should be routed to wastewater treatments systems or not.

6.6. Conclusion

Peri-urban catchments display multiple pollutant sources and pathways which affect surface water quality. Within these catchments, the complex land-use pattern and its spatial configuration present additional challenges to identify the specific sources of pollutants, particularly in a catchment with high spatial complexity such as the Portuguese *Ribeira dos Covões*.

This study revealed significant spatio-temporal variation in surface water quality, which vary between different physical-chemical parameters. Climatic conditions, land-use and lithology are parameters affecting catchment surface water chemistry. Some of the physical-chemical properties increase with greater urban land-use extent, particularly with impervious surface cover. Significant correlations between median event concentration and percentage impervious surface were found for EC and NO_2+NO_3 on dissolved phase of surface water. Over the study period, median EC increased from 182 µS cm^{-1} in *Quinta* (sub-catchment with lowest urban area, 25%), to 318 µS cm^{-1} in *Espírito Santo* (with greatest urban cover, 50%), whereas median NO_2+NO_3 concentrations increased from 0.35 mg L^{-1} to 1.46 mg L^{-1}. Significant positive correlations between major cations and urban impervious surface were also found (median values of 5.7-18.6 mg Na L^{-1}, 3.1-6.1 mg K L^{-1}, 19.8-34.4 mg Ca L^{-1} and 3.2-10.4 mg Mg L^{-1} in the monitored sites), but they could have been influenced by lithology differences between the study sites.

Greatest specific loads of chemical parameters were found in the highly urbanized *Espírito Santo* sub-catchment (mean event values of 203 kg COD km^{-2}, 4 kg Nk km^{-2} and 0.2 kg TP km^{-2}), but greater TS loads were maeasured in *Quinta* sub-catchment (mean event values ranged between 27 and 3943 kg km^{-2} over the 10 rainfall events monitored), encompassing 10% of its area under construction.

Hydrological connectivity seems to be an important key issue on surface water quality, since it determines the linkage between pollutant sources and stream network. Larger areas provide more opportunities for overland flow infiltration and retention, enhancing flow and pollutants pathways disruption. This may in part explain the lower specific pollutant loads observed at the catchment outlet. The relevance of landscape connectivity was also denoted by TS loads, with clear-felled located upslope woodland areas exposing lower TS contribution to the stream channel, than disturbed surfaces located nearby the stream and with overland flow linkage. Similarly, agricultural fields adjacent to the stream network could have led to higher nitrogen contributions than agricultural areas located at larger distances from watercourses. Nevertheless, in urban areas, the hydrological and, thus, pollutant sources connectivity with watercourses do not depend on location and distance, but rather on the urban drainage system itself. Surface water with direct contribution from impervious surfaces, provided by urban drainage system discharge, showed higher event median concentrations of EC, TP, Nk, NH_4 and Zn. Furthermore, leakages from the domestic wastewater drainage system may provide an important source of organic matter and nutrient contamination.

Although surface water quality is strongly influenced by the hydrological regime, the concentrations in surface water often show distinct temporal patterns. Chemical oxygen demand, nutrients (Nk, NH_4, NO_2+NO_3 and TP) and Mn, presented higher concentrations in the first rainfall events monitored after the summer, and generally decreasing concentrations through the wet season. This is thought to be a consequence of reduced dilution at times of low streamflow. Under these conditions, some minimum surface water quality standards were exceeded, notably Nk and NH_4 (> 2.0 mg L^{-1} and 1.0 mg L^{-1}), in all the studied catchments and sub-catchments (except in *Quinta*, with ~70% woodland area, as regards to NH_4). In addition, concentrations of these parameters, as well as some heavy metals (Zn, Cu and Cd) also exceeded the environmental standards during late winter storm events (>0.1 mg L^{-1} of Cu and Cd, and <0.5 mg L^{-1} of Zn), possibly due to increasing connectivity between sources and the stream network. Surface water quality in *Ribeira dos Covões*, occasionally exceeded the recommended guidelines for irrigation use as regards to TDS (>640 mg L^{-1}), pH (slightly higher than 9.0 in *Porto Bordalo*), Cu (>0.2 mg L^{-1} in *Espírito Santo*), Mn (>0.2 mg L^{-1} in *Porto Bordalo* and *ESAC*) and Cd (>0.01 mg L^{-1} in *ESAC*). Despite occasional exceedance of maximum recommended values, the guidelines for maximum admissible value were always accomplished.

Nevertheless, additional sampling during dry periods should be performed in order to assess water quality within *Ribeira dos Covões* better, since some pollutants may be diluted during rainfall events.

Further investigation is required to assess changes in spatial location of pollutant sources over the year better. In addition, other pollutants typically associated with human activities and urban land-uses, such as suspended sediments, BOD, oils, hydrocarbons and biological contaminants (e.g. coliforms), should be studied in order to improve the understanding of urbanization impacts on stream water quality.

The identification of pollutant sources and knowledge about the seasonal variation is important in order to establish spatially-explicit water management strategies to monitor and improve the local water quality at different time intervals. Moreover, a better understanding of the potential sources and sinks of pollutants should guide the stakeholders to design sustainable peri-urban areas. A planned land-use pattern at the catchment scale can minimize surface water quality problems and protect aquatic ecosystem services.

CHAPTER 7
FINAL DISCUSSION, CONCLUSIONS AND RECOMENDATIONS

7.1. Context

Land-use changes, including those associated with urbanization, can have major impacts on hydrological processes and streamwater quality. These modifications can be particularly significant and complex in peri-urban areas, due to the complex mosaic of the landscape. Understanding how different combinations and arrangements of land-uses affect overland flow generation and its speed and magnitude transfer via other parts of the catchment to the stream network is a major research question in hydrology.

This research has been the first study to assess the spatio-temporal variation of surface hydrological processes and their impact on stream water quality in a peri-urban catchment in a Portuguese setting. The study has used an integrated methodology based on field data acquisition at different scales: soil properties, runoff plots and catchment/sub-catchment scale, which is not usually considered in this type of studies. Real data acquisition is essential for understanding the system behaviour, and measurements at different scales provide important information for a better understanding on interactions between factors influencing processes and their integration at the catchment scale. Without data gathering, there is no basis for predictive modelling and risk management, as well as decision-making based on scientific knowledge to establish preventive actions in order to minimize the flood hazard.

