Universidade de Aveiro Departamento de Ambiente e Ordenamento
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Raquel Sofia e Vasconcelos Ferreira

Efeitos dos incêndios florestais na reserva de nutrientes do solo e sua exportação por escorrência superficial

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Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Ciências e Engenharia do Ambiente, realizada sob a orientação científica do Doutor Mário Miguel Azevedo Cerqueira, Professor Auxiliar do Departamento de Ambiente e Ordenamento da Universidade de Aveiro, com co-orientação do Doutor Jan Jacob Keizer, Bolseiro de Gestão de Ciência e Tecnologia, Universidade de Aveiro e da Doutora Dalila do Rosário Encarnação Serpa, bolseira de pós-doutoramento da Universidade de Aveiro

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“It always seems impossible until it’s done.”
Nelson Mandela

“The greatest progress in life is when you know your limitations, and then you have the courage to drop them.”
Yogi Bhajan

“Life is not easy for any of us. But what of that? We must have perseverance and above all confidence in ourselves. We must believe that we are gifted for something and that this thing must be attained.”
Marie Curie

o júri

presidente

Doutor Valeri Skliarov
Professor Catedrático, Departamento de Eletrónica, Telecomunicações e Informática, Universidade de Aveiro

Doutor Paulo Alexandre da Silva Pereira
Professor Catedrático, *Environmental Management Center, Mykolas Romeris University*

Doutor David Badia Villas
Professor Titular, *Escuela Politécnica Superior de Huesca, Universidad de Zaragoza*

Doutora Adélia de Jesus Nobre Nunes
Professora Auxiliar, Faculdade de Letras, Universidade de Coimbra

Doutor António José Diniz Ferreira
Professor Adjunto, Escola Superior Agrária de Coimbra, Instituto Politécnico de Coimbra

Doutora Maria Isabel da Silva Nunes
Professora Auxiliar, Universidade de Aveiro

Doutor Jan Jacob Keizer
Investigador Auxiliar, CESAM – Centro de estudos do Mar e Ambiente, Universidade de Aveiro (**Coorientador**)

Doutor Mário Miguel Azevedo Cerqueira
Professor Auxiliar, Universidade de Aveiro (**Orientador**)

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Sat Nam! Wahe Guru!

palavras-chave

Incêndios, Bacia Mediterrânica, erosão pela água, escorrência superficial, perda de catiões, perda de azoto, perda de fósforo, vegetação, geologia, orientação do declive, escala de micro-parcela e de encosta.

resumo

O objetivo deste trabalho foi realizar uma avaliação de perdas de nutrientes após incêndio por escorrência superficial, à escala de micro-parcela e à escala de encosta (embora de forma limitada) numa área recentemente queimada da região Mediterrânica, fornecendo estimativas das exportações de catiões, azoto e fósforo, num enquadramento paisagístico como este propenso ao fogo. Representa um importante complemento para o até agora modesto número de estudos sobre as perdas de nutrientes pós-fogo por escorrência superficial, realizado na região Mediterrânica, para antecipar os impactos dos incêndios recorrentes na produtividade do solo. Este trabalho é parte do projeto FIRECNUTS (PTDC/AGR-CFL/104559/2008) - efeitos de um incêndio nas reservas de nutrientes, dinâmica e exportações – e lida com estas lacunas de pesquisa, estudando a exportação de nutrientes selecionados (catiões, azoto e fósforo) numa área florestal recentemente queimada, no centro-norte de Portugal (Sever do Vouga). Os objetivos específicos foram comparar as exportações de catiões, assim como de azoto e fósforo nas formas totais e solúveis, principalmente à escala de micro-parcela: (i) para duas das espécies de árvores mais propensas ao fogo, i.e. eucalipto e pinheiro; (ii) para duas das geologias mais comuns na área, i.e. granito e xisto; (iii) para diferentes orientações do declive, i.e. face a norte e face a sul; (iv) com tempo-desde-incêndio durante os meses iniciais após incêndio e durante um período de monitorização mais extenso. As exportações de nutrientes foram particularmente acentuadas nos três meses após o fogo. No entanto, após este período inicial, foram observados também picos nas concentrações de nutrientes, em associação a eventos de precipitação intensa, com diferenças na variação de cada nutriente, e com o declínio das exportações de fósforo a seguir um padrão mais linear com o tempo desde o incêndio. Os resultados deste estudo enfatizaram a importância de uma camada protetora do solo (ou seja, com as agulhas das árvores queimadas de pinheiro) para minimizar a exportação de nutrientes pós-fogo. A geologia também foi identificada como uma variável importante na avaliação de riscos de erosão pós-incêndio e na definição de medidas de conservação do solo. A orientação do declive não foi uma variável decisiva neste estudo. Estes resultados mostram também que as escalas de tempo mais amplas são úteis para obter mais conhecimento sobre o ciclo hidrológico dos nutrientes e os complexos processos que ocorrem nas áreas de floresta queimada.

keywords

Wildfires, Mediterranean Basin, water erosion, overland flow, base cations loss, nitrogen loss, phosphorus loss, vegetation, geology, slope aspect, micro-plot and slope scale.

abstract

The aim of this work was to perform an evaluation of post-fire nutrient losses by overland flow at micro-plot scale, and at slope scale (although on a limited basis) in a recently burnt Mediterranean area, providing estimates of the range of base cations, nitrogen and phosphorus exports in a fire-prone landscape. It represents an important add-on to the up to now modest number of studies on post-fire nutrient losses by overland flow conducted in the Mediterranean region, for anticipating the impacts of recurrent fires on soil productivity. This work is part of the FIRECNUTS project (PTDC/AGR-CFL/104559/2008) - WildFIRE effects on topsoil Carbon and NUTrient Stocks, dynamics and exports – and addresses these research gaps by studying the export of selected nutrients (base cations, nitrogen and phosphorus) in a recently burnt forest area in north-central Portugal (Sever do Vouga).The specific objectives were to compare base cations exports together with nitrogen and phosphorus exports in the total and soluble forms by overland flow mainly at the micro-plot scale: (i) for the two predominant and fire-prone forest types in north-central Portugal, i.e. eucalypt and pine plantations; (ii) for the two prevailing parent materials in the region, i.e. granite and schist; (iii) for two different slope aspects, i.e. a slope facing north and a slope facing south; (iv) with time-since-fire during the initial months of the window-of-disturbance and for an extended monitoring period. In parallel, nitrogen and phosphorus stocks in the topsoil were also compared. Nutrient exports were particularly pronounced in the three months after fire. However, after this initial period, peaks in nutrients concentrations were also observed in association to intense rainfall events, with differences in the variation of each nutrient, with phosphorus exports decline following a more straightforward pattern with time since fire. The results of this study emphasized the importance of a protective soil layer (i.e. of scorched pine needle) for minimizing post-fire nutrient export. Parent material was also found to be an important variable when assessing post-fire erosion risks and defining soil conservation measures. Slope aspect was not a decisive variable in his study. These results also show that broader time scales are useful to gain insight into the hydrological and nutrient cycle complex processes in burnt forest areas.

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Abbreviations / Nomenclature

BEG	burnt eucalypt-granite site
BES	burnt eucalypt-schist site
BPS	burnt pine-schist site
BE-NW	burnt eucalypt site facing North-West
BE-SE	burnt eucalypt site facing South-East
Ca^{2+}	calcium cation
HCl	hydrochloric acid
HNO_3	nitric acid
H_2SO_4	sulphuric acid
HRU	Hydrological Response Unit
IPCC	Intergovernmental Panel on Climate Change
I_{30}	rainfall intensity during 30 min
K^+	potassium cation
Mg^{2+}	magnesium cation
Na^+	sodium cation
NO_3-N	nitrates
P_{av}	available phosphorus
PO_4-P	orthophosphates
SOM	soil organic matter
TKN	total Kjeldhal nitrogen
TN	total nitrogen
TP	total phosphorus
UES	unburnt eucalypt-schist site

Chapter 1 - Introduction

1.1 *Framework*

The role of wildfire as a selective force in the evolution of Mediterranean ecosystems and landscapes has long been overlooked (Naveh, 1990). Fire is now recognised worldwide as a natural phenomenon in Mediterranean regions but present-day fire regimes strongly reflect human activities such as the widespread planting of highly flammable pine and eucalypt forests (Lloret, 2004).

Throughout the past decades, wildfires have burned and affected increasingly large areas of land in Mediterranean ecosystems (Pausas et al., 2008). That trend is expected to continue, especially with projections of future climate changes with temperature rising and associated risk of intensified drought or more intense precipitation events, among other factors (Blake et al., 2010; Caon et al., 2014). The Intergovernmental Panel on Climate Change (IPCC) report concluded that global climate change will increase the risk of extreme fire events (IPCC, 2007). This tendency emphasizes the general reservations about the limits to the fire resilience of these ecosystems that have been continually devastated by fire over the past decades (Pausas et al., 1999; Pausas et al., 2008; Pereira et al., 2006b; Shakesby, 2011).

In Portugal, over the past decades, wildfires have devastated on average around 100 000 ha of land each year (Pereira et al., 2006a), with dramatically higher figures for dry years like 2003 and 2005. Due to the nature of the country's forestry activities as well as to a likely increase in fire-propitious meteorological conditions, fire frequency in Portugal is not expected to decrease in the foreseeable future (Pereira et al., 2006b). Such unprecedented frequencies and spatial extensions of wildfires have contributed to the increase of interest in studying wildfire effects.

1.2 *Brief summary of fire effects on soil and water resources*

Fire can considerably alter soils and their major ecological functions as the basis of many ecosystems resources. A global rise of fire occurrence, area burned or expansion of fire seasons has been acknowledged and many of the responses of soils to fire are as unique as the complex interactions among driver factors such as weather conditions during and following fire, type and growth of vegetation, soil characteristics or land management (Blake et al., 2010).

While wildfire is a natural disturbance, the more frequent occurrence of wildfires, often with high-intensity, can offset the ecological balance and have a significant negative impact on soil degradation, biological diversity and water cycle (Caon et al., 2014; Crouch et al., 2006). Wildfires have been considered as a significant, if not the main, cause of hydrological and geomorphological change in fire-prone landscapes (Shakesby and Doerr, 2006).

Vegetation and litter cover removal as well as soil physical and chemical alterations are usually designated as direct hydrological and geomorphological effects from wildfires. These changes are followed by indirect effects, such as reduced infiltration and increased sediment availability for transport. Finally, these effects will lead to an increase of overland flow generation and soil erosion (Figure 1.1; Shakesby and Doerr, 2006). This marked increase in overland flow and erosion not only cause on-site land degradation but can also cause increased sediment and nutrient inputs into adjacent streams or rivers, that can negatively affect the water quality in downstream aquatic systems, with potential contamination of drinking water supplies (Bowman and Boggs, 2006; Emelko et al., 2011; Shakesby, 2011; Smith et al., 2011).

Base cations, nitrogen and phosphorus are important limiting nutrients in forest soils ecosystems that can be significantly impacted by fire events. The combustion of litter and the surface horizons of soils frequently produces nutrient-rich erodible ash, organic matter and mineral material, that can be an increase in soil fertility, facilitating crop production, or it can destroy the protective vegetation canopy and forest floor, leading to a reduced infiltration capacity and potential transport of nutrient-enriched sediments from burnt slopes, by wind and water erosion (Shakesby and Doerr, 2006; Shakesby, 2011).

Neary et al. (2005), Shakesby and Doerr (2006), Ferreira et al. (2008), Shakesby (2011) and Caon et al. (2014) have recently gathered aspects of the principles and processes governing the complex relationships between fire and soil. Previous studies in the Mediterranean region (e.g. Cerdà and Lasanta, 2005; Cerdà and Robichaud, 2009; Ferreira et al., 2005a; Prats et al., 2012; Shakesby et al., 1996), have revealed strong and occasionally extreme responses in runoff generation and associated soil and nutrient losses following wildfire, in particular during the earlier stages of the so-called ‘‘window-of-disturbance’’ (Figure 1.1; Shakesby and Doerr, 2006).

This model represents a simplification of the sediment yield response to post-fire hydrological and geomorphological changes. Conversely, the role of each fire induced change to the post-fire hydrological and erosive response is still not entirely understood.

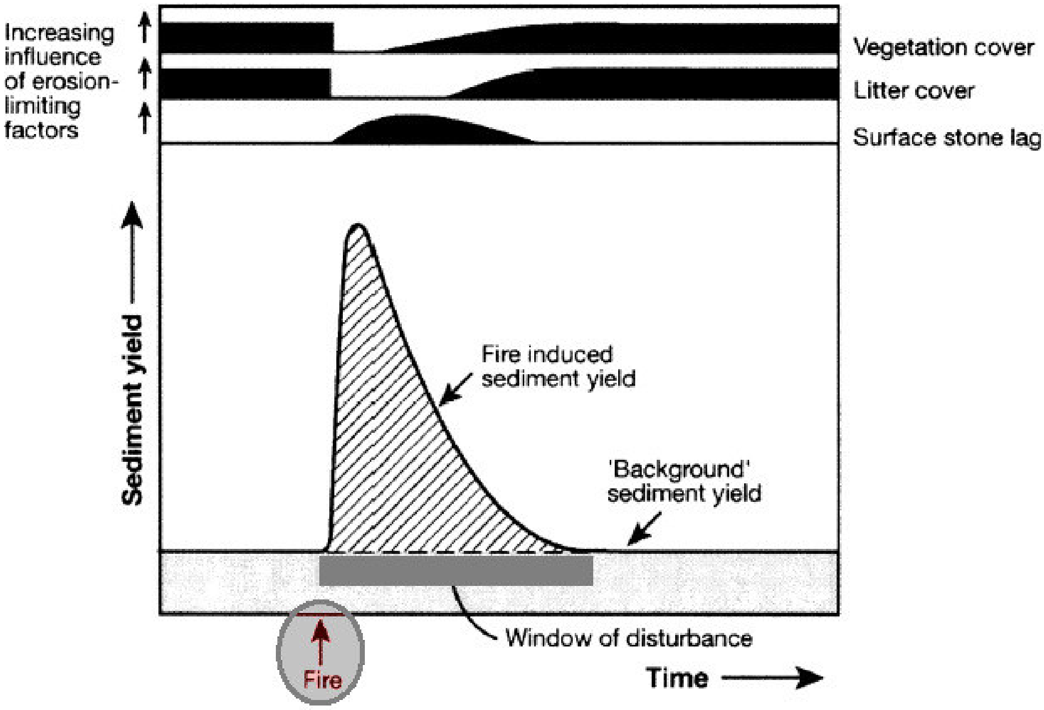

Figure 1.1 - The "window-of-disturbance" after wildfire, with the hypothetical decline in sediment yield and the role of three erosion-limiting factors: vegetation cover, litter cover, and stone lag development (Shakesby and Doerr, 2006).

In most cases, the first 4–6 months period after a fire present frequently bigger susceptibility to erosion because the lack of a protective litter and vegetation cover (Andreu et al., 2001; Bodí et al., 2014; Ferreira et al., 2005a; Thomas et al., 1999) promotes overland flow and erosion, but also because of the exhaustion of the nutrient-enriched ash layer (Caon et al., 2014; Cerdà and Doerr, 2008; Khanna et al., 1994; Knoepp et al., 2005; Pausas et al., 2008; Pereira et al., 2011; Shakesby, 2011; Thomas et al., 1999) and due to the maximum fire potential in summer (July–August), as a result of higher temperatures and rainfall deficit during this season, and the possibility of intense post-wildfire rainfall the following autumn–winter (November–January) (Andreu et al., 2001; Ferreira et al., 2005a).

A number of factors raise some concerns about the occurrence of wildfires in the Mediterranean basin, mainly because of the above mentioned direct and indirect effects. Wildfire frequency, severity and the size of burned areas, as well as the strong influence of human activities impact through land management practices, land-use changes such as land abandonment and widespread introduction of fire-prone species are viewed as drivers of the increase of the wildfire activity (Moreira et al., 2009; Shakesby 2011).

In Portugal, the number and severity of wildfires is not expected to decline in the future, as a result of the economic importance of the country's forestry activities using highly flammable species and the foreseeable raise in the occurrence of meteorological conditions favorable to fire (Carvalho et al., 2010; Moreira et al., 2009; Pereira et al., 2006b). Strong and sometimes extreme increases in runoff generation and the associated losses of sediments have also been observed for eucalypt and pine plantations, the two principal fire-prone forest types in north-central Portugal (Ferreira et al., 2005a; Prats et al., 2012; Shakesby et al., 1996).

Post-fire land management operations with heavy machinery (e.g. plowing; logging), leads to forest soil disturbances and have been acknowledged as an important cause for elevated soil erosion rates in some post-fire studies in the Mediterranean region (Shakesby et al., 1994; Fernández et al., 2004; Shakesby, 2011; Martins et al., 2013). An increase of the number of wildfires and recurrence at the same area, alongside the impacts of these generally used practices can be one of the major pressures to Mediterranean soils (Shakesby, 2011).

According to Shakesby (2011), post-fire soil losses in the Mediterranean are very important, although sediment losses are considered low when compared to other regions, because of the frequent presence in this region of shallow soils with a history of intense disturbances, in a nutrient-poor environment. More important than the quantity, or in any case on the same level of importance, the quality of the material that is being lost during post-wildfire erosion should be faced as a key focus of interest in this line of research (Shakesby, 2011). Minor post-fire soil losses could be significant for soil longevity in some areas, on account of soil organic matter and nutrient losses in solution or adsorbed onto eroded sediment particles (e.g. Kutiel and Naveh, 1987). The combination of high fire frequency and shallow soils in a nutrient-poor environment, characteristic of many fire-prone Mediterranean areas, increases the risk of soil fertility depletion (Pausas and Vallejo, 1999).

1.3 *Research on post-fire nutrient mobilization in the Mediterranean region: soil and overland flow*

Since the 1990s, when research activity into post-wildfire soil erosion in the Mediterranean region expanded (Shakesby, 2011), following the beginning of the dramatic increase in fire activity (Moreno et al., 1998; Pausas, 2004), several studies in this region have addressed the present-day hydrological response and erosion rates for areas affected by forest fires (e.g. Cammeraat and Imeson, 1999; Doerr et al., 2000; Ferreira et al., 2005b; Imeson et al., 1992; Shakesby et al., 1993, 1996, 2002), and soil nutrients dynamics after fire (e.g. Andreu et al., 1996; Gimeno-García et al., 2000; Pardini et al., 2003; Rodríguez et al., 2009).

Comparability among studies can be challenging due to several factors as fire behaviour and recurrence, precipitation regimes during the post-fire period, fire-induced changes according to different fire severity, and ecosystems specific features mixtures. Only a few studies in the Mediterranean have deal with fire-induced alterations on nutrient transport carried on by hydrological and erosion processes changes (e.g. Cancelo-González et al., 2013; DeBano et al., 1998; Díaz-Fierros et al., 1990; Lasanta and Cerdà, 2005; Machado et al., 2015). In Portugal, a small number of studies using experimental plots were performed focusing on these changes occurring in nutrient output by overland flow, and most of these only evaluated solute form losses (Coelho et al., 2004; Ferreira et al., 1997, 2005a; Thomas et al., 1999, 2000a, 2000b; Walsh et al., 1992).

Therefore, in spite of concerning the same land-cover types and having similarities in climate and type of soil, most of these studies presented results of different parameters, predominantly in the dissolved form, obtained by different methodologies. It is known that nutrients within ash on the soil surface (resultant of burning of litter and vegetation) are susceptible to both solution and physical erosion processes, increasing the potential for export of nutrients in both dissolved and particulate form (Lane et al. 2008), with particulate being the dominant form of loss (Sharpley et al. 1992).

Regardless of being generally recognized, there is less information currently available on the potential downstream environmental consequences of enhanced nutrient losses following wildfire in relation to impacts on water quality, which are intrinsically linked to post-fire hydrological and soil erosion processes (Blake et al., 2010). Hence, a better understanding of post-fire nutrient behaviour, in both dissolved and particulate forms, allows a more accurately interpretation of the evolution of nutrient losses and its effects on vegetation recovery, soil productivity and downstream water quality. This knowledge gap is being addressed by the present work.

The present work is part of the FIRECNUTS project (PTDC/AGR-CFL/104559/2008) - WildFIRE effects on topsoil Carbon and NUTrient Stocks, dynamics and exports – that addresses these research gaps by studying the export of organic carbon and selected key nutrients (base cations, nitrogen and phosphorus) in a recently burnt forest area in north-central Portugal (Sever do Vouga).

1.4 *Aims of the present work*

The general objective of this thesis is to contribute to deepen and broden the knowledge on the hydrological and erosion response focusing on the nutrient cycle complex processes in recently burnt forest areas and understand the ecological consequences of these processes.

Therefore, this thesis work pretends to gain insight into the magnitude of post-fire soil fertility losses in the Mediterranean region, which is crucial information for defining post-fire land management measures to reduce soil degradation.

For that matter, key nutrient exports (base cations, as well as nitrogen and phosphorus exports in the total and soluble forms: total nitrogen and nitrate; total phosphorus and ortophosphate) by overland flow were evaluated in a recently burnt forest area. This evaluation was done mainly at the micro-plot scale and on a limited basis at the slope scale (presented here only in one of the chapters).

The specific objectives were:

(i) to assess post-fire stocks of key nutrients in the topsoil and ash layer.

(ii) to describe the temporal variation in topsoil nutrient stocks and distribution following wildfire and post-fire management.

(iii) to quantify the post-fire nutrient losses by overland flow (under the influence of different features):

- for the two predominant and fire-prone forest types in north-central Portugal, i.e. eucalypt and pine plantations;
- for the two prevailing parent materials in the region, i.e. granite and schist);
- for two different slope aspects, i.e. a facing-north slope and a facing-south slope;
- with time-since-fire during the initial months of the window-of-disturbance and for an somewhat extended monitoring period.

(iv) to describe the temporal variation in key nutrient losses following wildfire and post-fire management.

(v) to establish the relationships between post-fire key nutrient losses and hydrological and erosion processes.

Site differences in soil nutrient dynamics are expected given the different features in terms of types of forest plantations, parent materials and slope aspects, as well as the shallow soil on this study area that brings the parent material close to the plant root zone (Yavitt, 2000).

1.5 *Outline of this thesis work*

This document starts with this Chapter 1, presenting the motivation and importance of this work, the outline of this thesis and a brief introduction to wildfire effects on soil nutrient stocks and exports by overland flow.

The organization of this thesis follows four main chapters, Chapters 2 to 5, in which these objectives were set. These chapters correspond to papers published or submitted for publication and stands by itself. These papers have been organized to cope with the objectives of this work, thus providing the framework for the rest of this thesis.

Chapter 2 present a short-term study on base cations losses in contrasting slopes in terms of vegetation (eucalypt vs. pine) and parent material (granite vs. schist), during a limited selection of major rainfall events over the six-months monitoring period. It presents also a comparison between micro-plot scale and slope scale, with comparison to an unburnt slope only at the slope scale.

Chapters 3 and 4 are based on the same study sites of Chapter 2, at the same contrasting slopes in terms of vegetation (eucalypt vs. pine) and parent material (granite vs. schist), presenting short-term nutrient losses for all the rainfall events over the six-months monitoring period, at the micro-plot scale. Chapter 3 presents results for nitrogen losses, while Chapter 4 deals with phosphorus losses.

To cope with the limitations of short-term studies, Chapter 5 presents a variation of nitrogen and phosphorus losses for all the rainfall events over an extended monitoring period, in contrasting slopes in terms of slope aspect. This was done in recently burnt eucalypt plantations, at the micro-plot scale, over a twenty-months monitoring period.

Chapter 6 provides the conclusions of the present work.

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Chapter 2 - Cation export by overland flow in a recently burnt forest area in north-central Portugal

Machado A. I.[a], Serpa D.[a], Ferreira R.V.[a], Rodríguez-Blanco M. L.[b], Pinto R.[a], Nunes M. I.[a], Cerqueira M. A.[a], Keizer J. J.[a]

[a]University of Aveiro and CESAM; [b]University of A Coruña, Faculty of Sciences

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Abstract

The current fire regime in the Mediterranean Basin constitutes a serious threat to natural ecosystems because it drastically enhances surface runoff and soil erosion in the affected areas. Besides soil particles themselves, soil cations can be lost by fire-enhanced overland flow, increasing the risk of fertility loss of the typically shallow and nutrient poor Mediterranean soils. Although the importance of cations for land-use sustainability is widely recognised, cation losses by post-fire runoff have received little research attention. The present study aimed to address this research gap by assessing total exports of Na^+, K^+, Ca^{2+} and Mg^{2+} in a recently burnt forest area in north-central Portugal. These exports were compared for two types of planted forest (eucalypt vs. maritime pine plantations), two types of parent materials (schist vs. granite) and for two spatial scales (micro-plot vs. hill slope). The study sites were a eucalypt plantation on granite (BEG), a eucalypt plantation on schist (BES) and a maritime pine plantation on schist (BPS). Overland flow samples were collected during the first six months after the wildfire. Cation losses differed strikingly between the two forest types on schist, being higher at the eucalypt than pine site. This difference was evident at both spatial scales, and probably due to the extensive cover of a needle cast from the scorched pine crowns. The role of parent material in cation export was less straightforward as it varied with spatial scale. Cation losses were higher for the eucalypt plantation on schist than for that on granite at the micro-plot scale, whereas the reverse was observed at the hill slope scale. Finally, cation yields were higher at the micro-plot than slope scale, in agreement with the general notion of scaling-effect in runoff generation.

Keywords

Wildfires, Base Cations, Overland Flow, Water Erosion, Mediterranean Basin

2.1 *Introduction*

In Portugal, like in other Mediterranean countries, wildfires are now widely accepted to be a natural phenomenon. However, fire frequency and intensity are considered to have increased dramatically since the 1960s (Pereira et al., 2006; Shakesby, 2011). As principal causes of this intensified fire regime have been appointed a combination of socio-economic factors, in particular the large-scale planting of fire-prone tree species such as eucalypt and pine, and the extensive abandonment of traditional land-use practices (Moreira et al., 2009; Shakesby et al., 2011).

The increase in fire occurrence is a matter of concern for the (semi-)natural ecosystems in the Mediterranean Basin because it exerts both immediate and lasting environmental and ecological impacts (Certini, 2005; Shakesby, 2011). Most of these impacts are directly or indirectly related to changes in the physical, chemical and biological properties of soils, which affect biogeochemical cycles, and may therefore increase the risk of soil degradation (Certini, 2005; Knoepp et al., 2005; Shakesby, 2011; Soto et al., 1997; Thomas et al., 2000a, 2000b).

During fires, macro-nutrients (N and P) and base cations (Na^{+}, K^{+}, Ca^{2+} and Mg^{2+}) contained in plant biomass and in the litter and soil organic layers may be lost through volatilization, convection (of ash and smoke), or particulate transport (Knoepp et al., 2005; Neary et al., 1999; Soto et al., 1997; Wanthongchai et al., 2008). After a fire, the elements deposited as ash or mineralized from burnt organic matter on the soil surface are often leached into the soil or lost by wind and water erosion (Caon et al., 2014; Knoepp et al., 2005; Neary et al., 1999; Soto et al., 1997; Wanthongchai et al., 2008).

Cation losses by hydrological processes are strongly affected by fire-induced changes in soil cover due to the (partial) combustion of vegetation and litter layer (Certini, 2005; Ferreira et al., 2005; Granged et al., 2011; Kutiel and Shaviv, 1992; Shakesby, 2011; Zavala et al., 2010). The increase in bare soil, which is known to enhance the erosive potential of rain drops (Certini, 2005; Fernandez-Raga et al., 2010), and the removal of vegetation and litter, promotes overland flow and the associated sediment losses (Ferreira et al., 2005, 2008; Granged et al., 2011; Prats et al., 2014; Shakesby and Doerr, 2006). Fire-induced changes in topsoil properties such as, infiltration capacity (Badía et al., 2014; Moody et al., 2013; Shakesby, 2011; Shakesby and Doerr, 2006), porosity (Granged et al., 2011), soil water repellency (Doerr et al., 2006; Keizer et al., 2008; Malvar et al., 2011), organic matter (Badía et al., 2014; Knoepp et al., 2005) and aggregate stability (Varela et al., 2010), can further enhance overland flow and losses in soil and soil fertility. The first rainfall events after a wildfire are often of major importance in terms of cation depletion (Badía et al., 2014; Knoepp et al., 2005; Shakesby, 2011).

The magnitude of post-fire cation losses is extremely variable, depending on a complex interplay of factors such as type and growth stage of the vegetation, fire behaviour and severity, local fire history, antecedent weather conditions, and site characteristics (Brais et al., 2000; Caon et al., 2014; Certini, 2005; Knoepp et al., 2005; Neary et al., 1999; Shakesby and Doerr, 2006). The temperature reached in soils during burning is particularly important for the direct fire effects on soil fertility (Caon et al., 2014; Certini, 2005). Low-intensity wildfires are usually associated with an increase, albeit ephemeral, in soil cation availability (Brais et al., 2000; Scharenbroch et al., 2012) whereas moderate- and high-intensity fires generally produce base cation losses (Certini, 2005; Shakesby, 2011).

The effects of fire on soil nutrient dynamics in forest areas have been addressed by various studies (Caon et al., 2014; Fernández et al., 2011; Johnson et al., 2007; Kutiel and Shaviv, 1992; Trabaud, 1994; Wanthongchai et al., 2008; Yildiz et al., 2010). However, post-fire export of base cations by overland flow has received little research attention; in spite the few-existing studies clearly suggested its relevance for soil productivity (Cancelo-González et al., 2013; Ferreira et al., 2005; Thomas et al., 1999, 2000b). Especially in the fire-prone regions of the Mediterranean Basin with their typically shallow and nutrient poor soils, fire-enhanced cation exports are particularly relevant for land-use sustainability (Ferreira et al., 2005, 2008; Shakesby, 2011).

In Portugal, post-fire cation export by runoff was studied by Thomas et al. (1999, 2000b) and Ferreira et al. (2005). These three studies assessed the losses for the two principal forest types in the study region - plantations of eucalypt (Eucalyptus globulus Labill.) and maritime pine (Pinus pinaster Ait.) - at different spatial scales ranging from micro-plot to catchment. However, Thomas et al. (1999, 2000b) and Ferreira et al. (2005) measured the losses of dissolved or exchangeable cations rather than the total losses, and, thus, most likely underestimated the full impacts of wildfires on soil fertility.

To address this research gap, the present study aimed at providing further insights into total cation exports by post-fire overland flow in recently burnt Mediterranean forests. To this end, total losses of Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} in post-fire runoff were quantified: i) for two contrasting spatial scales, i.e. that of micro-plot and hill slope; ii) for two contrasting forest types, i.e. the eucalypt and maritime pine plantations that are now dominating the north-central Portuguese mountains; and iii) for two contrasting bedrock types, i.e. schist and granite that are both widespread in north-central Portugal. These base cation losses by overland flow were furthermore compared with the stocks in the ash and uppermost soil layers, both immediately after the wildfire and at the end of this study as well as with the losses under long-unburnt conditions, albeit only at the slope scale and just for a eucalypt plantation. As post-fire hydrological and geomorphological activity in the study region is particularly intense during the early stages of the so-called “window of disturbance” (Ferreira et al., 2005, 2008; Malvar et al., 2011; Martins et al., 2013; Prats et al., 2014; Shakesby, 2011; Shakesby and Doerr, 2006), base cation losses were monitored during the first six months after a wildfire. Plans to continue the monitoring scheme had to be abandoned as the recently burnt study sites were terraced in preparation for a new eucalypt plantation.

2.2 *Material and Methods*

2.2.1 *Study area and study sites*

The study area was located within the Vouga River Basin, near the Ermida village in the Sever do Vouga municipality, Aveiro District, north-central Portugal (Figure 2.1). At the end of July 2010, a wildfire ravaged the area for two days and consumed almost 295 ha of forest lands (DUDF, 2011). The "Ermida" burnt area was predominantly covered by eucalypt plantations but also included a few, small maritime pine stands. The fire severity was, on overall, moderate, since the litter layer and undergrowth vegetation of herbs and shrubs were mostly completely consumed, whereas the tree crowns were typically only partially combusted (Shakesby and Doerr, 2006). Within the burnt area, three hill slopes were selected for this study for their moderate fire severity and, at the same time, contrasting forest types as well as parent materials (Table 2.1). The BEG study site concerned an eucalypt plantation on granite, the BES site an eucalypt plantation on schist and the BPS site a maritime pine slope on schist (Figure 2.1.). In addition, a long-unburnt (more than 20 years) eucalypt plantation on schist (UES) was selected just outside the burnt area, whilst a long-unburnt Maritme Pine site could not be located within reasonable distance (Figure 2.1.).

The climate of the study area can be classified as humid meso-thermal, with moderate but prolonged warm dry summers (Köppen: Csb; DRA-Centro, 2002). Mean annual temperature at the nearest climate station (Castelo Burgães: 40º 51' 10''N, 8º 22' 44''W at 306 m a.s.l.) was 14.9 oC (SNIRH, 2011: 1991-2011). Annual rainfall at the nearest rainfall station (Ribeiradio: 40º 73' 65''N, 8º 30' 08''W at 228 m a.s.l.) was, on average, 1609 mm but varied markedly between 960 and 2530 mm (SNIRH, 2011: 1991-2011). The study area is part of the Hespheric Massif, one of the region´s major physiographic units. This unit mainly consists of pre-Ordovician schists and greywackes but includes Hercynian granites at several locations (Ferreira, 1978). According to the existing soil map (1: 1 000 000; Cardoso et al., 1973), the soils in the study area are predominantly Humic Cambisols. However, the soils of the four study sites were also described in the field, and ranged from Humic Leptosols to Humic Cambisols at the BEG and BES sites; Lithic Leptosols to Humic Leptosols at the BPS site; and Umbric Leptosols at the UES site (IUSS, 2006). During the description of soil profiles,

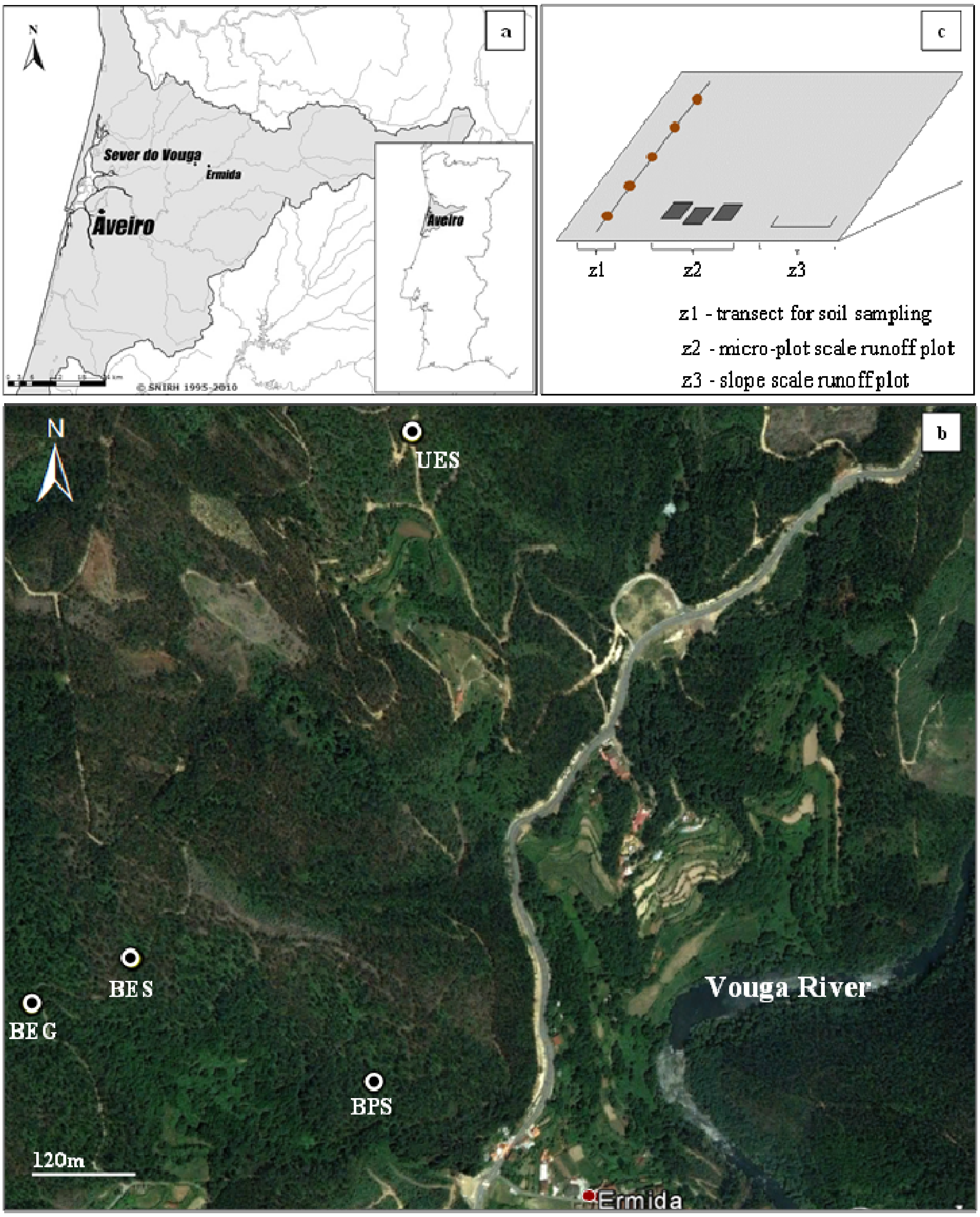

Figure 2.1 - Location of the Ermida study area within the Vouga River basin, north-central Portugal (a); location of the study sites (b): BEG – burnt eucalypt-granite site, BES – burnt eucalypt-schist site, BPS – burnt pine-schist site, UES – unburnt eucalypt-schist site; and schematic representation of the experimental set-up (c), dividing a study slope in the following strips: z1 – transect for soil sampling; z2 – micro-plot scale runoff plot; z3 – slope scale runoff plot..

topsoil (0-2 cm depth) samples were collected at five equally-spaced points along a transect immediately after the wildfire, and later analysed in the laboratory to determine bulk density [using the core method as described by Porta et al. (2003)], granulometric composition [following the international method of mechanical analysis as defined by Guítian and Carballas (1976)] and organic matter content [determined by loss on ignition at 550º C for 4 hours as described by Botelho da Costa (2004)]. The uppermost 2 cm of the soils at the study sites were rather coarse, with a loam to sandy-clay loam texture, and very rich in organic matter, ranging from 16 to 29 % (Table 2.1).