The research allies itself with WFD objectives in that it highlights nature's capacity to absorb or control overland flow and the relevance of spatial planning for flood prevention and aquatic ecosystems protection. It also stresses that preventing these problems at a planning stage and at the catchment scale is the most cost-effective solution.

7.2. The role of soil properties in different land-uses on potential overland flow processes

Land-use changes in the *Ribeira dos Covões* catchment were found to have affected soil properties greatly and via them to have influenced infiltration and overland flow processes. Woodland soils were found to have the highest organic matter content and the lowest bulk density, favoured by the great vegetation cover. However, the vegetation also releases hydrophobic compounds which form an impermeable surface soil layer and leads to infiltration-excess overland flow. This is particularly important in dry conditions, due to the widespread and stronger hydrophobic properties, particularly under eucalypt and pine stands, dominant on woodland-sandstone areas (median infiltration capacity: 0.3 mm h^{-1}). During the wet season, the switching properties of the hydrophobic substances and/or its leachate to deeper soil layers, lead to hydrophilic soil conditions and higher soil matrix infiltration capacity, which reached 8.3 mm h^{-1} at some sites.

In contrast, urban soils were found to be characterized by lowest soil organic matter content and greatest bulk density, possibly resulting from human trampling and vehicular traffic. The limited production of hydrophobic substances input, associated with only a minor and patchy vegetation cover, was found to lead to widespread hydrophilic conditions over the year. Nevertheless, the lower vegetation cover led to greater soil moisture increase during rainfall events, as a result of minor rainfall interception, but also favours enhanced soil drying between storms. During dry periods, matrix infiltration capacity was high (median 2.7 mm h^{-1}), whereas, in wet periods, increased soil moisture content reduced infiltration capacity (median 1.2 mm h^{-1}), favouring the development of saturation overland flow.

In agricultural fields, distinct land management associated with pasture, olive tree plantations and small gardens, dominant over sandstone soils, resulted in lower organic matter and higher bulk density than in the abandoned fields on limestone, with vegetation following the natural succession. In agricultural fields, the higher vegetation cover under limestone than sandstone also leads to greater soil hydrophobicity. Nevertheless, given the lower vegetation cover in agricultural-limestone than woodland soils, hydrophobicity was not so severe and widespread, breaking down more easily with rainfall events and requiring longer dry conditions to be re-established. Lower vegetation cover than woodland and higher surface roughness than urban soils may have led to greater soil moisture content in agricultural areas, particularly the ones overlaying limestone, due to the marly nature and hence higher silt-clay content. In agricultural sandstone areas soil matrix infiltration capacity was higher in summer (except in agricultural-limestone soils), decreasing with soil moisture increase through the wet seasons (median matrix infiltration capacity: 1.9 mm h^{-1} and 0.9 mm h^{-1}, respectively).

Distinct spatio-temporal variation of soil hydrological properties led to contrasting matrix infiltration capacity and overland flow sources between landscape units. In general, woodland and agricultural-limestone areas were more susceptible to overland flow during dry periods, due to soil hydrophobicity, whereas urban and agricultural-sandstone soils, with higher matrix infiltration capacity, may provide potential overland flow sinks. In contrast, during wet conditions, increasing soil moisture in urban and agricultural soils led to lower matrix infiltration capacity, while switching hydrophobic to hydrophilic conditions enhanced the infiltration capacity of woodland soils. The changing nature of overland flow sources and sinks of different land-uses would decrease flow connectivity over the hillslope, minimizing the impacts on the streamflow regime. This information should be considered in spatial urban planning in peri-urban catchments, in order to reduce connectivity of overland flow and maintain a more natural streamflow regime.

7.3. Impact of different woodland types on overland flow

Forest is generally associated with highly permeable soils. This was in general confirmed for the three woodland types of *Ribeira dos Covões* by the low overland flow recorded over two years (<3%). Nevertheless, dense eucalypt plantations produced twice as much overland flow than sparse eucalypt stands and oak woodlands.

Significant differences in soil properties, particularly hydrophobicity and soil moisture, were observed between woodland types. Despite being widespread in dry periods and almost absent during wettest seasons, hydrophobicity was generally low in oak soils, moderate in sparse eucalypt stands and severe/extreme in dense eucalypt plantations. Under dense eucalypt plantations, hydrophobicity required longer rainfall events to break down and was quickly re-established after just a few days without rainfall. Furthermore, hydrophobicity tended to increase with soil depth in eucalypt areas, but exhibited an opposite trend in oak woodland soils. Oak woodland soils revealed greater soil moisture content than eucalypt sites.

Differences in soil properties led to spatio-temporal variation in overland flow, despite the minor amounts produced. Infiltration-excess overland flow was the most important process within dense eucalypt plantations, as a result of the significantly greater soil hydrophobicity. Under driest conditions, when hydrophobicity was largest, overland flow attained 2.3% of the rainfall in dense eucalypt plantations, but it did not surpass 0.5% in sparse eucalypt stands and 0.4% in oak woodland. In dense eucalypt stands, overland flow increased with enhanced rainfall amount and intensity. On the other hand, in oak woodland, overland flow was mainly associated with saturation mechanisms, although it did not exceed 2.2% of the rainfall. In wettest periods, overland flow in dense and sparse eucalypt stands only attained 1.0% and 1.1% of storm rainfall. In oak stands, overland flow appeared to be linked to saturation of the shallow soil during the wettest periods. At the sparse eucalypt and oak sites, overland flow increased significantly with soil moisture content, perhaps produced due to the lower subsoil permeability, linked to its higher clay content and bulk density. The relatively low percentages of overland flow measured, both in hydrophobic and saturated soil matrix conditions, indicates the importance of water bypass via preferential flow paths provided by cracks and root holes.