Table 2.1 - General slope description. BEG – burnt eucalypt-granite site; BES – burnt eucalypt-schist site; BPS – burnt pine-schist site and UES – unburnt eucalypt-schist site.

Slope	BEG	BES	BPS	UES
General characteristics				
Forest type	*Eucalyptus*	*Eucalyptus*	*Pinus pinaster*	*Eucalyptus*
Bedrock	Granite	Schist	Schist	Schist
Geographical coordinates	40º43’56’’N 8º21’3’’W	40º43’58’’N 8º20’58’’W	40º43’54’’N 8º20’47’’W	40º44’16’’N 8º20’45’’W
Elevation (m.a.s.l.)	220	220	150	260
Slope angle (º)	25.6 ± 4.4	24.0 ± 6.0	24.0 ± 2.4	25.0 ± 3.5
Slope length (m)	77	48	36	25
Fire severity indicators				
Consumption of tree crowns	Partial	Partial	Partial	-
Consumption of shrub layer	Total	Total	Total	-
Consumption of herbs/litter	Total	Total	Total	-
Ash colour	Black	Black	Black	-
Topsoil properties				
0-2 cm depth				
Texture	sandy loam	loam	sandy-clay	sandy-clay
Sand fraction (%)	61	45	54	69
Silt fraction (%)	24	34	25	9
Clay fraction (%)	14	21	21	22
Organic matter (%)	29 ± 1	22 ± 1	19 ± 2	16 ± 1
0-5 cm depth				
Bulk density (g cm^{-3})	0.71 ± 0.11	0.78 ± 0.19	0.73 ± 0.13	0.88 ± 0.19

2.2.2 *Experimental design, field data and sample collection*

Each of the three recently burnt study sites was divided in 3 strips running from the base to the top of the slope section (Figure 2.1.). One of the strips was used for repeated collection of soil samples, another for measuring runoff at the micro-plot scale, and the remaining for measuring runoff at the slope scale. The strips for the runoff measurements were some 5 m wide, leaving the remaining part of the slope for destructive soil sampling. The long-unburnt site was less wide, so that it was decided not to install the micro-plots.

For this study, only samples of the topsoil (0-2 cm depth) were collected because moderate fires have been reported to mainly affect the upper 2 cm of soil (Badía-Villas et al., 2014a; 2014b). Soil samples were first collected on August 10 2010, before the occurrence of any rainfall after the wildfire, and then again on February 16 2011, before the terracing operations. At the first occasion, also samples of the ash layer were collected. Sampling was done at five equally-spaced points along a transect that was laid out from the base to the top of the slope section, and shifted 1-2 m across the slope between subsequent sampling occasions. At each transect point the ashes were collected over an area of 0.5 m^2 (0.5 m x 0.10 m) and the topsoil (0-2 cm depth) over an area of 0.25 m^2 (0.5 m x 0.5 m).

The study sites were instrumented with runoff plots by August 25 2010, before the occurrence of any significant post-fire rainfall, as registered by various rainfall gauges that had been installed across the burnt area (see underneath). This involved the installation, at the base of the slope section of three bounded micro-plots of approximately 0.28 m^2, at distances of 1-2 m from each other.

As prior studies in the region have found contradictory results on the role of slope position on post-fire runoff and erosion at the micro-plot scale (Malvar et al., 2015; Prats et al., 2014), the micro-plots were located at the base of the slope section where the forest stand was planted (i.e. at the bottom of the property). This allowed easy access and, thus, facilitated speedy data and sample collection, on the one hand, and, on the other, minimized the disturbance to the slopes, which was a concern as the slopes were located within an experimental catchment (Keizer et al., 2015). Four plot outlets of 0.5 m wide were also installed at the base of each slope section, together making up an unbounded slope-scale plot with a width of approximately 2 m and contributing areas of 62 m^2 (UES), 75 m^2 (BPS), 97 m^2 (BES) and 154 m^2 (BEG). The outlets of the runoff plots were connected, using garden hose, to one or more high-density polyethylene tanks of 30 or 70 L to collect the overland flow.

From August 25 2010 until February 23 2011, the runoff collected in the various tanks was measured at 1- to 2-weekly intervals, mainly depending on the occurrence of rainfall. Whenever the runoff in a tank exceeded 250 mL, a sample was collected in a 500 mL polyethylene bottle that had been previously rinsed with HCl (pH < 2.0) and distilled and deionised water. The samples were then transported to the laboratory in cool boxes and stored at 4 ºC for no longer than 24h. The 1- to 2-weekly field trips also involved measurement of the rainfall accumulated in four storage gauges (in-house design) that had been installed across the study area by the middle of August 2010. Their main purpose, however, was to validate the automatic recordings of two tipping-bucket rainfall gauges (Pronamic Professional Rain Gauge with 0.2 mm resolution) that had been installed at close proximity to two of the storage gauges.

2.2.3 *Laboratory work*

Upon arrival at the laboratory, the ash and soil samples were air dried. The base cation content of the first 2 cm of the topsoil was determined for each soil sample individually (n=5; Figure 1), whereas the base cations content of the ash layer was determined for one composite sample per site and sampling occasion (as the amounts of ash were limited). The soil and composite ash samples were digested with HNO_3 and H_2SO_4 in teflon vessels placed in a sand bath at 250ºC (APHA, 1998). After digestion, samples were filtered through paper filters and then analysed for their Na, K, Ca and Mg concentrations using a Perkin Elmer Analyst 200 Atomic Absorption Spectrophotometer. Because of logistic constraints, only about half of the runoff samples that were collected during the 6-month study period could be analysed for this study. The runoff samples analysed here were those collected following the two monitoring periods (i.e. read-outs) of each month with the highest rainfall amounts, so that the runoff samples from in total 12 read-out periods were included in this study. The analysis of total base cations (i.e. dissolved plus particulate forms) in the selected samples either started shortly upon arrival at the laboratory or, whenever that was not possible, was delayed up to a maximum period of 6 months, after first acidifying the sample with HNO_3 to a pH below 2 and then storing it at 4ºC. The Na, K, Ca and Mg concentrations in runoff samples were determined using the same procedure as described above for ash and soil samples. Total suspended sediment concentration of the selected runoff samples was also determined, using the standard gravimetric method (APHA, 1998).

2.2.4 *Data analysis*

Differences in base cation contents of the ash and soil samples as well as differences in base cation exports by runoff and the respective concentrations were evaluated for the pairs of study sites with contrasting forest types (BES vs. BPS), parent materials (BES vs. BEG) and fire regimes (BES vs. UES). This was done with the Student's t-test if the assumptions of normality and homogeneity of variance were not rejected. If one or both of them were indeed rejected, square root and logarithmic transformations of the data were tried first and, if unsuccessful, the non-parametric Mann-Whitney Rank Sum test was applied (Zar, 1999). Relationships between the base cation exports at the different study sites for each read-out were explored by means of the Spearman rank correlation coefficient (Zar, 1999). The Spearman rank correlation coefficient was also computed to assess how well selected environmental variables (rainfall amount and intensity, total overland flow, sediment losses) could explain the export of Na, K, Ca and Mg, both at the micro-plot and slope scale (Zar, 1999). All statistical analyses were performed using SigmaPlot 11.0 package software, employing a significance level of 0.05.

2.3 ***Results and discussion***

2.3.1 *Base cation contents in ash and topsoil*

In the ashes collected at the different eucalypt and pine sites immediately after the wildfire, the common order of abundance of base cations was Ca^{2+} > K^{+} > Mg^{2+} > Na^{+} (Table 2.2.). These results are consistent to those found by Gabet and Bookter (2011) which also analysed ash cations by acid digestion, however if exchangeable forms were quantified, the order of cation abundance would be expected to differ: Ca^{2+} > Mg^{2+} > K^{+} > Na^{+} (Ferreira et al., 2005; Khanna et al., 1994).

The comparison between ash cation contents at the eucalypt site (BES) and the maritime pine site on schist (BPS) did not reveal significant differences (Student's t-test, $p>0.05$) between the two types of tree plantations (Table 2.2.). Nonetheless, base cation contents were, on average, consistently higher in the ashes collected at the BPS than BES site (Table 2.2.). Between-site differences in ash cation contents could reflect differences in either vegetation or litter layer, or both (Bodí et al., 2014; Ferreira et al., 2005; Khanna et al., 1994; Pereira et al., 2011; Soto and Diaz-Fierros, 1993).

Table 2.2 - Average (± standard deviation) base cation concentrations/stocks in the ash and topsoil layers of burnt slopes, immediately (August 2010) and sixth months (February 2011) after fire. BEG – burnt eucalypt-granite site; BES – burnt eucalypt-schist site; BPS – burnt pine-schist site and UES – unburnt eucalypt-schist site. For each cation, different symbols, letters and numbers correspond to significant differences ($p<0.05$) among slopes with respectively, different parent material (BEG vs BES), vegetation (BES vs BPS) and fire regime (BES vs UES).

	Cation	Sampling period	Layer	Site			
				BEG	BES	BPS	UES
Contents ($mg\ g^{-1}$)	Na^+	Aug-10	Ash	1.96 ± 0.42	1.21 ± 0.18[a]	1.94 ± 0.11[b]	-
			Soil	0.67 ± 0.33[*]	0.63 ± 0.19[*,a,1]	0.76 ± 0.14[a]	0.67 ± 0.15[1]
		Feb-11	Soil	0.65 ± 0.38[*]	0.50 ± 0.14[*,a,1]	0.65 ± 0.09[a]	0.62 ± 0.15[1]
	K^+	Aug-10	Ash	7.77 ± 1.46	8.41 ± 0.98[a]	9.40 ± 1.28[a]	-
			Soil	10.83 ± 1.24[*]	10.30 ± 1.21[*,a,1]	12.75 ± 1.02[a]	11.86 ± 1.37[1]
		Feb-11	Soil	11.30 ± 1.47[*]	9.78 ± 1.98[*,a,1]	11.70 ± 1.09[a]	10.12 ± 2.26[1]
	Ca^{2+}	Aug-10	Ash	14.91 ± 0.87	12.51 ± 1.59[a]	22.78 ± 0.16[a]	-
			Soil	1.37 ± 0.16[*]	1.14 ± 0.38[*,a,1]	1.25 ± 0.09[a]	0.27 ± 0.15[2]
		Feb-11	Soil	2.02 ± 0.44[*]	2.18 ± 0.84[*,a,1]	2.23 ± 0.28[a]	0.23 ± 0.11[2]
	Mg^{2+}	Aug-10	Ash	3.83 ± 0.70	2.79 ± 0.38[a]	4.04 ± 0.25[a]	-
			Soil	1.16 ± 0.73[*]	0.72 ± 0.44[*,a,1]	0.87 ± 0.53[a]	0.67 ± 0.44[1]
		Feb-11	Soil	1.02 ± 0.23[*]	0.64 ± 0.31[*,a,1]	0.90 ± 0.14[a]	0.54 ± 0.07[1]
Stocks ($g\ m^{-2}$)	Na^+	Aug-10	Soil	9.5 ± 4.7	9.8 ± 3.0	11.2 ± 2.0	11.8 ± 2.6
		Feb-11	Soil	9.2 ± 5.4	7.7 ± 2.2	9.4 ± 1.3	11.0 ± 2.6
	K^+	Aug-10	Soil	153.8 ± 17.6	160.7 ± 18.9	186.2 ± 14.9	208.7 ± 24.1
		Feb-11	Soil	160.5 ± 20.9	152.6 ± 30.9	170.8 ± 15.9	178.0 ± 39.8
	Ca^{2+}	Aug-10	Soil	19.5 ± 2.3	17.8 ± 5.9	18.3 ± 1.3	4.7 ± 2.6
		Feb-11	Soil	26.7 ± 6.3	34.0 ± 13.1	21.6 ± 4.1	4.0 ± 1.9
	Mg^{2+}	Aug-10	Soil	16.5 ± 10.4	11.3 ± 6.9	12.7 ± 7.7	11.8 ± 7.7
		Feb-11	Soil	14.4 ± 3.3	9.9 ± 4.8	4.0 ± 2.0	9.5 ± 1.2

In the present work, the separate role of understory vegetation and litter layer is impossible to untangle, since the wildfire fully consumed these two compartments at all study sites (see Table 2.1), as is usually the case in the study region (Ferreira et al., 2005, 2008; Maia et al., 2012; Malvar et al., 2013). However, as base cation concentrations were consistently higher at the BPS than BES site, one might hypothesize that litter layers influenced ash cation contents since long-unburnt maritime pine stands in the study region typically have more developed litter layers than long-unburnt eucalypt stands. As a result of their well-developed litter layers, pre-fire carbon stocks and cation contents in the organic soil horizon of maritime pine stands (Nunes et al., 2010) are usually higher than in eucalypt stands (Ribeiro et al., 2002), so one might presume that soil organic matter combustion contributed to the higher cation contents in BPS ashes. On the other hand, tree combustion could have also played a role in the cation availability in ashes because trees were partially consumed by fire (Table 2.1). The pronounced difference in Ca^{2+} contents, in particular, possibly reflected the difference in tree composition, since the Ca^{2+} content at the BEG site was also markedly lower than at the BPS site. Such a pine vs. eucalypt contrast in ash Ca^{2+} content could well involve differences in combustion characteristics, since eucalyptus leaves (Ribeiro et al., 2002) have higher cation contents than pine needles (Nunes et al., 2010).

Na^{+}, Ca^{2+} and Mg^{2+} ash contents immediately after the wildfire were, on average, higher than topsoil contents, whereas the opposite was true for K^{+} (Table 2.2.). The natural availability of this cation in soils (cf. UES data; Table 2.2) together with its high temperature threshold (i.e. temperature at which a given cation is volatilized) in soils [760-774ºC; cf. Bodí et al. (2014) and Knoepp et al. (2005)], might account for the different pattern of K+ ash/soil concentrations. Since the present, moderate-severity fire (with NIR-based estimates of Maximum Temperature Reached at 0-2 cm depth ranged from 325 to 405 ºC; Pedrosa, 2012) was unlikely to have produced important K^{+} losses from the topsoil through volatilization and since K^{+} is not the most abundant cation in vegetation and litter (Nunes et al., 2010; Ribeiro et al., 2002), K^{+} contents were expected to be higher in the soil than in the ashes. On the other hand, differences between ash and soil concentrations were particularly pronounced in the case of Ca^{2+}, with lower (90–95 %) concentrations in soil than ash samples, as would be expectable from previous studies (Ferreira et al., 2005; Johnson et al., 2007; Pereira et al., 2012). The reason behind these findings is two-fold. On one hand it can relate to the natural composition of litter layers and vegetation, which is typically Ca^{2+} enriched (Nunes et al., 2010; Ribeiro et al., 2002), and on the other, to the temperature threshold (1240-1484 ºC) for Ca^{2+} in soils, which is higher than for the other cations (Bodí et al., 2014; Knoepp et al., 2005). As a consequence, Ca^{2+} and K^{+} swapped places in the order of predominance of base cations in the topsoil compared to the ash layer.

The comparison of the topsoil base cation contents, in August 2010, at the recently burnt and long-unburnt eucalypt plantations on schist (BES vs. UES) suggested that the wildfire did have a significant (Mann-Whitney Rank Sum test, $p<0.01$) direct effect but just in the case of Ca^{2+} (Table 2.2). The combustion of belowground biomass and topsoil organic matter during fire is likely to have promoted a Ca^{2+} increase in soils since this material is typically Ca^{2+} enriched (Knoepp et al., 2005; Nunes et al., 2010; Ribeiro et al., 2002). Likewise, the incorporation of Ca^{2+} enriched ground ash (Table 2.2) into the soils could have influenced Ca^{2+} availability since substantial increases in soil Ca^{2+} contents have been reported after ash deposition (Badía et al., 2014; Bodí et al., 2014; Caon et al., 2014; Kutiel and Shaviv, 1992). The relative proportion of cations in soils also seems to have been affected by fire, as reported by other authors (Caon et al., 2014; Knoepp et al., 2005), since the order of abundance of cations at the BES site ($K^+ > Ca^{2+} > Mg^{2+} > Na^+$) was clearly different than at the UES site ($K^+ > Mg^{2+} > Na^+ > Ca^{2+}$). Like in the case of the ash layer, base cation contents in the topsoil did not reveal significant differences (Student's t-test, $p>0.1$) between the two types of tree plantations on schist (Table 2.2). Also in agreement with the ash results, the average topsoil contents of all four cations, immediately after fire, were consistently higher at the maritime pine (BPS) than eucalypt site (BES). This could be due to a somewhat higher soil burnt severity at the eucalypt site, as its higher organic matter content (Table 2.1) would presume higher base cation contents (Granged et al., 2011; Knoepp et al., 2005; Soto and Diaz-Fierros, 1993; Terefe et al., 2008). Topsoil base cation contents did not differ significantly between the two types of parent material either (Student's t-test and Mann-Whitney Rank Sum test, $p>0.3$). All four base cations did, however, consistently revealed higher concentrations at the eucalypt site on granite (BEG) than schist (BES), most likely due to the higher organic matter content of BEG soils (Table 2.2) which increases cation exchange capacity and their retention in soils (Granged et al., 2011; Knoepp et al., 2005; Terefe et al., 2008).

From August 2010 to February 2011, a decrease in soil cation contents was observed at the long-unburnt site (UES), possibly as result of erosion, cation leaching into deeper soil layers, and/or plant uptake (Bodí et al., 2014; Cerdà and Doerr, 2008; Khanna et al., 1994; Knoepp et al., 2005). For the burnt slopes, a similar justification can be given for the lower Na^+, K^+ and Mg^{2+} soil contents observed six months after the fire, but the same is not true for Ca^{2+} since its contents almost doubled between the two sampling periods (Table 2.2). In the case of this element, the results most likely reflected leaching of Ca^{2+}-enriched-ash into the soil (Ferreira et al., 2008; Knoepp et al., 2005; Kutiel and Shaviv, 1992; Soto and Diaz-Fierros, 1993; Wangthongchai et al., 2008), since substantially higher Ca^{2+} concentrations were observed in ashes than in soils (Table 2.2). Despite the temporal variations, the relative proportion of cations in soils was maintained at the long-unburnt ($K^+ > Mg^{2+} > Na^+ > Ca^{2+}$) and burnt eucalypt site on schist (K+ > Ca2+ > Mg2+ > Na+), suggesting that the influence of fire was still present after a six month period (Caon et al., 2014). Differences among sites with distinct types of vegetation (BPS vs. BES) and parent material (BEG vs. BES) were also maintained between the two sampling periods, which reinforces the hypothesis of processes occurring within the "window of disturbance" (Ferreira et al., 2005, 2008; Shakesby and Doerr, 2006).

2.3.2 *Base cation export by overland flow*

2.3.2.1 *Micro-plot scale*

The 12 read-outs selected for this study, which represent the two monitoring periods of each month with the highest rainfall amounts, corresponded to 962 of the 1205 mm of rainfall that fell over the entire study period, and amounted, on average, to 74 % of the overland flow produced by the micro-plots over this 6-months period. The associated total base cation losses at the three recently burnt sites differed markedly for the four elements (Table 2.3). At all three sites, total Mg^{2+} exports were lowest and total K^+ exports highest, with relative differences between the two cations ranging from a factor of 3 to 5. The relative order of total Ca^{2+} and Na^+ losses, on the other hand, was possibly related to parent material, since Ca^{2+} export was, on average, higher at the two sites on schist (BES and BPS) but lower at the site on granite (BEG). Assuming the ash layer to be the principal source of the exported cations, either in its dissolved or particulate form, K^+ and Na^+ were over-represented in the observed exports. K^+ was the most exported cation but ranked second in the ashes, while Na^+ was the least abundant in the ashes but ranked second/third in terms of exports (Table 2.2 and Table 2.3). Ca^{2+} and Mg^{2+}, on the other hand, were under-represented because their rank in post-fire overland flow was lower than in the ashes (Table 2.2 and Table 2.3). Such a preferential transport of monovalent over divalent cations would agree well with their higher solubility in water (Brais et al., 2000; Cancelo-González et al., 2013; Certini, 2005; Knoepp et al., 2005; Soto and Diaz-Fierros, 1993). The lower affinity of monovalent cations to bind to soil organic matter might also account for these results as they are less likely to be retained in soils (Cancelo-González et al., 2013; Knoepp et al., 2005; Soto and Diaz-Fierros, 1993). In fact, the exports of monovalent cations tended to represent a larger fraction of the topsoil cation stocks (Table 2.2 and Table 2.3) than the exports of divalent cations (11- 93% vs. 4-27%). This could indicate that the topsoil acted as a source of K^+ and Na^+ losses at the micro-plot scale once the ash layer was exhausted as a source, whereas it acted as a sink of divalent cations and, in particular, Ca^{2+}.

Table 2.3 - Total (dissolved plus particulate) average (± standard deviation) cation losses, overland flow, runoff coefficients (%) and sediment losses at the micro-plot scale for the 12 selected read-outs during the first six months following a wildfire. BEG – burnt eucalypt-granite site; BES – burnt eucalypt-schist site and BPS – burnt pine-schist site. For each line, different symbols and letters correspond to significant differences ($p<0.05$) among slopes with respectively, different parent material (BEG vs BES) and vegetation (BES vs BPS).

Variable		BEG	BES	BPS
Cation losses (g m^{-2})				
	Na^{+}	1.19 ± 0.69*	1.89 ± 0.15*, a	0.88 ± 0.21a
	K^{+}	1.52 ± 0.71*	5.54 ± 0.73+, a	1.63 ± 0.16b
	Ca^{2+}	0.74 ± 0.31*	2.17 ± 0.44+, a	1.02 ± 0.41b
	Mg^{2+}	0.55 ± 0.29*	1.60 ± 0.33+, a	0.35 ± 0.11b
Overland flow (mm)º		236 ± 203*	319 ± 26*, a	230 ± 74a
Runoff coefficient (%)		25 ± 20*	33 ± 1*, a	24 ± 7a
Sediment losses (g m^{-2})		50 ± 44*	200 ± 69+, a	85 ± 69b

º Total rainfall associated = 962 mm

Despite the higher ash and soil cation contents at the BPS site (cf. Section 2.3.1) cation losses by overland flow were 2 to 5 times higher under eucalypt (BES) than pine (Table 2.3 and Figure 2.2).

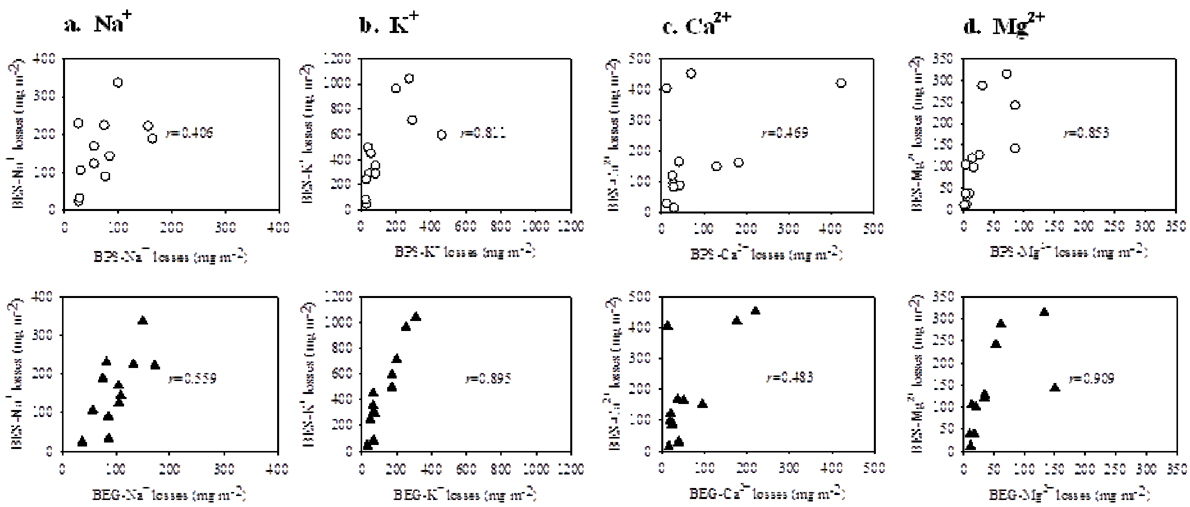

Figure 2.2 - Correlations between cation losses in sites with different vegetation (BES vs. BPS) and parent material (BES vs. BEG), at micro-plot scale. Data points correspond to the average cation losses in each of the 12 read-outs analysed for the present study.

From the Spearman Rank correlation analysis presented in Table 2.4, the environmental variables governing cation export at burnt slopes seem to vary depending on pre-fire vegetation. At the BES site, losses of dominant ash and soil cations like K^+ and Ca^{2+} were highly correlated to variables related to hydrological processes (Table 2.4), in particular to rainfall intensity (r=0.65 for K^+; r=0.87 for Ca^{2+}) and overland flow (r=0.52 for K^+; r=0.81 for Ca^{2+}). Malvar et al. (2015) and Prats et al. (2014) also found that rainfall intensity was a key factor in the post-fire response of micro-plots in recently burnt eucalypt stands in the study region, especially in terms of sediment losses. The higher soil hydrophobicity combined with a slower recovery of litter and ground vegetation under burnt eucalypt stands were likely to have promoted overland flow and the associated cation losses (Table 2.3) at the BES site (Doerr et al., 1998; Knoepp et al., 2005; Malvar et al., 2011, 2013; Thomas et al., 1999, 2000b), particularly under intense rainfall.

Table 2.4 - Spearman Rank correlations between environmental variables (rainfall amount and maximum intensity during 30 minutes - I30, overland flow and suspended sediments) and cation losses (averages per read out), at micro-plot scale. Values significantly different from zero at $\alpha \leq 0.05$ are presented in bold.

Slope	Variable	Na^+	K^+	Ca^{2+}	Mg^{2+}
BEG	Rainfall (mm)	0.29	0.21	0.06	-
	I_{30} (mm h^{-1})	**0.66**	**0.65**	**0.63**	0.34
	Overland flow (mm)	**0.54**	**0.61**	0.35	0.22
	Sediments (g m^{-2})	0.10	0.00	0.20	-
BES	Rainfall (mm)	0.13	0.21	**0.64**	0.07
	I_{30} (mm h^{-1})	0.34	**0.65**	**0.87**	0.39
	Overland flow (mm)	0.40	**0.52**	**0.81**	0.36
	Sediments (g m^{-2})	-0.07	0.08	0.47	0.09
BPS	Rainfall (mm)	0.21	0.01	0.00	-
	I_{30} (mm h^{-1})	0.49	0.50	0.53	0.35
	Overland flow (mm)	0.38	0.37	0.31	0.12
	Sediments (g m^{-2})	**0.67**	**0.78**	**0.80**	**0.66**

At the pine site (BPS), on the other hand, cation export was strongly correlated with sediment losses (Table 2.4), which suggests that cation losses occurred especially in particulate form. This stronger dependence on erosion processes confirms the idea of other authors (Knoepp et al., 2005; Kutiel and Shaviv, 1992; Martins et al., 2013; Thomas et al., 2000a, 2000b) that the existence of a needle cover, resulting from needle cast from the partially combusted crowns of resinous trees, may act as a protection for soils, thereby limiting overland flow and the associated sediment and cation losses at burnt pine sites.

Parent material also played an important role in cation export (Table 2.3 and Figure 2.2) since losses were 1.5 to 4 times higher on schist (BES) than on granite (BEG). As cations are adsorbed on the surface of negatively charged materials such as organic colloids, higher exports would be expected from the organically-poor schist soils than granite soils (Table 2.1) due to the existence of fewer cation exchange sites (Granged et al., 2011; Knoepp et al., 2005; Terefe et al., 2008; Shakesby 2011). On the other hand, the sandy texture of granite soils might have provided greater water infiltration capacity at micro-plot scale (Boix-Fayos et al., 2006; Shakesby, 2011), thereby generating lower amounts of overland flow and consequently lower cation exports at the BEG site (Table 2.3). Differences between the relative order of total Na^{+} and Ca^{2+} losses on granite and schist seem to be linked to soil properties and hydrological processes. The high correlation coefficients between Na^{+} losses and overland flow at the BEG site (Table 2.4) suggest that the export of the highly-soluble Na^{+} ions was promoted by the lack of Na^{+}-adsorption sites in granite soils (possibly due to the higher availability of divalent cations), especially since lower amounts of overland flow were required for Na^{+} mobilization at the BEG site than at the BES site (Table 2.3). As a consequence, Na^{+} exports were also higher at the BEG site than at the BES site. In the case of the divalent cations which are less easily mobilized as monovalent ions (Cancelo-González et al., 2013; Soto and Diaz-Fierros, 1993; Úbeda et al., 2009), however, the amount of overland flow generated was a limiting factor in promoting promote Ca^{2+} export at the BEG site (r=0.35) but not at the BES site (r=0.81).

2.3.2.2 *Slope scale*

At slope scale, the 12 read-outs selected for this study amounted, on average, to 92 % of the total overland flow produced by the open-plots. As regards to the associated total cation losses, values were, on average, 2-fold lower (Table 2.5) at the long-unburnt (UES) than at the recently burnt eucalypt plantations on schist (BES). Fire disruption of soil structure and hydraulic properties might account for these findings (Ferreira et al., 2005; 2008; Shakesby, 2011; Thomas et al., 1999, 2000b), since sediment losses were higher at the burnt site, but not the overland flow (Table 2.5).

Table 2.5 - Total (dissolved plus particulate) average cation losses, overland flow, runoff coefficients (%) and sediment losses at slope scale, for the 12 selected read-outs during the first six months following a wildfire. BEG – burnt eucalypt-granite site; BES – burnt eucalypt-schist site; BPS – burnt pine-schist site and UES – unburnt eucalypt-schist site. For each line, different symbols, letters and numbers correspond to significant differences ($p<0.05$) among slopes with respectively, different parent material (BEG vs BES), vegetation (BES vs BPS) and fire regime (BES vs UES).

Variable		**BEG**	**BES**	**BPS**	**UES**
Cation losses ($g\ m^{-2}$)					
	Na^+	0.16^{*}	$0.04^{+,a,1}$	0.05^{a}	0.05^{1}
	K^+	1.04^{*}	$0.10^{+,a,1}$	0.09^{a}	0.04^{2}
	Ca^{2+}	0.35^{*}	$0.05^{+,a,1}$	0.05^{a}	0.02^{1}
	Mg^{2+}	0.18^{*}	$0.02^{+,a,1}$	0.02^{a}	0.01^{1}
Overland flow (mm)°		24.0^{*}	$10.5^{+,a,1}$	10.8^{a}	14.3^{1}
Runoff coefficient (%)		2.4^{*}	$0.9^{+,a,1}$	0.8^{a}	1.5^{1}
Sediment losses ($g\ m^{-2}$)		140.2^{*}	$6.1^{+,a,1}$	3.5^{a}	1.2^{2}

° Total rainfall associated = 962 mm

For this site (BES), the addition of ash to the soils might have increased soil water retention, leading to lower runoff generation (Ebel et al., 2012). However, the ash layer was not able to prevent the detachment of soil particles by rainsplash erosion. An analysis of the amount of overland flow associated to each read-out seems to support this idea since runoff, unlike sediment losses, was higher at the BES than UES site in the second trimester after fire.

On the other hand, at the unburnt site, the high hydrophobicity of soils under eucalypt stands particularly after a dry season might have also been responsible for the higher runoff amounts observed in the first trimester after the fire, since high soil moisture levels are required to break soil water repellency (Keizer et al., 2005; Santos et al., 2013). As regards to sediments, the existence of a soil protective layer (litter and vegetation) at unburnt sites, most likely prevented sediment losses during the period of intense overland flow. The Spearman Rank correlation analyses presented in Table 2.6 clearly suggest that differences in cation exports between unburnt and burnt sites must be related to differences in hydrological and erosion processes, since little effect of environmental variables were found at the UES site, unlike at the BES site (Figure 2.3 and Table 2.6). The relative order of cation exports also differed between UES and BES (Table 2.6).

Table 2.6 - Spearman Rank correlations between environmental variables (rainfall amount and maximum intensity during 30 minutes - I30, overland flow and suspended sediments) and cation losses, at slope scale. Values significantly different from zero at α≤0.05 are presented in bold.

Slope	Variable	Na^+	K^+	Ca^{2+}	Mg^{2+}
BEG	Rainfall (mm)	**0.69**	**0.69**	0.42	0.49
	I_{30} (mm h^{-1})	0.04	0.36	**0.79**	**0.54**
	Overland flow (mm)	**0.62**	**0.71**	**0.50**	**0.61**
	Sediments (g m^{-2})	**0.59**	**0.74**	**0.62**	**0.65**
BES	Rainfall (mm)	**0.67**	**0.81**	0.46	**0.50**
	I_{30} (mm h^{-1})	0.21	**0.69**	**0.74**	0.48
	Overland flow (mm)	**0.73**	**0.81**	0.39	**0.50**
	Sediments (g m^{-2})	**0.68**	**0.76**	**0.61**	**0.74**
BPS	Rainfall (mm)	0.36	0.25	0.28	0.12
	I_{30} (mm h^{-1})	0.36	0.40	0.52	0.31
	Overland flow (mm)	0.24	0.01	-0.04	-0.10
	Sediments (g m^{-2})	**0.64**	**0.73**	**0.74**	**0.71**
UES	Rainfall (mm)	**0.59**	0.47	**0.52**	0.36
	I_{30} (mm h^{-1})	0.36	0.22	0.49	0.24
	Overland flow (mm)	0.08	-0.11	0.07	-0.17
	Sediments (g m^{-2})	0.48	0.39	**0.58**	0.34

At the UES site, highly-reactive easily-mobilized monovalent cations (Na^+ > K^+) presented the highest export rates and divalent cations (Ca^{2+} > Mg^{2+}) the lowest (2 to 7 times), as would be expected in undisrupted systems (Ferreira et al., 2005; Thomas et al., 1999, 2000a, 2000b). In the BES site, on the other hand, K^+ and Ca^{2+} were respectively the first and second most exported cations, possibly as a result of the depletion of the cation-enriched ash layer as hypothesized at the micro-plot scale (cf. Section 2.3.2.1). For the other burnt sites (BEG and BPS), K^+ was also the element with the highest export rates, but the relative order of export of the other cations differed from the BES site.