Results from runoff plots highlight the important role that woodland areas have on water infiltration and retention during rainfall events, even considering the differences in overland flow mechanisms. The protection of this land-use within peri-urban catchments, including downslope of urban expansion, is of utmost importance to minimize the impacts of enhanced urban runoff. Nevertheless, oak woodland is more favourable to mitigate floods than eucalypt plantations.

7.4. Catchment hydrology and water quality, and potential impacts of the landscape pattern

Ribeira dos Covões has a relatively low annual runoff coefficient (14-22%) despite the high urbanization rate (40% in 2012). This is thought to be a consequence of the low storage capacity of the catchment, linked to high potential evapotranspiration and high permeability linked to the limestone and sandstone lithology. The low annual BFI (37-39%) can also be explained by this high permeability of the generally deep soil, but may also in part result from valley infill favouring subsurface flow beneath the river discharge gauging station.

The seasonal Mediterranean climate is a major hydrological driver on streamflow and pollutant loads. During the summer, discharge is limited and dominated by baseflow (63%). Infiltration-excess is the dominant overland flow process and is more prone in areas of degraded (highly compacted and without vegetation cover) and hydrophobic soils, and on impervious urban surfaces. The low streamflow provides little dilution effect resulting in highest concentrations of chemical oxygen demand and nutrients (nitrogen and phosphorus). During the first rainfall events after the summer, nitrogen (kjeldahl nitrogen and ammonium) and manganese concentrations occasionally exceeded Portuguese surface water quality standards, but total solids also showed greatest concentrations.

Over the wet season, increasing rainfall favours overland flow production, due to increasing soil moisture, which led to greater streamflow and pollutant loads. Saturation overland flow was more prone in late winter, favoured by water table rise in valley bottoms and saturation of shallow soils on limestone hillslopes. Under saturated conditions, higher flow connectivity down hillslopes led to greater peak flows and also some pollution problems, in the form of high kjeldahl nitrogen and ammonium, and some heavy metals (zinc, copper and cadmium), exceeding Portuguese environmental guidelines.

Hydrology and hydrochemistry varied with lithology. Sandstone plays an important role on streamflow outlet delivery, with *Ribeiro da Póvoa* (56% of the catchment area) supplying 51% of *ESAC* discharge and 50% of storm flow (Figure 7.1). Within this lithology, stream network denotes a perennial flow regime, favoured by the greater baseflow (annual BFI ranged between 25-33% at upstream gauging stations and 37-38% in downstream locations). In limestone areas, the ephemeral regime is the product of low baseflow (~2% annual BFI), but annual storm flow represents 35% of *ESAC* storm flow. Streamwater chemistry within limestone areas showed higher pH as well as calcium, magnesium and manganese concentrations, whereas sandstone exhibited higher sodium loads.

Land-use was also an important parameter influencing the catchment hydrological response. Across the catchment, increasing urban land-use was associated with greater runoff and storm runoff coefficients, though these varied with lithology. Storm runoff coefficients ranged from 3% in *Covões* to 21% in *Espírito Santo* sub-catchments, with the lowest and highest urban land-use (15%-17% and 47-49%) respectively (Figure 7.2).