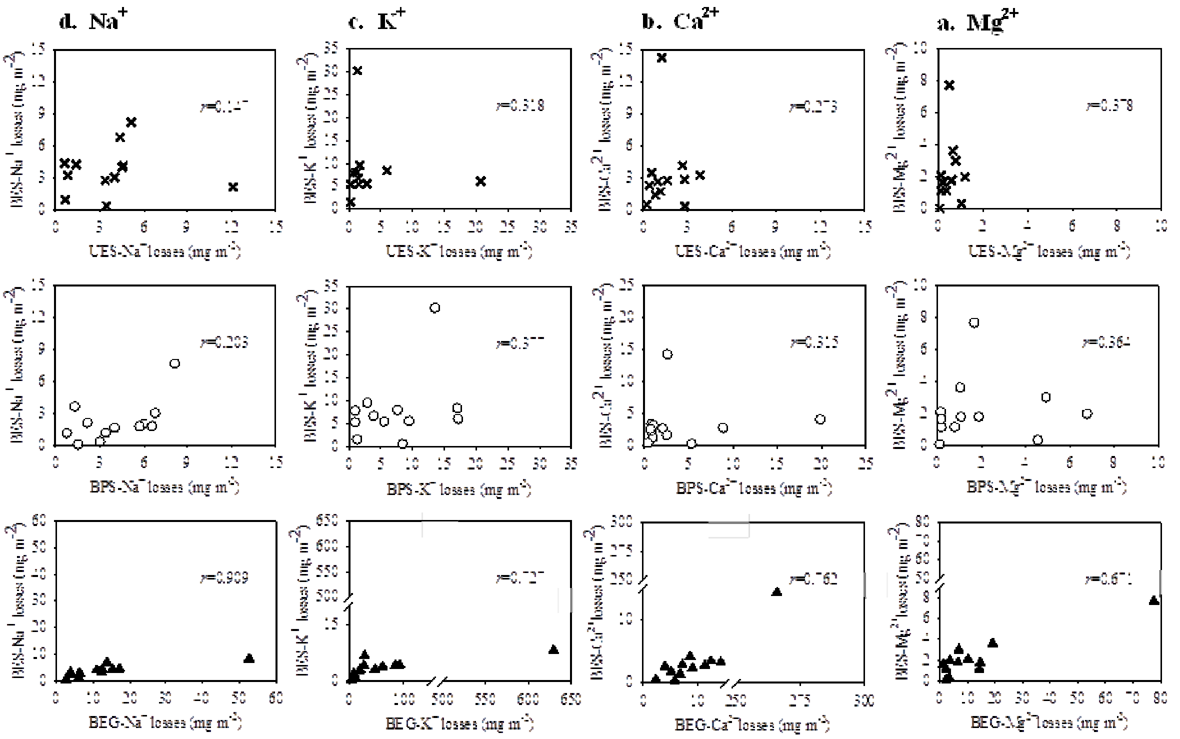

Figure 2.3 - Correlations between cation losses in sites with different fire regime (BES vs. UES), vegetation (BES vs. BPS) and parent material (BES vs. BEG), at slope scale. Data points correspond to the average cation losses in each of the 12 read-outs analyzed for the present study.

At the BPS site, the exports of highly reactive-highly soluble cations (K^{+}>Na^{+}) were higher than that of less reactive-less soluble divalent cations ($Ca2^{+}$>Mg^{2+}). At the BEG site, cation exports followed the order of soil cation contents (cf. Section 3.1), thereby suggesting that cation losses were more dependent on soil erosion than on metal reactivity (i.e. solubility in water and affinity to bind to organic matter).

For the burnt slopes, differences in cation exports were also identified between micro-plot and slope scale. In comparison to the micro-plot scale, a substantial decrease (one order of magnitude) in cation exports was observed at slope scale (Table 2.3 and Table 2.5).

Although a higher number of micro-plots would have been desirable to capture the heterogeneity within each slope, in the present study, the cation exports measured at the three micro-plots did not encompassed slope-scale exports. Therefore, one can presume that the lower cation exports were largely the result of lower overland flow and erosion rates at the slope scale (Table 2.5) since cation exports were strongly dependent on hydrological and erosion processes (Table 2.6). This seems to agree with the current opinion that runoff and erosion decrease with increasing spatial scale (Boix-Fayos et al., 2006; Coelho et al., 2004; Ferreira et al., 2005, 2008; Shakesby, 2011), especially due to re-infiltration opportunities resulting from a high spatial variability of soil water repellency, macroporosity and vegetation patterns following fire (Boix-Fayos et al., 2006; Ferreira et al., 2008; Shakesby, 2011).

When comparing sites with different pre-fire vegetation features (Table 2.5 and Figure 2.3), similar cation exports were observed at eucalypt (BES) and pine plantations (BPS) on schist, in opposition to what was observed at micro-plot scale (cf. Section 2.3.2.1). The improvement of hydrological connectivity at larger scales might have reduced the water erosion at the BES site (Table 2.5), since cations losses were highly correlated to sediment losses (Table 2.6), unlike at micro-plot scale (Figure 2.3). Despite these results, cation exports were, on average, lower at the BPS than BES site, which confirms the importance of a soil protective layer for the reduction of cation losses in burnt areas (cf. Section 2.3.2.1).

Parent material, on the other hand, had a significant effect (Mann-Whitney Rank Sum test, $p<0.01$) on base cation exports in burnt areas, since higher cation losses (one order of magnitude) were found at the granite (BEG) than at the schist (BES) site (Table 2.5), as opposite to the micro-plot scale (Table 2.3). These findings seem to support the idea that processes occurring at larger scales are more likely to resemble the natural hydrological and erosive response of burnt slopes, since higher overland flow and associated sediment and cation losses as found in the present study (Table 2.5), have been reported for sandy soils (Knoepp et al., 2005; Shakesby, 2011).

2.3.3 *Cation concentrations in overland flow*

2.3.3.1 *Micro-plot scale*

Immediately after the first post-fire rainfall event, all burnt sites exhibited a peak in total base cation concentrations (Figure 2.4) as a response to the leaching of the cation rich-easily erodible ash layer (Ferreira et al., 2005; Thomas et al., 1999). As the ash reservoir diminished and eroded sediments progressively coarsened (which causes a reduction of the cations sorption capacity to eroded soil particles), a sharp decrease in cation levels was observed, particularly in the first two months following fire (Figure 2.4). From this point one, cation concentrations were maintained at low levels and slight peaks occurred only as a response to extreme rainfall events, as referred by other authors (Ferreira et al., 2005; Soto et al., 1997).

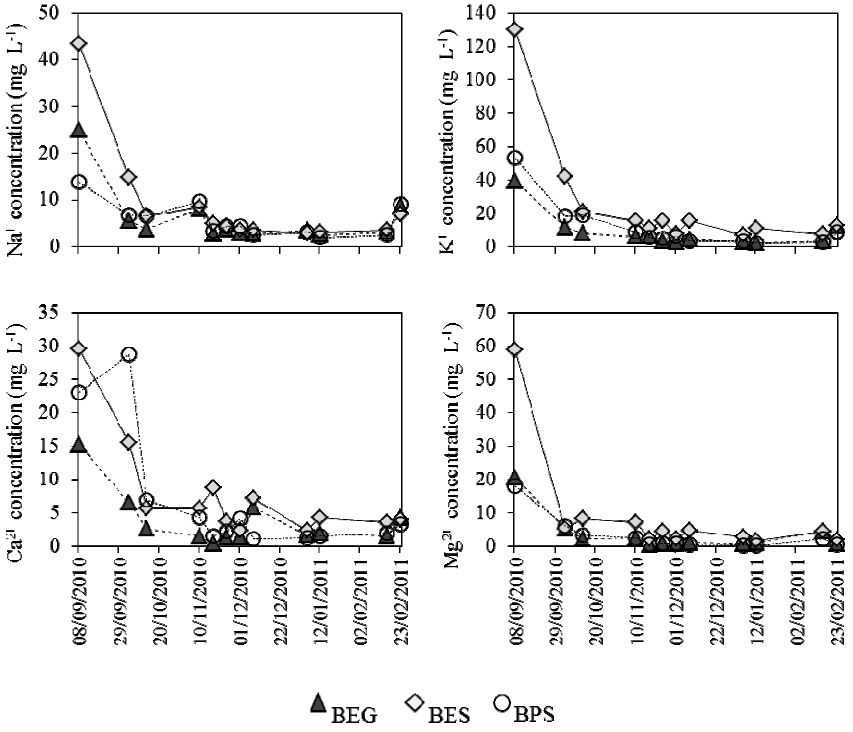

Figure 2.4 - Cation concentrations in overland flow (mg L^{-1}) at micro-plot scale. BEG – burnt eucalypt-granite site; BES – burnt eucalypt-schist site and BPS – burnt pine-schist site.

2.3.3.2 *Slope scale*

The comparison between cation concentrations at the long-unburnt (UES) and burnt eucalypt plantations on schist (BES), confirms the impact of wildfires as higher cation concentrations were found at BES than UES site (Figure 2.5). The increase of bare soil areas as a result of the (partial) combustion of vegetation and litter layer (Ferreira et al., 2005; Soto et al., 1997; Soto and Diaz-Fierros, 1993; Thomas et al., 1999, 2000b), possibly promoted overland flow and the associated sediment and cation losses at the BES site (Table 2.5). In comparison to the micro-plot scale, at a larger scale, cation concentrations exhibited clear differences between burnt sites as well as a more complex variation pattern (Figure 2.5). At the granite site (BEG), several cation peaks were observed within the first 6 months after fire, whereas at schist sites (BES and BPS) high cation levels were only found during a short period of time (1 to 2 months) after burning (Figure 2.5). A potential explanation for these patterns involves the existence of a continuous source of cations on granite – the topsoil, and a finite source on schist – the cation-rich ash layer (Ferreira et al. 2005). As a consequence, higher cation exports were found on granite than on schist (Table 2.5 and Figure 2.3).

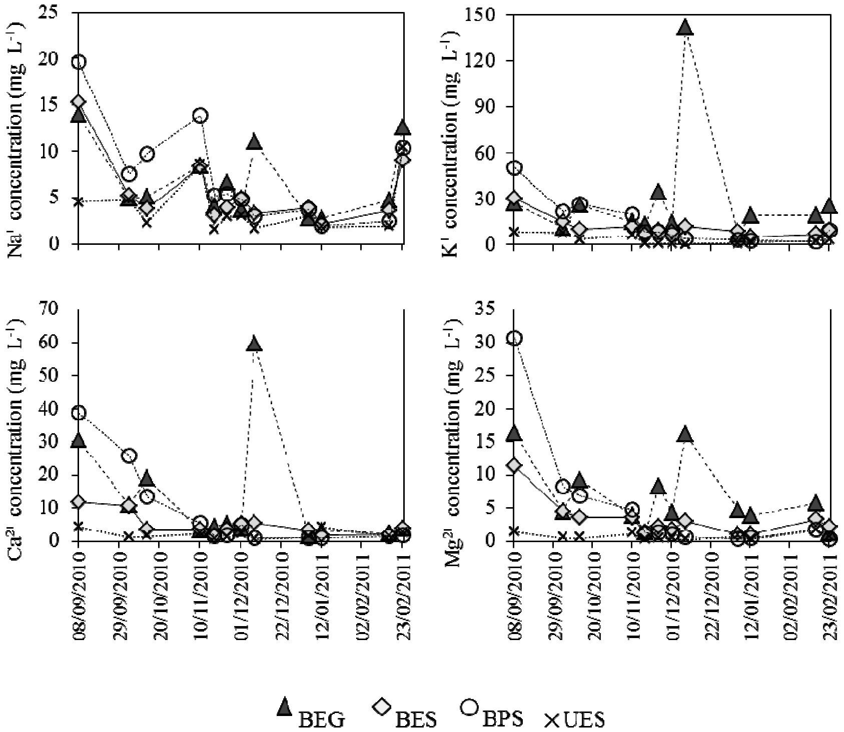

Figure 2.5 - Cation concentrations in overland flow (mg L^{-1}) at slope scale. BEG – burnt eucalypt-granite site; BES – burnt eucalypt-schist site; BPS – burnt pine-schist site and UES – unburnt eucalypt-schist site.

2.4 *Conclusions*

The present study clearly demonstrated the effects of wildfires on cation mobilization by overland flow. Cation exports were particularly intense in the two months after fire but after this initial period, peaks in cation concentrations were also observed in association to intense rainfall events.

These results suggest that wider time scales (i.e. wider than 6 months) are needed to evaluate the full extension of wildfires on forest lands. Nevertheless, it seems reasonable to recommend that post-fire management efforts should focus on the first 3 months after fire, to minimize the loss of soil fertility and degradation of burnt forest areas.

The present work also showed that scale size is an important factor when studying the effects of wildfires on soil degradation, since different responses were observed at micro-plot and slope scale. At smaller scales, cation losses were higher than at larger scales, possibly because runoff and erosion decreases at larger scales as a result of changes in the soil infiltration patterns.

These findings confirm the idea that although micro-plots may be suitable to quickly characterize the hydrological and erosion response in burnt forest areas, studies carried out at a larger scale are probably closer to reality due to a better representation of the natural connectivity within forest systems.

Studies at broader spatial scales, as well as wider time scales, are therefore recommended to assess the effective risk of post-fire soil fertility loss, which has important implications for the recovery process of burned Mediterranean forests as well as for post-fire land management.

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Chapter 3 - Short-term nitrogen losses by overland flow in a recently burnt forest area in north-central Portugal: A study at micro-plot scale

R.V. Ferreira[a], D. Serpa[a], A.I. Machado[a], M.L. Rodríguez-Blanco[b], L.F. Santos[a], M.T. Taboada-Castro[b], M.A. Cerqueira[a], J.J. Keizer[a]

[a]University of Aveiro and CESAM; [b]University of A Coruña, Faculty of Sciences

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Abstract

Over the past decades, wildfires have affected extensive areas of the Mediterranean region with negative impacts on the environment. Most of the studies on fire-affected areas have focused on sediment losses by overland flow, whereas few have addressed post-fire nutrient export. The present study aimed to address this research gap by assessing nitrogen (nitrate and total nitrogen) losses by overland flow in a recently burnt area in north-central Portugal. To this end, three burnt slopes were selected for their contrasting forest types (eucalypt vs. pine) and parent materials (granite vs. schist). The selected study sites were a eucalypt site on granite (BEG), a eucalypt site on schist (BES) and a maritime pine site on schist (BPS). Overland flow samples were collected during the first six months after the wildfire on a 1- to 2-weekly basis, after which this study had to be cancelled due to bench terracing of some of the sites. A peak in total nitrogen concentrations was observed in burnt areas immediately after the first post-fire rainfall event as a response to the erosion of the N-enriched ash layer. After this initial peak, smaller peaks were observed throughout the study period, mainly as a response to overland flow and/or erosion events. Nitrogen export differed strikingly between the two types of forests on schist, being higher at the eucalypt than at the pine site, due to the lack of a protective soil layer. Parent material did not play an important role on nitrogen export by overland flow since no significant differences were found between the eucalypt sites on granite and schist. The present study provides some insight into the differences in post-fire soil fertility losses between forest types and parent materials in the Mediterranean region, which is crucial information for defining post-fire land management measures to reduce soil degradation.

Keywords

Wildfire, Micro-Plot Scale, Overland Flow, Nitrogen Loss, Vegetation, Geology

3.1 *Introduction*

The increasing frequency of wildfires over the past decades has raised the concern over the resilience capacity of Mediterranean ecosystems to fire (Pausas et al., 2008; Pereira et al., 2006; Shakesby, 2011). By altering vegetation and soil properties, a fire typically disrupts the hydrological and geomorphological processes in forest areas (Shakesby, 2011; Shakesby and Doerr, 2006), so recurrent wildfires are likely to affect the functioning of natural systems. In the Mediterranean region, in particular, fires have been reported to increase overland flow generation and the associated soil and nutrient losses (Caon et al., 2014; Certini, 2005; Ferreira et al., 2005; Machado et al., 2015; Pausas et al., 2008; Shakesby, 2011; Thomas et al., 1999, 2000a, 2000b), increasing the risk of degradation of the already shallow and poor Mediterranean soils (Ferreira et al., 2005; Shakesby, 2011; Shakesby and Doerr, 2006).

Post-fire nutrient losses by water occur mainly during the earlier stages of the so-called ''window-of-disturbance'' (Shakesby and Doerr, 2006). This has typically been attributed to the (partial) consumption of the protective litter and vegetation cover, which promotes overland flow generation and soil erosion (Andreu et al., 2001; Bodí et al., 2014; Ferreira et al., 2005; Prats et al., 2013; Thomas et al., 1999). However, also the exhaustion of the nutrient-enriched ash layer deposited after the fire has been suggested as an important factor (Caon et al., 2014; Khanna et al., 1994; Knoepp et al., 2005; Pausas et al., 2008; Pereira et al., 2005; Shakesby, 2011; Thomas et al., 1999). Nonetheless, the magnitude of post-fire nutrient losses appears to be extremely variable, depending on an interplay of factors such as fire severity and recurrence (Bodí et al., 2014; Brais et al., 2000; Caon et al., 2014; Knoepp et al., 2005; Neary et al., 1999; Shakesby and Doerr, 2006), post-fire rainfall patterns (Bodí et al., 2014; Shakesby and Doerr, 2006), vegetation type and recovery (Caon et al., 2014; Cerdà and Doerr, 2008; Certini, 2005; Knoepp et al., 2005; Neary et al., 1999), terrain steepness (Bodí et al., 2014; Certini, 2005; Neary et al., 1999; Shakesby and Doerr, 2006) and soil characteristics (Certini, 2005; Neary et al., 1999; Shakesby and Doerr, 2006).

In spite of the relevance of soil nutrient status for the productivity of Mediterranean forest ecosystems (Andreu et al., 1996; Durán et al., 2010; Ferreira et al., 2005; Gimeno-García et al., 2000; Pardini et al., 2003; Rodríguez et al., 2009), post-fire nutrient losses by overland flow have been poorly studied in the Mediterranean Basin (e.g. Cancelo-González et al., 2013; DeBano et al., 1998; Díaz-Fierros et al., 1990; Lasanta and Cerdà, 2005; Machado et al., 2015). In the case of Portugal, few studies have measured post-fire nitrogen export by overland flow (Coelho et al., 2004; Ferreira et al., 1997, 2005; Thomas et al., 2000a, b; Walsh et al., 1992). Like the present study, most of the prior studies investigated nitrogen losses for the two principal forest types in north-central Portugal, i.e. plantations of eucalypt (Eucalyptus globulus Labill.) and maritime pine (Pinus pinaster Ait.), but they only evaluated solute losses and not total nitrogen losses (i.e. solute + particulate fraction). Furthermore, prior studies involved larger spatial scales than this study, i.e. 16 m^2 plots (Ferreira et al., 1997, 2005; Thomas et al., 2000a, b; Walsh et al., 1992) and small catchments (Ferreira et al., 1997, 2005), which typically have more complex hydrological and erosion responses.

A better understanding of post-fire nutrient export behaviour, in both its dissolved and particulate forms, is therefore crucial for a more reliable assessment of soil fertility losses following wildfires as well as of their potential eutrophication effects on downstream aquatic systems.

The present study aims to address this knowledge gap, by evaluating total nitrogen exports by post-fire overland flow in a recently burnt area of the western Mediterranean Basin. Since it proved impossible to find a long-unburnt pine plantation in the immediate surroundings of the burnt area and since it was preferred to instrument a nearby long-unburnt eucalypt plantation with slope-scale plots rather than of micro-plots (see for more details in Machado et al., 2015), this study does not allow to assess the effects of fire on nitrogen losses by overland flow. Instead, the main purpose of the current work was to compare post-fire nitrogen losses for different combinations of land cover and parent material. The specific objectives were to quantify total nitrogen as well as nitrate losses by overland flow at the micro-plot scale for: (i) two contrasting forest types - i.e. eucalypt and maritime pine plantations, which dominate the north-central Portuguese mountains; (ii) for two contrasting bedrock types - i.e. schist and granite, which are the prevailing parent materials in north-central Portugal. These losses were furthermore related to the nitrogen stocks of the ash layer and the topsoil, for a better understanding of the N cycle following fire.

As two of the three study sites were terraced 6 months after the fire in preparation for a new eucalypt plantation, the present study had to be restricted to the immediate post-fire period because this technique completely altered the topography of the slopes (Martins et al., 2013). Although this constitutes a drawback compared to the initial plans to monitor runoff and erosion during the first 2-3 years after fire, prior studies in the study region have suggested that the post-fire hydrological and erosion response is strongest during the first 4 to 6 months after the wildfire (e.g. Ferreira et al., 2005, 2008; Malvar et al., 2011; Martins et al., 2013; Prats et al., 2014; Shakesby, 2011; Shakesby and Doerr, 2006).

3.2 *Materials and Methods*

3.2.1 *Study area and sites*

The study area was located within the Vouga River Basin, near the Ermida village in the Sever do Vouga municipality, north-central Portugal (Figure 3.1).

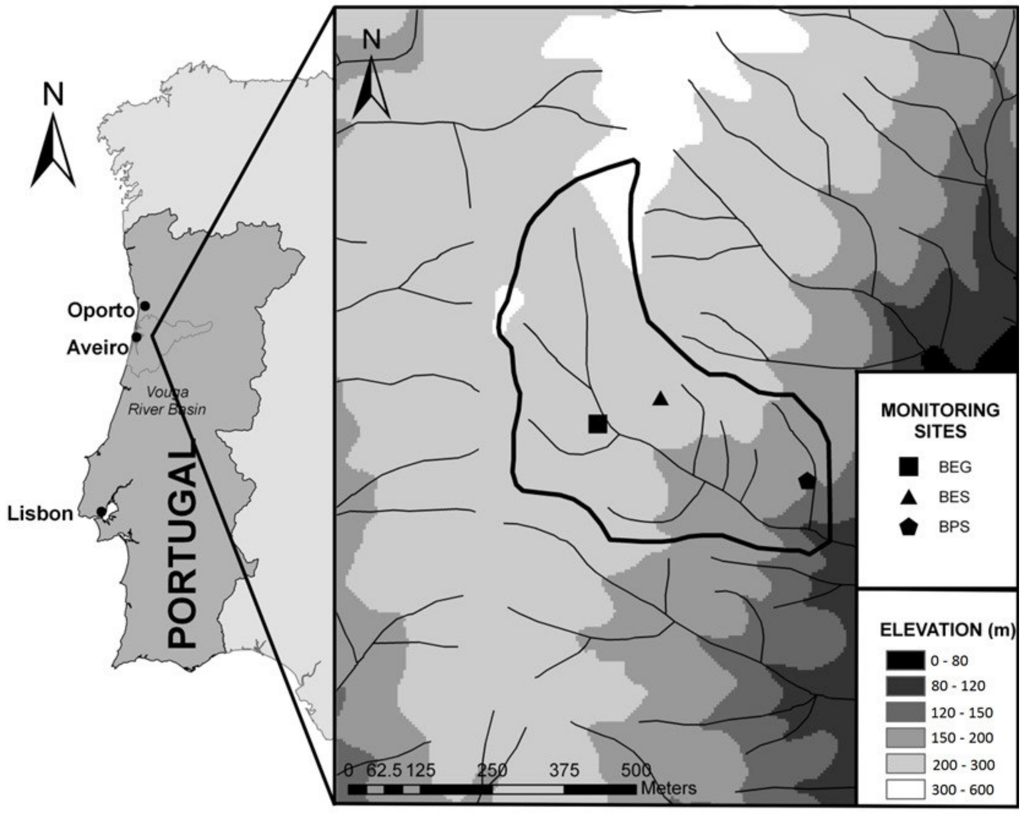

Figure 3.1 - Location of the Ermida study area within the Vouga River basin, north-central Portugal. Location of the study sites: BEG — burnt eucalypt-granite site, BES — burnt eucalypt schist site and BPS — burnt pine-schist site. Bold line represents the Ermida catchment.

The area was burnt between July 26 and July 28 2010 by a wildfire that consumed, in total, 295 ha of forest (DUDF, 2011). Before the fire, the "Ermida" study area was predominantly covered by commercial eucalypt (Eucalyptus globulus Labil.) plantations but also included some maritime pine (Pinus pinaster Ait.) stands. Fire severity was, on overall, moderate, since ashes were black, the litter layer and understory vegetation (herbs and shrubs) was almost completely consumed by fire, and tree crowns were only partially combusted (Shakesby and Doerr, 2006). According to Near Infrared (NIR) spectroscopy measurements, the maximum temperatures reached by topsoil (0-2 cm layer) during fire varied from 325 to 405ºC in the study area (Pedrosa, 2012). Within the burnt area, three hill slopes were selected for this study for their contrasting forest types and parent materials (Figure 3.1). The BEG study site concerned an eucalypt plantation on granite, the BES site concerned an eucalypt plantation on schist and the BPS site a maritime pine site on schist.

The climate of the study area can be classified as humid meso-thermal with moderate but prolonged warm dry summers (Köppen; Csb, DRA-Centro, 2002). The mean annual temperature at the nearest climate station (Castelo-Burgães: 40°51′10″N, 8° 22′44″W at 306 m a.s.l.) was 14.9 °C (1991–2011; SNIRH, 2011), with average monthly temperatures ranging from 8.9 °C in January to 21 °C in July. Annual rainfall at the nearest rainfall station (Ribeiradio: 40°73′65″N, 8°30′08″W at 228 m a.s.l.) was, on average, 1655 mm, but varied markedly between dry (960 mm) and wet (2530 mm) years (1991–2011; SNIRH, 2011).

The study area is part of the Hesperic Massif, one of the region's major physiographic units. This unit is dominated by pre-Ordovician schists and greywackes but also includes Hercynian granites (Pereira and FitzPatrick, 1995). The granites exhibit evidences of granular disintegration, otherwise designated by arenisation, with accumulation of sand particles and gravel. The soils are mapped as Humic Cambisols (1:1000000; Cardoso et al., 1973), but according to a field survey carried out in the area, soils range from Humic Leptosols to Humic Cambisols at the BEG and BES sites; and from Lithic Leptosols to Humic Leptosols at the BPS site (IUSS, 2006). The topsoil (0–2 cm) at the study sites was rather coarse, with a loam to sandy-clay loam texture, and high (19–29%) organic matter content (Table 3.1).

3.2.2 *Experimental set-up, field data and sample collection*

Each of the study sites was divided into 2 strips running from the base to the top of the slope section. One of the strips was used for repeated collection of soil samples and the other for measuring overland flow at the micro-plot scale. Samples and plots at each site were treated as independent observations, although this can be questioned given the reduced distances between the samples/plots. This possible form of pseudo-replication is, however, typically difficult to avoid in wildfire studies (Hurlbert, 1984; Mantgem et al., 2001); in the case of the study area, due to the impossibility to find three or more slopes that were sufficiently similar in land cover, parent material, terrain characteristics (exposition, slope angle) and fire severity to be considered replicate sites. Worth stressing is that the samples/plots from each of the present study sites typically exhibited considerable variability, suggesting that they can indeed be considered independent observations.

Table 3.1 - General slope description. BEG – burnt eucalypt-granite site; BES – burnt eucalypt-schist site; and BPS – burnt pine-schist site.

Slope	**BEG**	**BES**	**BPS**
General characteristics			
Forest type	*Eucalyptus globulus*	*Eucalyptus globulus*	*Pinus pinaster*
Parent material	Granite	Schist	Schist
Geographical coordinates	40º43'56'' N	40º43'58'' N	40º43'54'' N
	8º21'3'' W	8º20'58'' W	8º20'47'' W
Elevation (*m.a.s.l.)*	220	220	150
Slope angle (º)	25.6 ± 4.4	24.0 ± 6.0	24.0 ± 2.4
Slope length (m)	77	48	36
Fire severity	moderate	moderate	moderate
Topsoil properties			
[0-2] cm depth			
Texture	Sandy loam	Loam	Sandy-clay loam
Sand fraction (%)	61.3	44.7	53.6
Silt fraction (%)	24.3	33.8	25.1
Clay fraction (%)	14.4	21.5	21.3
Organic matter (%)	29	22	19
[0-5] cm depth			
Bulk density ($g.cm^{-3}$)	0.71 ± 0.11	0.78 ± 0.19	0.73 ± 0.13

For this study, only samples of the topsoil (0-2 cm depth) were collected because moderate fires are widely known for affecting mainly the upper 2 cm of soil (Badía et al., 2014; Mataix-Solera et al., 2011; Zavala, 2014). Soil sampling was done on 2 occasions: first, on August 10 2010, roughly two weeks after the wildfire and before the occurrence of any rainfall; and then again, on February 16 2011, before terrace construction. At the first occasion, ash samples were collected along with soil samples. At both occasions ash and/or soil sampling was done at five equally-distant points along a transect that was laid out from the base to the top of the slope section. At each point of the transect ashes were collected over an area of 0.25 m^2 (0.5 m × 0.5 m) and topsoil (0-2 cm depth) over an area of 0.06 m^2 (0.25 m × 0.25 m). At the second sampling occasion, the transect was shifted approximately 1-2 m across the slope.

The study sites were instrumented with overland flow plots on August 25 2010, before the occurrence of post-fire rainfall. This involved the installation, at the base of the slope section, of three replicate bounded micro-plots of approximately 0.28 m^2, at distances of 1-2 m from each other. The main criteria for the location of the micro-plots were: i) the easy access, as it facilitates speedy data and sample collection, and ii) the minimization of slope disturbance, which was a concern because the slopes were located within an experimental catchment (Keizer et al., 2015). The outlets of the micro-plots were connected, using garden hose, to one or more high density polyethylene 30 to 70 L barrels to collect overland flow.

From August 2010 to February 2011, overland flow was measured at 1- to 2-weekly intervals, depending on the occurrence of rainfall. Whenever the overland flow in a barrel exceeded 250 mL, a sample was collected in a 500 mL polyethylene bottle that had been previously rinsed with HCl (pH < 2.0) and distilled and dionized water. The samples were then transported to the laboratory in cool boxes and stored at 4ºC for no longer than 24 h. The 1- to 2-weekly field trips also involved measurement of rainfall accumulated in 4 storage gauges (in-house design) that had been installed across the study area by the middle of August 2010. Their main purpose, however, was to validate the automatic recordings of two tipping-bucket rainfall gauges (Pronamic Professional Rain Gauge with 0.2 mm resolution) that had been installed in close proximity to two of the storage gauges.

3.2.3 *Laboratory analyses*

Upon arrival to the laboratory, the ash and soil samples were air dried and sieved manually with a 2 mm sieve. Total nitrogen content (TKN) in ashes and soils was determined using the Kjeldahl method (Bremner, 1979). Aside from nitrogen, soil samples were also analysed for: i) bulk density, using the core method as described by Porta et al. (2003); ii) soil particle size, following the international method of mechanical analysis as defined by Guitián and Carballas (1976); and iii) organic matter, determined by loss on ignition at 550ºC for 4 h, as described by Botelho da Costa (2004).

Overland flow samples were analysed for total nitrogen (i.e. dissolved plus particulate N forms) and nitrate (NO_3-N) using a flow injection FIAstarTM 5000 analyser (FOSS-Tecator). Prior to analysis, overland flow subsamples (50 mL) for determining NO_3-N concentrations were filtered with 0.45 µm Millipore© membrane filters. Subsamples (50 mL) for analysing TN were subjected to an oxidative digestion, using peroxodisulphate/alkali (Oxisolv®, Merck) and then filtered. Total suspended solids (TSS) in overland flow samples were quantified gravimetrically through filtration of 50 to 150 mL of water by a glass fibre filter, followed by drying to a constant weight at 105 ºC (APHA, 1998).

3.2.4 *Data analyses*

Differences in total Kjedahl nitrogen (TKN) ash and topsoil contents between sites with different forest type (BES vs. BPS) and parent material (BEG vs. BES) were evaluated by a a one-way ANOVA followed by a multi-comparison Tukey's test, if the assumptions of normality (checked by the Shapiro-Wilk test) and homogeneity of variance (checked by the Levene's test) were not rejected. If one or both of them were rejected, logarithmic transformations of the data were performed to comply with the assumptions of the ANOVA (Zar, 1999).

Regarding NO_3-N and TN exports in overland flow and their respective concentrations, a one-way ANOVA followed by a Tukey's test was performed to test differences between sites with contrasting vegetation (BES vs. BPS) and parent material (BEG vs. BES), after checking for data normality and homogeneity of variance. Whenever one or both of the ANOVA assumptions were not met, logarithmically transformed data was used in the analysis (Zar, 1999). Between-site differences in overland flow and sediment losses were also evaluated by a one-way ANOVA followed by a Tukey's test.

The influence of environmental variables (rainfall amount and intensity, overland flow and sediment losses) on nitrogen losses by overland flow was assessed by the Pearson's correlation coefficient. In the case of the variables that had not met the normality assumption by the above-mentioned Shapiro-Wilk test, the coefficients were computed for the transformed data.

All statistical analyses were performed with SigmaPlot 11.0 package software, using a significance level of 0.05.

3.3 *Results*

3.3.1 *Ash and topsoil nitrogen contents*

The average total Kjeldahl nitrogen (TKN) content in ash and topsoil layers at the three study sites are shown in Table 3.2. No significant differences were observed between the ashes collected at sites with contrasting forest type or parent material (ANOVA: F = 0.847, p = 0.455). At all the study sites, TKN contents immediately after the wildfire (August 2010) were on average roughly twice as high in the ashes than in the topsoil (Table 3.2).

The comparison of topsoil nitrogen contents in August 2010 did not reveal significant differences (ANOVA: F = 0.325, p = 0.729) between the two types of tree plantations (BES vs. BPS) on schist (Table 3.2). Topsoil TKN contents did not differ significantly between the two types of parent material (BEG vs. BES) either (ANOVA: F = 0.325, p = 0.729). From August 2010 to February 2011, a significant decrease (58 to 75%) in soil TKN contents was observed at all three study sites (Table 3.2). However, six months after the fire (Table 2), there were also no significant differences between sites with distinct types of vegetation and parent material (ANOVA: F = 0.801, p = 0.476).

Table 3.2 - Average (± standard deviation; n = 5) total Kjeldahl nitrogen (TKN) concentrations/stocks in the ash and topsoil layers of the three study sites, immediately (August 2010) and sixth months after fire (February 2011). BEG — burnt eucalypt-granite site; BES — burnt eucalypt-schist site; and BPS — burnt pine-schist site.

	Sampling date	Layer	**BEG**	**BES**	**BPS**
TKN concentrations	Aug 2010	Ash	1.92 ± 0.29	1.72 ± 0.63	1.58 ± 0.32
(mg g^{-1})		Soil	0.91 ± 0.15	0.81 ± 0.36	0.78 ± 0.26
	Feb 2011	Soil	0.23 ± 0.15	0.26 ± 0.19	0.32 ± 0.04
TKN stocks	Aug 2010	Soil	12.9 ± 2.2	12.7 ± 5.6	11.4 ± 3.8
(g m^{-2})	Feb 2011	Soil	3.2 ± 2.1	4.1 ± 3.0	5.0 ± 1.0

3.3.2 *Nitrogen exports by overland flow*

The average exports of nitrate (NO_3-N) and total nitrogen (TN) in the first 6 months after fire are presented in Figure 3.2. At all the study sites, peaks of NO_3-N and TN exports were generally associated to major runoff events. Nitrate exports, however, represented only a small fraction (1 to 6%) of TN exports. The comparison of NO_3-N (ANOVA: F = 6.732, p = 0.003; Tukey's test: p = 0.004) and TN exports (ANOVA: F = 4.346, p = 0.019; Tukey's test: p = 0.016) between sites with contrasting types of vegetation revealed significant differences between the eucalypt and the pine site on schist (Figure 3.2).

Global TN losses over the entire study period (Table 3.3) were almost four times as high at the BES site (1.32 g m-2) than at the BPS site (0.35 g m-2). For NO3-N, differences between the two sites were even more pronounced, being about 10 times higher at the BES site (0.04 g m-2) than at the BPS site (0.004 g m-2). Parent material, on the other hand, did not play an important role in post-fire nitrogen exports (Figure 3.2 since no significant differences were found for either NO3-N losses (ANOVA: F = 6.732, p = 0.003; Tukey's test: p = 0.834) or TN losses (ANOVA: F = 4.346, p = 0.019; Tukey's test: p = 0.130) at the BEG and BES sites. In terms of global exports, however, TN losses were more than two times higher at the BES site (1.32 g m-2) than at the BEG site (0.62 mg m-2), whereas NO3-N exports were very similar at the two sites (BEG = 0.03 g m-2; BES = 0.04 g m-2).