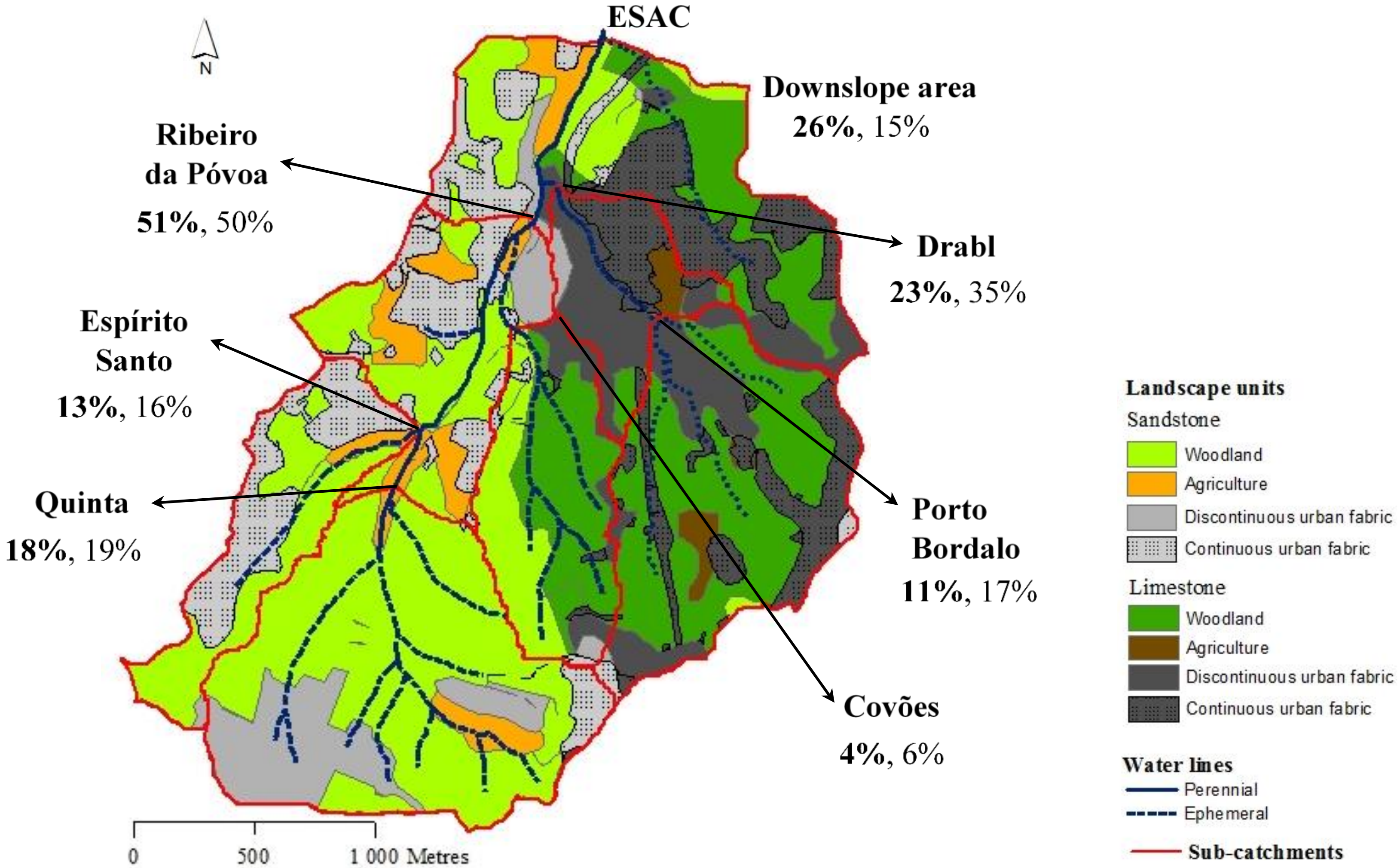


Figure 7.1 - Contributions from upslope sub-catchments to ESAC streamflow (bold percentage values) and storm flow between 2010/11 and 2012/13 water years.

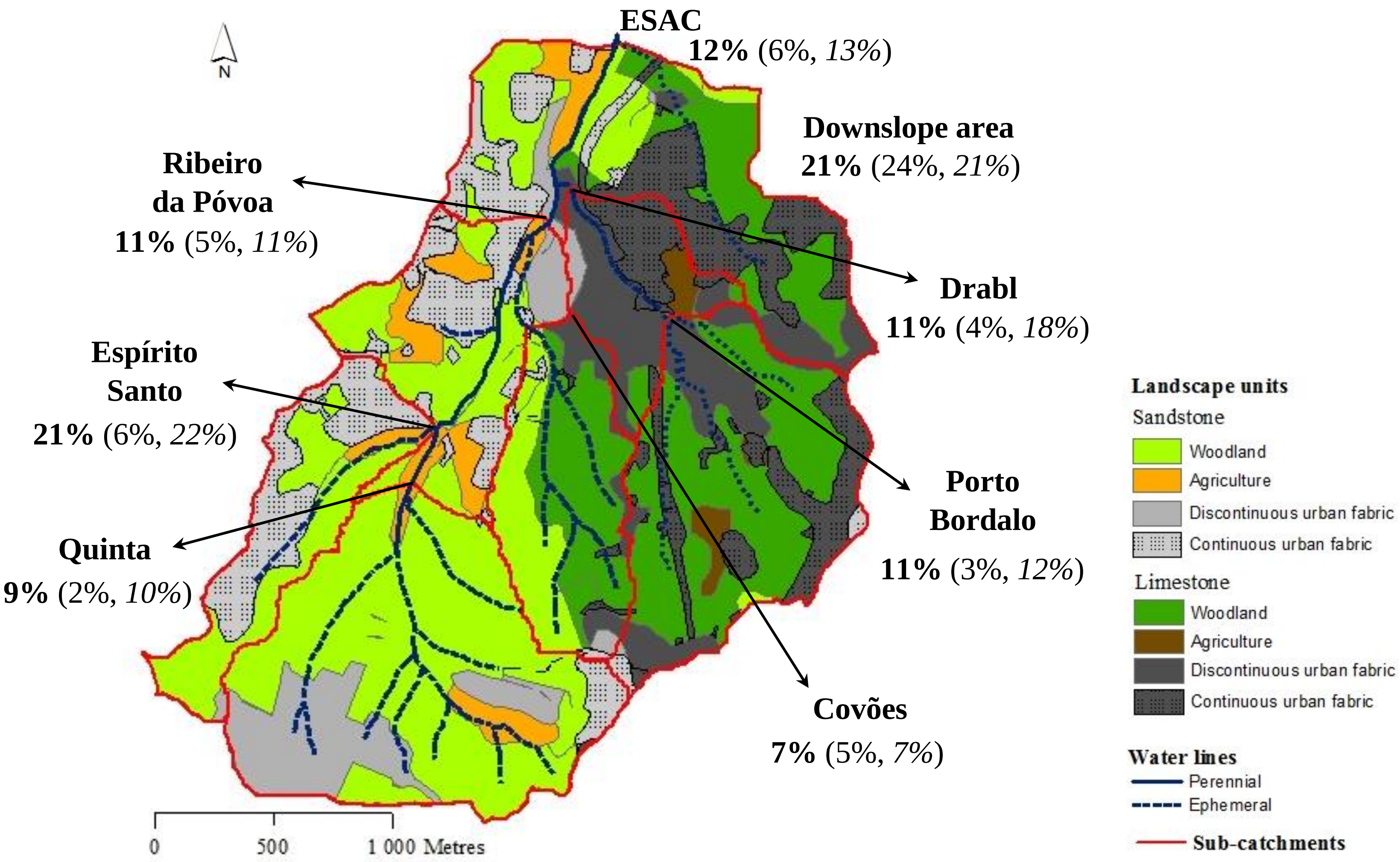


Figure 7.2 - Storm runoff coefficients (bold values) of *Ribeira dos Covões* catchment and its sub-catchments between 2010/11 and 2012/13 water years. Values in brackets represent storm runoff coefficients during dry (summer) and wet (italic values) periods over the study period.

Impermeable surfaces represent important sources of overland flow, not only within urban land-uses but also at the catchment scale, particularly during driest periods. In the *Espírito Santo* and *Drabl* sub-catchments of greatest urban cover (47% and 43%), winter streamflow was only 2-4 times higher than in dry periods, whereas in less urbanized areas the seasonal streamflow difference were greater, attaining as much as 21 times in *Quinta* (9-25% urban land-use). However, in terms of storm runoff coefficient, small differences were found between dry and wet seasons in the downslope area of the catchment (downstream *Ribeiro da Póvoa* and *Drabl*), covered by 51% of urban land-use, but also in *Covões* sub-catchment, where the reduced urban area (15%) is mostly located downslope, with storm runoff being piped to the stream (Figure 7.2). These differences highlight the role of impermeable surfaces on overland flow generation. During the rainy seasons, increasing soil moisture content led to enhanced flow connectivity over the landscape, traduced on higher storm runoff coefficients during wet conditions (Figure 7.2).