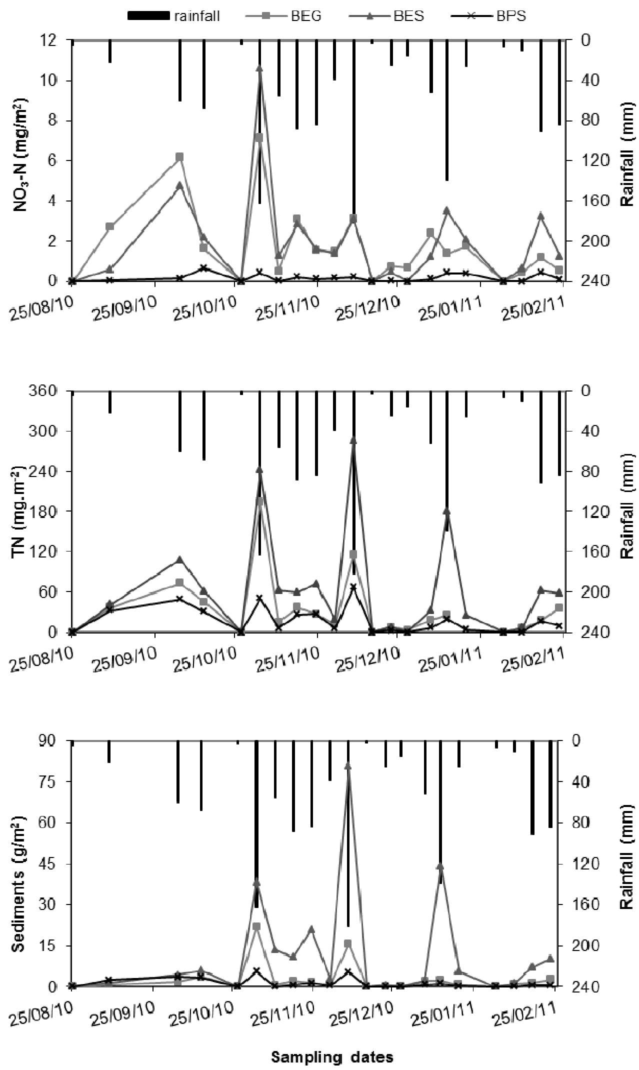

Figure 3.2 - Average overland flow amounts, and nitrate (NO_3-N) and total nitrogen (TN) losses by overland flow within the first 6 months after fire. BEG – eucalypt-granite site; BES – eucalypt-schist site and BPS – pine-schist site.

Table 3.3 - Average (± standard deviation) of total nitrogen losses (NO_3-N and TN), overland flow, runoff coefficients and sediment losses at the three study sites for the first 6 months following fire (no. of plots per site = 3; no. of read-outs per plot = 21). Different letters within rows correspond to significant differences ($p < 0.05$) among slopes with different types of parent material (BEG *vs.* BES). Different symbols within rows correspond to significant differences ($p < 0.05$) among slopes with different types of vegetation (BES *vs.* BPS). BEG – eucalypt-granite site; BES – eucalypt-schist site and BPS – pine-schist site.

Variables	**BEG**	**BES**	**BPS**
***Nitrogen export* (g m^{-2})**			
NO_3-N	0.03 ± 0.02^{a}	0.04 ± 0.01^{a,*}	0.004 ± 0.002^{+}
TN	0.62 ± 0.37^{a}	1.32 ± 0.30^{a,*}	0.35 ± 0.09^{+}
Environmental variables			
Overland flow (mm)º	320 ± 245^{a}	419 ± 14^{a,*}	298 ± 105*
Runoff coefficient (%)	26 ± 20^{a}	34 ± 1^{a,*}	25 ± 9*
Sediment losses (g m^{-2})	54 ± 45^{a}	249 ± 113^{b,*}	26 ± 13^{+}

º Total rainfall associated = 1218 mm

3.3.3 *Environmental variables and post-fire nitrogen export*

From the Pearson correlation coefficients presented in Table 4, TN export at the three study sites was strongly associated to the amount ($r \geq 0.66$) and intensity of rainfall ($r \geq 0.76$) as well as to overland flow amount ($r \geq 0.72$) and sediment losses ($r \geq 0.82$). As regards to nitrate, the environmental variables governing the export of this inorganic nitrogen form differed with pre-fire vegetation (Table 3.4).

At the BES site, NO_3-N losses were highly correlated with hydrological variables (rainfall amount, rainfall intensity, and overland flow), whereas at the BPS site no significant correlations were found between NO_3-N exports and the environmental variables investigated in the present study. Comparing the two sites with contrasting parent materials, differences were also observed between environmental variables controlling NO_3-N exports at the granite and schist sites. At the BEG site NO_3-N exports were highly correlated with both hydrological variables and sediment losses, whereas at the BES site they were mostly dependent on hydrological variables (Table 3.4).

Table 3.4 - Pearson's correlations between environmental variables (i.e. rainfall amount, maximum rainfall intensity during 30 min – I_{30}, overland flow and suspended sediments) and nitrogen losses by overland flow (averages per read out). Significant values ($p \leq 0.05$) are presented in bold.

Slope	N form	**Rainfall** (mm)	**I_{30}** ($mm\ h^{-1}$)	**Overland flow** (mm)	**Sediments** ($g\ m^{-2}$)
BEG	**TN**	**0.73**	**0.83**	**0.94**	**0.95**
	NO_3-N	0.47	**0.73**	**0.75**	**0.67**
BES	**TN**	**0.93**	**0.87**	**0.91**	**0.93**
	NO_3-N	**0.67**	**0.80**	**0.87**	0.43
BPS	**TN**	**0.66**	**0.76**	**0.73**	**0.82**
	NO_3-N	0.38	0.49	0.42	0.32

3.3.4 *Nitrogen concentrations in overland flow*

The variation patterns of nitrate (NO_3-N) and total nitrogen (TN) concentrations in overland flow within the first 6 months after fire are presented in Figure 3.3.

At the eucalypt sites (BEG and BES) a major peak in NO_3-N concentrations was observed for the first post-fire rainfall event (Figure 3.2 and Figure 3.3), whereas a clear peak in NO_3-N concentrations was lacking at the pine site (BPS). For the subsequent study period, all slopes revealed complex patterns in NO3-N concentrations, which appeared to be largely independent from rainfall amounts as well as from overland flow and sediment losses at each site (Figure 3.2 and Figure 3.3).

As regards to TN, a major peak was also observed for the first post-fire rainfall event but this peak has occurred at all three study sites, unlike was the case for NO_3-N (Figure 3.2 and Figure 3.3). After this initial peak, smaller peaks in TN levels were observed throughout the study period, mainly in association with peaks in overland flow or sediment losses (Figure 3.2 and Figure 3.3).

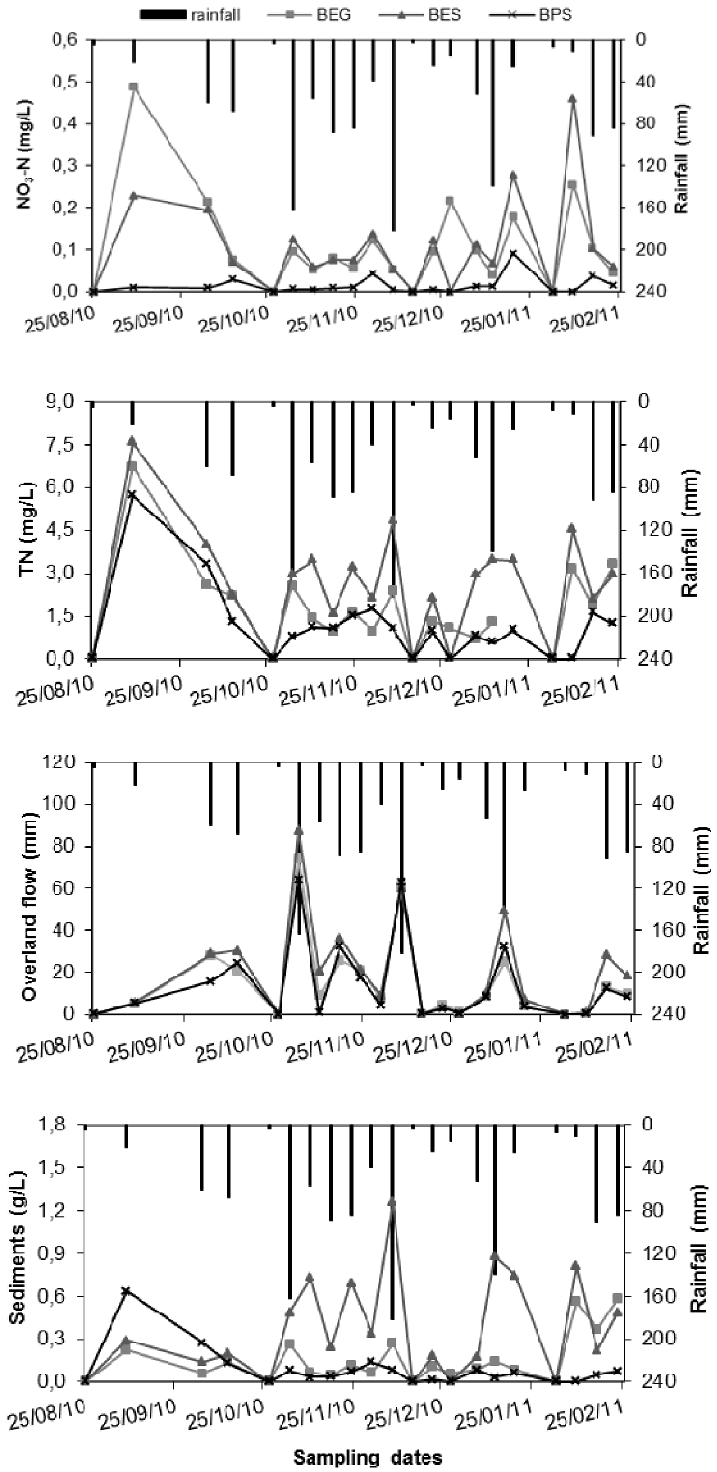

Figure 3.3 - Average sediment losses, and nitrate (NO_3-N) and total nitrogen (TN) concentrations in overland flow within the first 6 months after fire. BEG – eucalypt-granite site; BES – eucalypt-schist site and BPS – pine-schist site.

3.4 *Discussion*

3.4.1 *Nitrogen contents in ash and topsoil*

In the present study, the ashes collected at sites with contrasting types of vegetation (BES vs. BPS) did not present significantly different TKN contents (Table 3.2). As fire severity was similar at the two study sites, these results most likely reflected the pre-fire N contents in aboveground vegetation and litter layer, which were found to have similar N levels in unburnt eucalypt (Ribeiro et al., 2002) and maritime pine stands (Nunes et al., 2010) in the study region. Sites with contrasting parent materials also presented similar TKN ash contents, which agree with the fact that forest stands in the study region commonly have similar topsoil nitrogen contents on unburnt granite and schist soils, independently from the type of tree plantation (Magalhães et al., 2011). For all the burnt sites, TKN ash contents immediately after the wildfire were, on average, higher than topsoil contents. The reason behind these findings is probably related to the natural composition of plant biomass and litter layers, as they are typically richer in N than soils (Nunes et al., 2010; Ribeiro et al., 2002).

The comparison of topsoil TKN contents, immediately after the wildfire, revealed no significant differences between the two types of tree plantations on schist, in agreement with the results for the ash layer (Table 3.2). These results could be related to similar N contents in belowground biomass and topsoil organic matter in unburnt eucalypt (Ribeiro et al., 2002) and pine sites (Nunes et al., 2010). This hypothesis is also supported by the similar organic matter contents in BES (22%) and BPS (19%) soils, immediately after fire (Table 3.1). Topsoil TKN contents did not differ between the two types of parent material either, in accordance to what was found by other authors for unburnt forest areas in central Portugal (Magalhães et al., 2011). An explanation for these findings would also be the existence of comparable organic matter contents in granite (29%) and schist (22%) soils (Table 3.1).

From August 2010 to February 2011, a decrease in soil TKN contents was observed at all three burnt sites. This could have involved two mechanisms, i.e. N leaching into deeper soil layers as well as N losses by runoff and soil erosion (Bodí et al., 2014; Caon et al., 2014; Cerdà and Doerr, 2008; Certini, 2005; Khanna et al., 1994; Knoepp et al., 2005; Pausas et al., 2008; Shakesby, 2011; Thomas et al., 1999). Six months after the fire, no significant differences in TKN contents were found among sites with distinct forest (BES vs. BPS) or with different parent materials (BEG vs. BES), in line with what was found immediately after the fire.

3.4.2 *Nitrogen exports by overland flow*

Despite the similar ash and topsoil N contents in eucalypt and pine sites, NO_3-N and TN losses were consistently higher at the eucalypt site on schist than at the pine site on schist (Table 3.2 and Table 3.3). The stronger soil water repellency in eucalypt than in pine stands, as has been observed in the study region both before and after wildfires (Doerr et al., 1998; Keizer et al., 2005a, b; Santos et al., 2013), combined with a somewhat slower recovery of litter and ground vegetation under burnt eucalypt stands (Doerr et al., 1998) were likely to have promoted overland flow and the associated sediment and N losses at the BES site. On the other hand, the existence of a needle cover at the pine site, resulting from needle cast from the partially combusted pine crowns, might have reduced overland flow and the associated sediment and nutrient transport (Knoepp et al., 2005; Kutiel and Shaviv, 1992) by increasing surface storage and resistance against flow and, at the same time, decreasing splash erosion (Martins et al., 2013; Prats et al., 2012, 2013; Shakesby et al., 1996; Thomas et al., 2000a, b). Other studies in the study region have also found needle cast following low and moderate severity fires to be highly effective in reducing runoff and especially erosion (Martins et al., 2013; Prats et al., 2012, 2013; Shakesby et al., 1996; Thomas et al., 2000a, b). In the case of soluble N forms, like NO_3-N, the existence of a needle cover was particularly relevant in preventing losses by overland flow, since NO_3-N exports were not significantly related to any of the hydrological variables at the BPS site as opposed to the BES site (Table 3.4).

TN exports, on the other hand, were apparently less affected by the needle cover, since a strong relationship was found between TN losses and hydrological/erosion variables at both the BPS and BES site. As post-fire TN transport results mainly from an increase in the export of particulate N forms (Soto et al., 1997), one might conclude that the existence of a needle cover was particularly important for the protection of the easily-erodible solute-enriched ash layer, as reported by other authors for the nearby Caramulo Mountains (Ferreira et al., 2005; Shakesby, 2011; Thomas et al., 1999). The fact that a peak in NO_3-N concentrations was observed in both eucalypt sites immediately after the first significant post-fire rainfall event but not at the pine site seems to corroborate this idea (Figure 3.2 and Figure 3.3). Overall, the needle cover was effective in reducing soil fertility losses since TN exports represented only 6% of topsoil N stocks at the BPS site as opposed to 15 % at the BES site.

Parent material did not have a significant effect on N losses by overland flow. Even so, global TN exports were higher at the BES site than at the BEG site (Table 3.3). From the Pearson's correlations presented in Table 3.4, the hydrological/erosion variables governing

TN export were the same at the BES and BEG slopes. Therefore, one might hypothesize that the differences between these two sites were most likely related with the coarser texture of the granite soils (Table 3.1), which was also reported by Wahren et al. (2016) for the study region. A coarser texture can be expected to increase water infiltration and reduce runoff, particularly at the micro-plot scale (Boix-Fayos et al., 2006; Shakesby, 2011). This seems to be supported by the work of Wahren et al. (2016) since lower annual runoff coefficients were reported for Hydrological Response Units (HRU's) with shallow soils derived from granite than from schist. As a result, lower amounts of overland flow and lesser sediment losses were generated at the BEG site, ultimately leading to lower TN exports. The fact that the TN losses represented twice as much of the topsoil N stock at the BES site (15 %) than at the BEG site (7%) also seems to support the idea that erosion by water was the main factor explaining the differences between granite and schist soils (Table 3.2 and Table 3.3).

In the case of NO_3-N, on the other hand, differences in global exports were minimal between granite and schist soils (Table 3.3). As larger amounts of overland flow were generated at the BES than BEG site, and as overland flow had a strong influence on NO3-N export at both sites (Table 3.4), one might hypothesize that the lower topsoil organic matter content at the BES site (Table 3.1) influenced the availability of inorganic N forms in soils, by limiting mineralization processes (Caon et al., 2014; Thomas et al., 2000b).

3.4.3 *Nitrogen concentrations in overland flow*

Nitrogen concentrations in overland flow exhibited a very distinct variation pattern than N losses (Figure 3.2 and Figure 3.3). Unlike N exports, peaks in N concentrations were not clearly associated with the major runoff events (Figs. 2 and 3). In fact, almost all plots exhibited a marked peak in NO_3-N and TN concentrations during the first significant post-fire rainfall event. These peaks probably reflected the detachment and transport of the N enriched, easily erodible ash layer and of the partially combusted organic material on the ground surface, as also suggested by previous studies in the region (Ferreira et al., 2005, 2008; Thomas et al., 1999). No such peak, however, was found for NO_3-N concentrations at the BPS site but this could be explained by the post-fire needle cast providing a protective cover to the solute-enriched ash layer (Ferreira et al., 2005; Shakesby, 2011; Thomas et al., 1999).

As the ash layer became exhausted and erosion started to affect the topsoil, peaks in TN concentrations were mainly associated with major rainfall events, as a result of peaks in overland flow and associated sediment losses (Figure 3.2 and Figure 3.3). In contrast, peaks in NO_3-N concentrations were often unrelated to rainfall events, possibly because nitrification processes are largely dependent on microbial activity (Badía, 2000; Caon et al., 2014; Murphy et al., 2006).

3.5 *Conclusions*

The present study focused on post-fire nitrogen mobilization by overland flow at the micro-plot scale. The fact that this work was carried out in the Mediterranean region is important for anticipating the impacts of recurrent fires on soil productivity because fire frequency is expected to increase in the future as a result of climate changes.

The main findings of the present work were that:

i) the existence of a protective litter layer (i.e. of scorched pine needles) at the burnt pine site considerably reduced post-fire N export compared to the burnt eucalypt site, mainly by decreasing overland flow generation and the associated sediment losses. This information can be considered relevant for post-fire land management since it emphasizes that spontaneous mulching can be highly effective to reduce soil (fertility) losses and, thereby, will make further soil conservation measures superfluous.

ii) overland flow and soil (fertility) losses were markedly lower at the eucalypt site on granite than at that at the eucalypt site on schist, probably due to the coarser texture and, thus, higher infiltration capacity of the granite soils. This parent material-related difference in post-fire erosion risk is important for defining priorities in post-fire land management and, in particular, for the application of soil conservation measures such as mulching.