The proximity of urban land-use to the stream network is an important parameter influencing streamflow. In most urban cores located upstream, overland flow is usually routed and/or piped to downslope permeable soils, mostly into woodland areas but also into agricultural fields. Overland flow discharge into areas of permeable soil facilitates water infiltration and/or retention leading to minor contributions to the stream network. In contrast, urban areas located near the stream network have a greater impact on streamflow, particularly if storm runoff is piped directly to the water lines. During the study period, the 2% enlargement of the urban area of *Covões*, mostly downstream and with overland flow piped directly into the stream, led to a 6% storm runoff coefficient increase. On the other hand, the enlargement of urban area within *Quinta* (from 9 to 25%), did not reflect on storm runoff increase, due to greater overland flow retention/infiltration opportunities in downslope permeable soils, enhanced by larger distance to the tributary. The 7% growth in urban cover of *Porto Bordalo*, located in upslope areas far away from the stream, also did not affect the runoff coefficient. This was also due to obstructions to overland flow in downslope areas by several structures, including road embankments, houses, walls and surface depressions within construction sites.

Urban impervious surfaces also led to quicker response time. In *Porto Bordalo* and *Covões*, where the urban overland flow is partially piped to the tributaries, peak flow was usually reached in 5-10 minutes after the peak rainfall. Despite the largest urban land-uses in *Espírito Santo* and *Drabl*, response time was ~20 minutes. This was due to overland flow being routed into soils rather than being piped to the stream network. Despite the highest annual peak denoted an increasing tendency with urban areas expansion, the analysis of storm events did not show a clear impact of urbanization on peak flow during the three years of study.

Urban land-use and impervious area also affected surface water quality. Increasing imperviousness led to greater specific loads of chemical oxygen demand, nitrogen (kjeldahl nitrogen) and phosphorus. Hydrological connectivity between sources of pollutants and the stream network, however, is an important parameter affecting surface water quality. Direct discharge of urban runoff into stream led to higher concentrations, particularly of phosphorous and zinc. Erosion of bare soil by overland flow supplied considerable sediment when overland flow was connected to the water lines (e.g. the enterprise park construction site). But when sediment sources were not hydraulically connected with the stream network, particularly if they were located upslope of woodland, the impact on surface water quality was minimal. Similarly, higher loads of nitrogen were measured in streams surrounded by agricultural fields.

In peri-urban catchments a dispersed settlement of urban structures, particularly located upslope, and the maintenance of permeable soils should be considered in order to minimize streamflow impacts, not only as regards to the magnitude of the flow but also to water quality. In *Ribeira dos Covões*, the proximity of some houses to the stream network and the expected future urbanization increase, controlling additional overland flow production and preventing it from reaching the stream network, would be very important to mitigate flood hazards and aquatic ecosystems degradation.

7.5. Overland flow processes at different scales and impacts on catchment surface hydrology

The research in *Ribeira dos Covões* indicates that different physical processes may dominate at different spatio-temporal scales. Based on soil properties, such as particle size distribution, bulk density and hydrophobicity, spatial differences between land-uses, but also within the same land-use, provide differences in soil matrix infiltration capacity which can support different overland flow processes. However, the relatively low soil matrix infiltration capacity values measured at a very small soil scale with a minidisc infitrometer did not corroborate with the high permeability indicated by the runoff plot experiments and catchment hydrology. This could be because of the dominance of other physical processes acting at larger scales.

Plot experiments highlighted the important role of preferential flow paths on hillslope, associated with macropores such as cracks, root holes or wormholes, on infiltration of water to deeper soil layers with a minimum contribution of the soil matrix. In addition, at the hillslope scale, surface roughness can be an important parameter. Thus the greater surface concavities and litter layer of woodland areas have a higher potential for overland flow retention. However, after the retention capacity is exceeded, flow connectivity will be established downslope.

Land management in agricultural fields can also influence surface roughness, particularly through ploughing. Also ancestral stone walls, used in agricultural and woodland areas in order to promote water retention, are also effective in breaking flow connectivity. In urban areas, impervious surfaces not only promote greater overland flow and quicker transport due to surface smoothness, though pervious soil areas can lead to overland flow infiltration. Some urban features such as retention basins, embarkments and walls, may provide surface water retention, although their role under large storm events may be limited and could exacerbate flood damages in case of failure.

At the hillslope scale, soil depth and lithology could be also relevant parameters influencing hydrological processes. In shallow soils overlying marly limestone, soil saturation and sub-surface lateral flow is prone to occur. Furthermore, lithology is also associated with baseflow delivery, representing a minor contribution in limestone areas, but a considerable fraction of the sandstone streamflow.

Apart from the spatial scales, hydrological processes are, to some extent, related with time scales. Infiltration-excess, resulting from heavy rainfall events, is usually observed in short periods of time, varying between minutes to hours, according with rainfall duration. Saturation is typically slower, since overland flow is determined by building up soil moisture. It can endure several days, particularly if saturated areas are influenced by water table level. Subsurface lateral flow is often associated with response times of a day or longer (Bloschl and Sivapalan, 1995). Furthermore, baseflow at the catchment level, due to delayed water sources and groundwater contribution, is usually linked to time-scales of months and years.

All these spatio-temporal scales determine the catchment hydrology but also its hydrochemical properties. Overland flow sources and the mechanisms of transport over the hillslope will influence the connectivity between pollutant sources and the stream network. Nevertheless, greater distances create more opportunities for water infiltration and/or surface retention, if storm drainage systems are not installed.

In general, considering the potential sources and sinks of overland flow and their contribution to catchment hydrology, the landscape of *Ribeira dos Covões* can be divided into several hydrological units: 1) woodland-sandstone areas, characterized by hydrophobic soils and thus, susceptible to infiltration-excess overland flow in summer storms and after dry periods; 2) woodland-limestone areas and agricultural fields overlying limestone, which are associated with high surface roughness but usually shallow soils, and hence more prone to saturation overland flow especially in wet periods; 3) agricultural-sandstone areas and upslope urban areas (without overland flow being piped to the stream network), characterized by a low susceptibility to generate overland-flow; and 4) urban areas located near the stream network, characterized by high and rapid overland flow contribution to the streamflow, both from impervious surfaces (especially if directly piped to the ephemeral stream network) and easily saturated urban soils.

7.6. Implications

7.6.1. *Ribeira dos Covões* catchment

Despite the dominance of woodland areas, this peri-urban catchment has undergone rapid urbanization, which is expected to continue in the near future. The current mosaic of land-uses seems to favour water infiltration, traduced by the relatively low storm runoff coefficients (Figure 7.2). Some of the urban areas are dispersed over the catchment and located in upslope positions, which not only represent safe areas in terms of flood hazard, but also allow downslope areas to act as sinks for overland flow infiltration and/or retention. Nevertheless, there are urban cores placed on valley bottoms, and the proximity between some infrastructures, namely houses, to the stream network, highlight the vulnerability to floods (Figure 7.3). A few flood events have already brought inconvenience and damage to the local population. This problem is expected to become more frequent, considering the upslope urban areas planned for the near future (Figure 7.3).

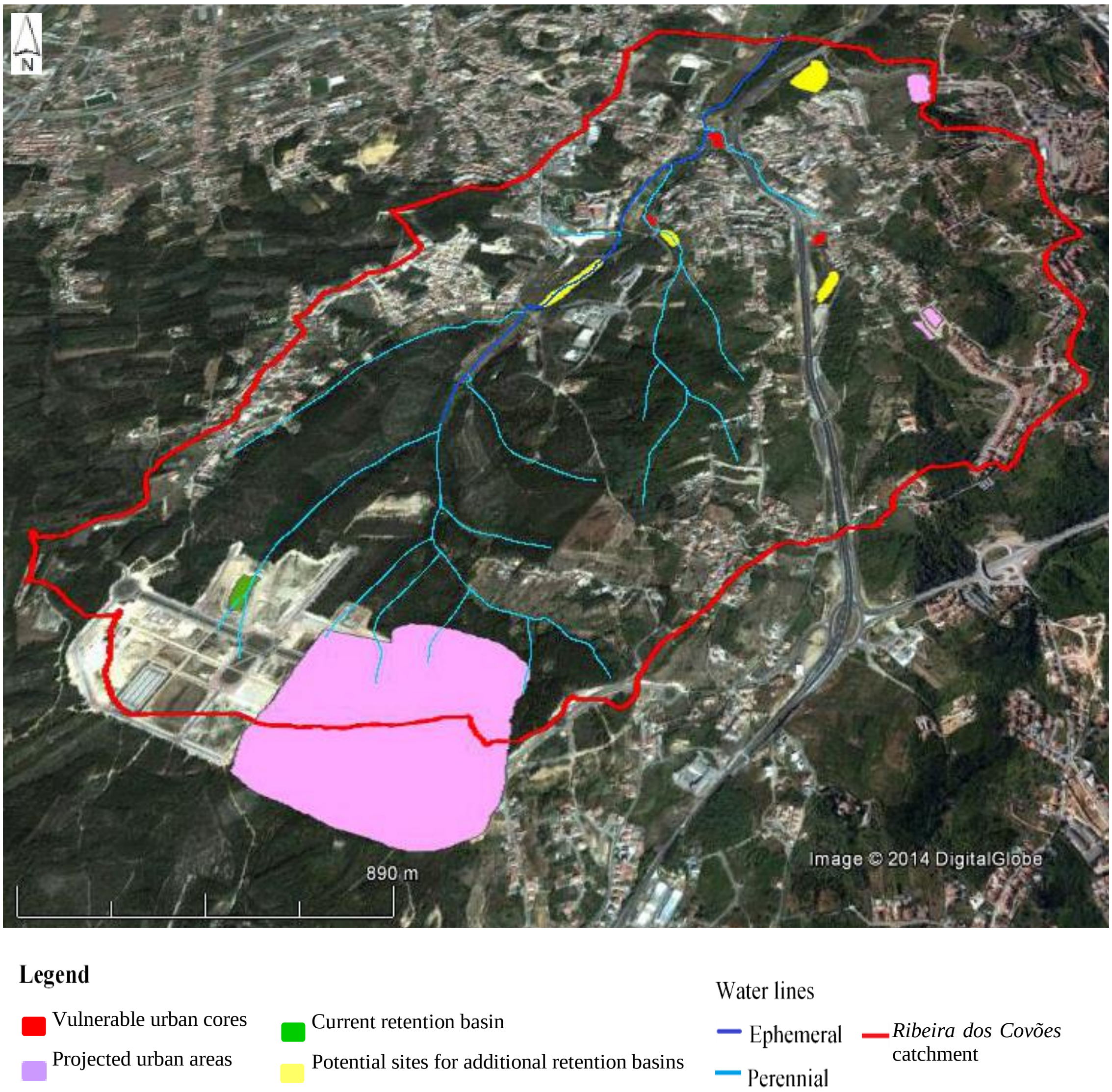


Figure 7.3 – Location of most vulnerable houses (based on reports of local citizens of previous flood events), projected urban cores and potential sites for installing retention basins (adapted from Google Earth, 2014).

The projected urban cores and extent of the existing ones are well positioned within the catchment, considering the topography, hydrology and accessibility. However, despite the downslope opportunities for overland flow infiltration, increasing impervious area would affect streamflow and enhance flood hazard in downslope urban areas. The most appropriate solution to protect the most vulnerable citizens would be to relocate them in other urban spaces, and convert these areas into additional stream bank. However, this would be a drastic measure which would bring conflicts with local population and high financial costs.

The most cost-efficient solution to protect downslope urban areas from flood hazard, would be to enhance overland flow infiltration and/or retention in upslope areas, and prevent additional run-off from the new urban cores. The establishment of green areas within the urban cores would not only have aesthetical value but also create permeable areas which could enhance water infiltration. Other potentially useful measures would be to construct infiltration trenches immediately downslope of urban structures and retention basins in open fields. Suggested locations for these preventive structures are shown on Figure 7.1 and were selected based on the streamflow amount resulting from upslope urban cores but also in the overland flow from the highway. In addition to reducing the flow connectivity over the landscape, these structures would also delay the overland flow and retain sediments, which would be important to reduce suspended sediment loads in stream water.

In the enterprise park area under current construction, the overland flow is routed at the moment to a retention basin, which delays the flow delivery into the stream network (Figure 7.1). However, discharge from the retention basin has already caused the stream to overflow onto downslope agricultural fields. This is mostly because of the small size of the channel section, thus its enlargement seems to be the only effective solution to reduce the flooding hazard, erosion and potential pollution of these fields with urban pollutants, particularly nutrients and metals.

An important problem observed within the study catchment is the lack of cleaning and maintenance of features of the urban drainage network. Sediments tend to clog drains and channels, thus reducing their drainage capacity and leading to overflow. These problems can be easily solved with regular cleaning and dredging activities.

Inspections and maintenance operations to the wastewater drainage system would be also important, in order to prevent sewage leakages and surface water contamination.

7.6.2. Urban land management

Land-use changes, particularly of peri-urban areas, should be planned so as to minimize hydrological changes and flood hazard resulting from urban development. These goals could be partially achieved through appropriate spatial planning at the catchment scale. Physical catchment characteristics, such as geology, topography and soil properties, should be considered in order to evaluate the potential uses. Importantly, however, a landscape pattern comprising a strategically positioned combination of land-uses should be designed to favour water infiltration and detention. As this study has demonstrated, during the year, different land-uses are prone to provide potential sources and sinks of overland-flow. Thus a mosaic of mixed land-uses that will break flow connectivity across the landscape can be designed so as to restrict the amount of overland flow reaching the stream network, leading to smaller changes in streamflow storm peaks, less water quality degradation and hence only minor impacts on aquatic ecosystems.

In Portugal, municipalities are the responsible authorities for land-use planning, through the development of the Municipal Master Plan. These plans should try to incorporate land-use patches in any development proposal to reduce overland flow sources and provide infiltration areas. Besides the spatial location and extent of each land-use, these municipal plans should also limit the maximum area of impervious surfaces. Adequate provision of permeable surfaces breaking up the impervious area could greatly increase infiltration and reduce peak flows at the stream network.

The safeguarding of soils with greatest infiltration capacity is recognised at a Portuguese national level. A network of sites with ecological interest, in which maximum infiltration areas are included, has been established (National Ecological Reserve). All the areas included in this reserve have several usage restrictions, in order to preserve their ecological role (Ministry of Planning and Territory, 1990). These areas include stream beds and areas threatened by floods (defined as areas covered by water during medium floods). Moreover, with the purpose of minimizing flood damage, national legislation imposes tight construction restrictions within 10 m of non-navigable streams (Ministries of Marine and Public Constructions, 1971), though, this protection distance is not always adhered to.

Although improved landscape planning and protection of maximum infiltration areas are cost-efficient methods to reduce overland flow, additional measures can be required in order to maximize upstream overland flow reduction. It could be important to combine nonstructural (associated with planning process) and structural (e.g. stormwater detention structures, such as dykes and dams) measures to mitigate flood risks. Sustainable urban drainage systems, incorporating features such as infiltration trenches and small detention ponds, have been considered as cost-effective means to control overland flow and associated pollutant loads and partially restore a more natural hydrologic regime to a catchment (Parikh et al., 2005).

7.7. Challenges and limitations of the research

Catchment hydrology is a result of the complex interplay of several biophysical parameters, such as climate pattern, topography, geology and soil properties, land-use and land cover as well as their historical evolution. The requirement of knowledge in all these fields in a holistic approach to understanding hydrological and hydrochemical processes represented the most challenging issue in this research study. Despite this research contributed to a better understanding of the impact of a Portuguese peri-urban style, the influence of each landscape unit and the result of different combinations and arrangements of land-uses on overland flow connectivity and streamflow discharge, particularly, surface water chemistry remains not fully understood and some aspects require further investigation.

Besides the complexity to understand overland flow processes at different spatial and time scales, and its influence on transfer mechanisms over the hillslope, additional challenges were posed by the influence of urban drainage systems. They significantly affect the connectivity between overland flow and pollutant sources and the stream network. Over the study period, there were contacts with the local authorities responsible for the design, development and maintenance of the urban drainage system. However, despite their interest in the outcomes of this research, the bureaucratic process for formal requests for drainage system information, and its approval by the company managers, did not allow the supply of this information in time. Because of this lack of information transfer, the discussed impact of the drainage system was based on field observations and information from local citizens, rather than from arguably more accurate official sources. It was not possible to calculate the directly connected impervious area and, thus, quantify the connectivity over the catchment and adequately assess its impact on streamflow response.

Longer-term monitoring data would be also valuable for a better understanding of the spatio-temporal overland flow processes, since the hydrological years covered in this study were years of below- or near-average annual rainfall. It is important to measure and understand how catchment hydrology change under rainiest conditions, and particularly during severe rainfall events, since these will be the most endangering for local people, and the ones where the impacts most need to be minimized.

Limited human resources also represented an important constraint to the study, given the time required to install and maintain the extensive monitoring network involved. Time required for field measurements was not always compatible with the quick hydrological response of *Ribeira dos Covões* catchment, which led to a relatively low number of high flow measurements at all the gauging stations. It also affected the temporal resolution of surface water sampling in storm hydrographs. The type of water level recorders used in the gauging stations was not always the best, considering the small water depths and the occasional changes on the channel surface, resulting from some sedimentation associated with major rainfall events. Although frequent field visits and manual data acquisition made it possible to correct streamflow data series, this took several months to achieve.

Vandalism and theft significantly affected data acquisition by parts of the monitoring network. This was particularly the case with the streamflow record from *Iparque* and *Mina*, where the resultant short and broken flow records and uncertainties of their quality prevented them being included in the analysis. In addition, theft of soil moisture sensors installed in woodland runoff plots also hindered continuous data acquisition at different soil depths. Soil sampling and soil moisture measurements in the laboratory were the alternative solutions found, but they did not allow monitoring of soil moisture behaviour through rainfall events.

As regards surface water quality assessment, few storm events were able to be sampled as a result of limited human resources, particularly to perform laboratory analysis. The analytical methods used for different water quality parameters were largely determined by the laboratory conditions and equipment. Thus the high detection limits of the heavy metal analytical procedures constrained the assessments of spatio-temporal variations in metal concentrations. Also the study was not able to include assessment of chemical parameters, such as biochemical oxygen demand, as well as oils and fats, that are usually considered as important urban pollutants.

7.8. Fields for future research

A prime need of future research will be the incorporation of more detailed information of the artificially constructed urban drainage system in order to improve the understanding of the connectivity, between different urban land-uses and the stream network. This information, coupled with the field data acquired, should be used as data inputs for, and to calibrate and validate, spatially-distributed hydrological models. The application of modelling tools will allow an improved assessment of the impact of the location and extension of different landscape mosaic features, as well as the testing of future urbanization scenarios and the best locations for mosaic elements and mitigation measures. Such information should be coupled with flood risk assessment and should guide future catchment management.

Further investigation of surface water quality is also important. Greater spatial and temporal resolution of water sampling is required in order to identify pollutant sources, their transport mechanisms and understand the seasonal variation on surface water quality. Identifying critical source areas and their connectivity with the stream network over the year is needed in order to select appropriate preventive measures and settings, which may be specific to different target pollutants. Water quality data should be also considered together with the hydrological modelling, so that best spatial arrangement of land-uses is based upon both flood risk management and aquatic ecosystems protection.

This research has also highlighted some complementary themes that should be investigated in the future, such as establishing practical guidelines and rules to provide hydrological connectivity breaks, which should be considered under current planning legislation and catchment management.

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ANNEX

SAMPLING OF SURFACE WATER

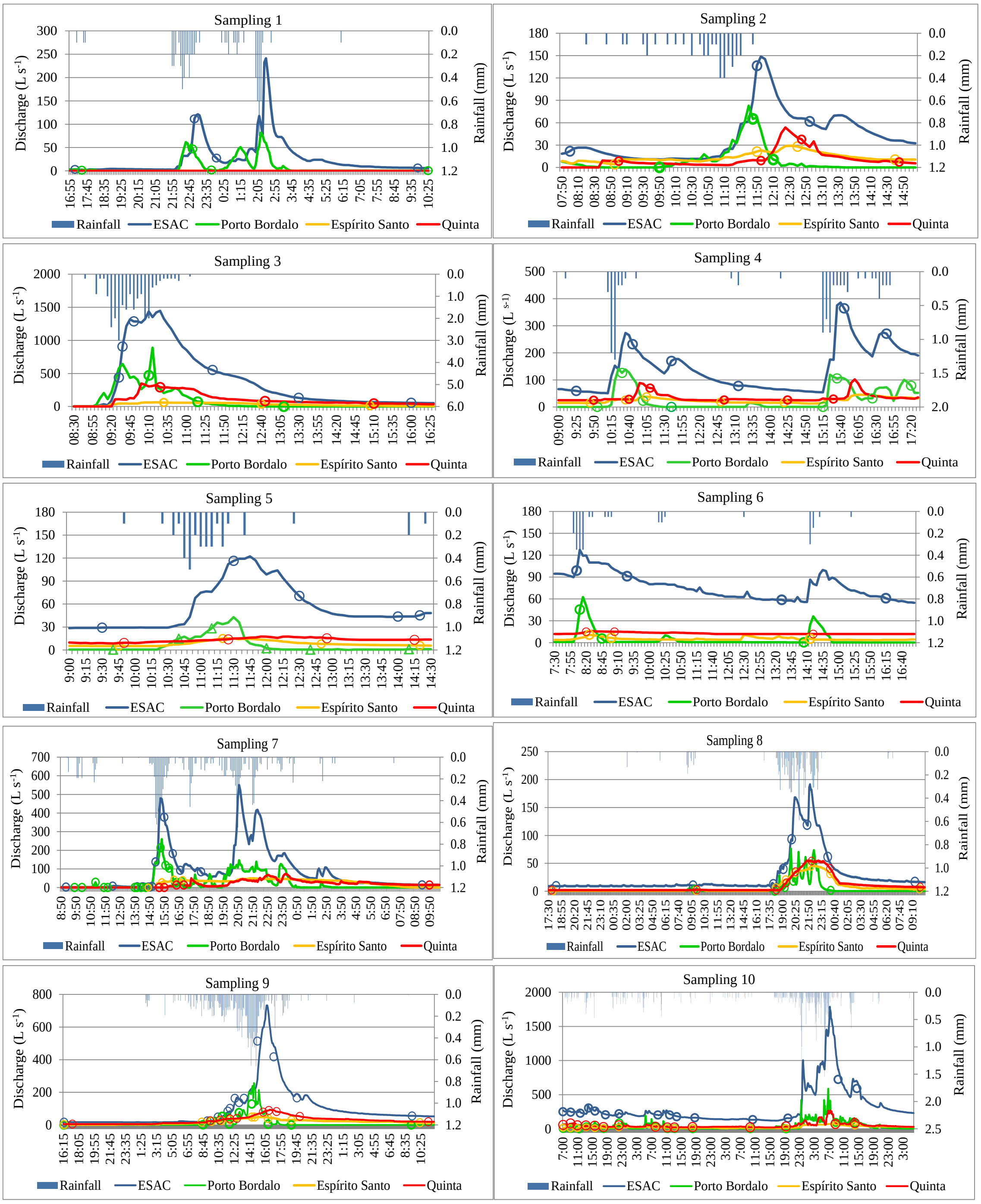

Figure 1 - Variation of rainfall and discharge for the four monitoring catchments, through ten sampling events (note scale differences). Circles represent sampling time.