The results of this study must nonetheless be interpreted with some caution because micro-plots may not fully represent post-fire hydrological and erosive processes at the field scale, which is the key management unit in north-central Portugal due to the reduced size of land properties.

Furthermore, the lack of data from pre-fire or unburnt sites prevents the assessment of fire effects on N losses by overland flow, so this work only provides estimates of the range of N exports in a fire-prone landscape.

Even so, the present findings are viewed as an important contribution to the current knowledge of post-fire nutrient mobilization and redistribution and of the resulting soil degradation in the Mediterranean Basin, especially since such information continues to be scarce for this region and since Mediterranean soils are typically nutrient poor.

Future studies are, however, recommended to address broader spatial scales as well as wider time scales to fully understand post-fire nutrient dynamics.

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Chapter 4 - Short-time phosphorus losses by overland flow in burnt pine and eucalypt plantations in north-central Portugal: A study at micro-plot scale

R.V. Ferreira[a], D. Serpa[a], M.A. Cerqueira[a], J.J. Keizer[a]

[a]University of Aveiro and CESAM

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Abstract

Over the past decades, wildfires have affected vast areas of Mediterranean ecosystems leading to a variety of negative on- and off-site environmental impacts. Research on fire-affected areas has given more attention to sediment losses by fire-enhanced overland flow than to nutrient exports, especially in the Mediterranean region. To address this knowledge gap for post-fire losses of phosphorus (P) by overland flow, a recently burnt forest area in north-central Portugal was selected and instrumented immediately after a wildfire. Three slopes were selected for their contrasting forest types (eucalypt vs. pine) and parent materials (granite vs. schist). The selected study sites were a eucalypt site on granite (BEG), a eucalypt site on schist (BES) and a maritime pine site on schist (BPS). Micro-plots were monitored over a period of six months, i.e. till the construction of terraces for reforestation obliged to the removal of the plots. During this 6-month period, overland flow samples were collected at 1- to 2-weekly intervals, depending on rainfall. Total P and PO_4-P losses differed markedly between the two types of forests on schist, being lower at the pine site than at the eucalypt site, probably due to the presence of a protective layer of pine needle cast. Parent material did not play an important role in PO_4-P losses by overland flow but it did in TP losses, with significantly lower values at the eucalypt site on granite than that on schist. These differences in TP losses can be attributed to the coarser texture of granite soils, typically promoting infiltration and decreasing runoff. The present findings provided further insights into the spatial and temporal patterns of post-fire soil fertility losses in fire-prone forest types during the initial stages of the window-of-disturbance, which can be useful for defining post-fire emergency measures to reduce the risk of soil fertility losses.

Keywords

Wildfire, Micro-Plot Scale, Overland Flow, Phosphorus Export, Forest type, Parent material

4.1 *Introduction*

Wildfires are a widespread phenomenon, acting as a major driver of ecosystem change all over the world (Caon et al., 2014; Coombs and Melack, 2013; Doerr and Cerdà, 2005; Kugbe et al., 2014; Lane et al., 2008; Pereira et al., 2014a; Tsibart et al., 2014; Wang et al., 2015).

In the Mediterranean region, wildfires have affected increasingly large areas of land throughout the past decades (Pausas et al., 2008). This trend is expected to continue, especially since projections of future climate change foresee rising temperatures and increasing risks of drought spells in this fire-prone region (Anaya-Romero et al., 2015; Blake et al., 2010; Caon et al., 2014). While wildfires are a natural disturbance in many ecosystems, more frequent fires and more severe fires can offset the ecological balance of the ecosystems and have a significant negative impact on soil fertility, soil biological diversity as well as on the water cycle (Caon et al., 2014; Crouch et al., 2006; Malvar et al., 2015a).

Soil fertility is particularly affected by recurrent wildfires because the heating-induced changes in soil physical, chemical and biological properties deeply affect the biogeochemical cycles of carbon, nitrogen and phosphorus (Caon et al., 2014; Certini, 2005; Knoepp et al., 2005; Shakesby, 2011).

In the case of phosphorus, the combustion of vegetation as well as of litter by fire frequently produces a layer of P-enriched ash and charcoal that can be easily lost by leaching into the soil and/or lost by wind or water erosion (Bodí et al., 2011, 2014; Johnson et al., 2007; Pereira et al., 2014a, 2014b). Also the P pool of the topsoil itself can be markedly affected by fire since heating promotes the mineralization of topsoil organic matter and, thereby, the release of inorganic P (Badía et al., 2014; Certini, 2005; Kutiel and Shaviv, 1992). The fate of inorganic P following fire depends strongly on pre- and post-fire soil properties (Certini, 2005; Murphy et al., 2006). In acidic soils, inorganic P tends to adsorb to newly formed Al, Fe and Mn oxides and hydroxides (Certini, 2005; Murphy et al., 2006; Otero et al., 2015), whereas in neutral or alkaline soils it especially binds to Ca-minerals or precipitates as Ca phosphate (Badía et al., 2014; Certini, 2005; Murphy et al., 2006). Nonetheless, P sorption/desorption processes are highly dynamic (Otero et al., 2015), so even small changes in soil pH as often observed after fire can easily cause desorption of inorganic P from metal oxides or calcium compounds formed immediately after fire (Kutiel and Shaviv, 1992;

Murphy et al., 2006). As the topsoil P reservoir is depleted by fire-enhanced overland flow and erosion (Caon et al., 2014; Certini, 2005; Ferreira et al., 2005; Pausas et al., 2008; Shakesby, 2011; Thomas et al., 1999, 2000a, 2000b), and P is exported in both its dissolved and particulate forms, there can be a loss of soil fertility (Caon et al., 2014; Johnson et al., 2007; Knoepp et al., 2005; Neary et al., 1999; Soto et al., 1997).

In the Mediterranean Basin, the effects of fire on soil P availability have been addressed by various studies (Badía et al., 2014; Caon et al., 2014; Johnson et al., 2007; Kutiel and Shaviv, 1992; Otero et al., 2015). Post-fire losses of P by overland flow, however, have been poorly investigated (Cancelo-González et al., 2013; DeBano et al., 1998; Díaz-Fierros et al., 1990; Lasanta and Cerdà, 2005). In Portugal, particularly few studies have measured post-fire P export by overland flow (Coelho et al., 2004; Ferreira et al., 1997, 2005; Thomas et al., 1999, 2000a, 2000b; Walsh et al., 1992), especially considering the more than 100.000 ha that are burnt each year. These prior studies investigated P losses for the two principal forest types in north-central Portugal, i.e. plantations of eucalypt (Eucalyptus globulus Labill.) and maritime pine (Pinus pinaster Ait.) but at larger spatial scales than in the present work, i.e. 16 m2 plots (Ferreira et al., 1997, 2005; Thomas et al., 2000a, 2000b; Walsh et al., 1992), small (Ferreira et al., 1997, 2005) and large catchments (Santos et al., 2015a, 2015b). Perhaps more importantly, these prior studies only addressed soluble P losses and not total P losses (i.e. solute + particulate fraction). Hence, a better understanding of overall losses of nutrients after fire, in both dissolved and particulate forms, is required for a more accurate assessment of the risks of post-fire soil fertility losses and its possible impacts on forest recovery.

The present study aims to address this knowledge gap by determining the exports of total phosphorus (TP) and dissolved inorganic phosphorus (PO_4-P) by post-fire overland flow in a recently burnt forest area in the Mediterranean. The current work, however, does not quantify the effects of fire on P losses since comparable but long unburnt could not be found in the vicinity of the study sites. Instead it intends to compare these losses for different combinations of forest type and parent material. To this end, TP and PO4-P losses by overland flow were quantified at the micro-plot scale for: i) two contrasting forest types, i.e. eucalypt and maritime pine plantations, which dominate the north-central Portuguese mountains and are both fire-prone; and ii) two contrasting bedrock types, i.e. schist and granite, which are the prevailing parent materials in north-central Portugal. Phosphorus losses by overland flow were further compared with their stock in the ash and upper soil layer, for a better appreciation of the relevance of these losses for the P cycle following fire.

As all three study sites were (partially) terraced with a bulldozer 6 months after the fire, completely changing the topography of the terrain (Martins et al., 2013), the present work was forcedly limited to the immediate post-fire period.

4.2 *Materials and Methods*

4.2.1 *Study area and sites*

The study area was located within the Vouga River Basin, near the Ermida village in the Sever do Vouga municipality, north-central Portugal (Figure 4.1). Between July 26 and July 28 2010 a wildfire consumed a total of 295 ha of forest in this area (DUDF, 2011). Before the fire, the Ermida study area was covered predominantly by commercial eucalypt plantations (*Eucalyptus globulus* Labil.) but also included some maritime pine stands (*Pinus pinaster* Ait.). Fire severity was classified as moderate, because ashes were predominantly black, the litter layer and understory vegetation were almost completely consumed by the fire and tree crowns were only partially combusted (Table 4.1; Shakesby and Doerr, 2006).

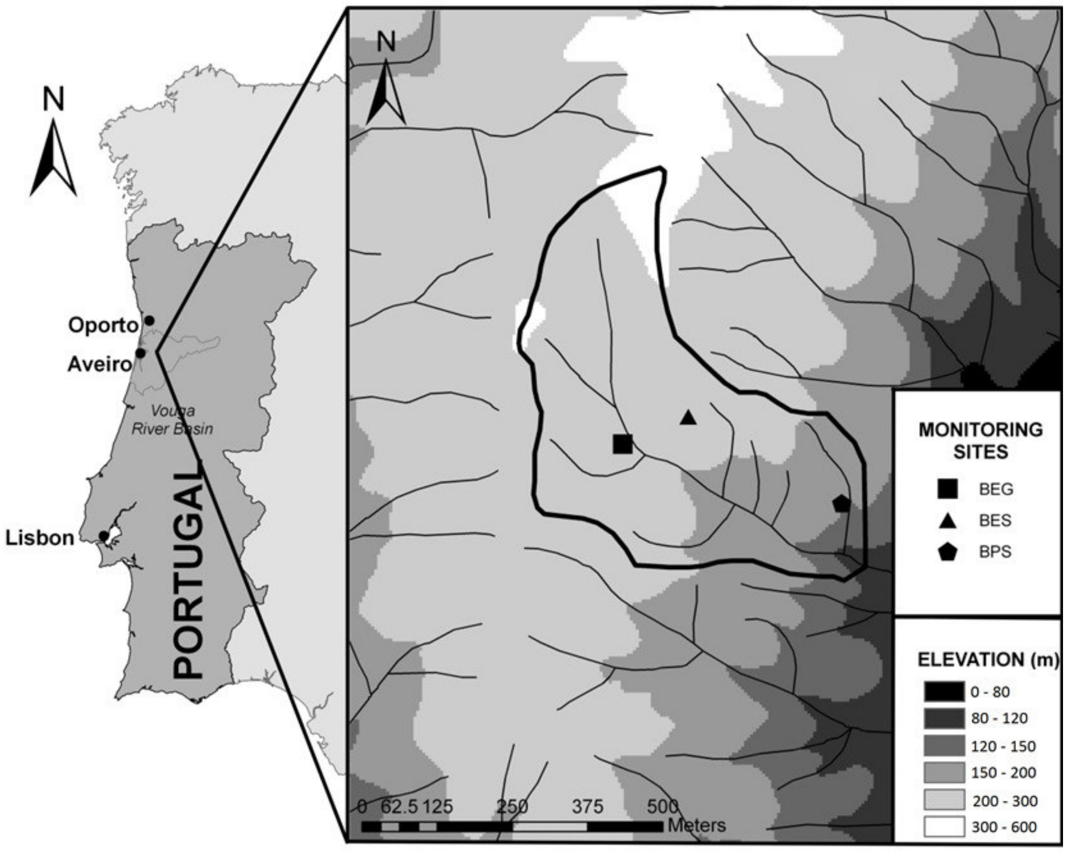

Figure 4.1 - Location of the Ermida study area within the Vouga River basin, north-central Portugal. Location of the study sites: BEG — burnt eucalypt-granite site, BES — burnt eucalypt schist site, and BPS — burnt pine-schist site. The bold line represents the Ermida catchment.

Table 4.1 - General slope description. BEG – burnt eucalypt-granite site; BES – burnt eucalypt-schist site; and BPS – burnt pine-schist site.

Slope	**BEG**	**BES**	**BPS**
General characteristics			
Forest type	*Eucalyptus globulus*	*Eucalyptus globulus*	*Pinus pinaster*
Parent material	Granite	Schist	Schist
Geographical coordinates	40º43'56'' N	40º43'58'' N	40º43'54'' N
	8º21'3'' W	8º20'58'' W	8º20'47'' W
Elevation (*m a.s.l.)*	220	220	150
Slope angle (º)	25.6 ± 4.4	24.0 ± 6.0	24.0 ± 2.4
Slope length (m)	77	48	36
Fire severity	moderate	moderate	moderate
Topsoil properties			
[0-2] cm depth			
Texture	Sandy loam	Loam	Sandy-clay loam
Sand fraction (%)	61.3	44.7	53.6
Silt fraction (%)	24.3	33.8	25.1
Clay fraction (%)	14.4	21.5	21.3
Organic matter (%)	29	22	19
[0-5] cm depth			
Bulk density ($g.cm^{-3}$)	0.71 ± 0.11	0.78 ± 0.19	0.73 ± 0.13

In addition, Maximum Temperatures Reached based on Near Infrared (NIR) spectroscopy measurements (see Guerrero et al., 2007; Maia et al., 2012) varied from 325 to 405ºC for the uppermost 2 cm (Pedrosa, 2012).

The climate of the study area can be classified as humid meso-thermal with moderate but prolonged warm dry summers (Köppen; Csb, DRA-Centro, 2002). The mean annual temperature at the nearest climate station (Castelo-Burgães: 40°51′10″N, 8° 22′44″W at 306 m a.s.l.; 15 km north of the study area) was 14.9 °C (1991–2011; SNIRH, 2011), with average monthly temperatures ranging from 8.9 °C in January to 21 °C in July. Annual rainfall at the nearest rainfall station (Ribeiradio: 40°44′12″N, 8°18′03″W at 228 m a.s.l.; 5 km east of the study area) was, on average, 1655 mm, but varied markedly between dry (960 mm) and wet (2530 mm) years (1991–2011; SNIRH, 2011).

The study area is part of the Hesperic Massif, a physiographic unit that is dominated by pre-Ordovician schists and greywackes but locally includes Hercynian granites (Pereira and FitzPatrick, 1995). The soils are mapped as Humic Cambisols (1:1000000; Cardoso et al., 1973), but according to a field survey carried out on January 2011, soils ranged from Humic Leptosols to Humic Cambisols at the eucalypt sites, and from Lithic Leptosols to Humic Leptosols at the pine site (IUSS, 2006). The topsoil (0-2 cm) at the study sites was rather coarse, with a loam to sandy-clay loam texture, and high (19–29%) organic matter content (Table 4.1).

4.2.2 *Experimental set-up, field data and sample collection*

Within the burnt area, three hill slopes were selected for their contrasting forest types and parent materials, *i.e.* Burnt Eucalypt on Granite (BEG) *vs.* Burnt Eucalypt Schist (BES) *vs.* Burnt Pine on Schist (BPS) (Table 4.1).

At each site, a baseline experimental design was implemented which comprised dividing it into two strips running from the base to the top of the slope section. One of these strips was used for repeated collection of soil samples and another for monitoring overland flow at the micro-plot scale. A necessary limitation of this work was that samples and plots within each slope were treated as replicates. Although this can be considered as a form of pseudo-replication, this is typically difficult to avoid in wildfire studies (Hurlbert, 1984; van Mantgem et al., 2001), due to the impossibility to find three or more slopes that are similar enough (in terms of land cover, parent material, terrain characteristics and fire severity) to be considered replicate sites.

Soil sampling was limited to the topsoil (0-2 cm depth) since moderate fires are widely known for affecting mainly the upper 2 cm of soil (Badía et al., 2014; Zavala et al., 2014). Sampling was performed on 2 occasions: on August 10 2010, approximately two weeks after the wildfire and before any post-fire rainfall occurrence; and on February 16 2011, immediately before the start of the bench terracing. At the first occasion, ash samples were collected along with soil samples. At both occasions ash and/or soil sampling was done at five equally-distant points along a transect that was laid out from the base to the top of the slope section. At each point of the transect ashes were collected over an area of 0.25 m^2 (0.5 m × 0.5 m) and topsoil (0-2 cm depth) over an area of 0.06 m^2 (0.25 m × 0.25 m).

The study sites were instrumented with overland flow plots on August 25 2010, before the occurrence of any post-fire rainfall. This involved the installation, at the base of the slope section, of three bounded micro-plots of approximately 0.28 m^2, at distances of 1-2 m from each other. The outlets of the micro-plots were connected to high density polyethylene barrels to collect overland flow. The placement of the micro-plots at the bottom of the slope section was done to facilitate access and, thus, field measurements and runoff sample collection as well as to minimize disturbance which was a concern since the sites were located within an experimental catchment (Keizer et al., 2015). From August 2010 to February 2011, overland flow was measured at 1- to 2-weekly intervals, depending on the occurrence of rainfall. Whenever the overland flow in a barrel exceeded 250 mL, a sample was collected in a 500 mL polyethylene bottle that had been previously rinsed with hydrochloric acid (pH < 2.0), and distilled and deionized water. The samples were then transported to the laboratory in cool boxes and stored at 4ºC for no longer than 24 h before laboratory analysis.

4.2.3 *Laboratory analyses*

Upon arrival to the laboratory, the ash and soil samples were air dried and then sieved manually with a 2 mm sieve. Available phosphorus (P_{av}) content in ash and soils was determined by the Bray method (Bray and Kurtz, 1945), using a mixture of ammonium fluoride (0.03 M) and hydrochloric acid (0.025 M) as extractant. The extracted P was analyzed spectrophotometrically as orthophosphate by the molybdenum blue method (APHA, 1998). Soil samples were also analysed for: i) soil particle size, following the international method of mechanical analysis as defined by Guitián and Carballas (1976); and ii) organic matter content, which was determined by loss on ignition at 550ºC for 4 h, as described by Botelho da Costa (2004). In addition, bulk density of the upper 5 cm of soil was determined using the core method, as described by Porta et al. (2003).

Overland flow samples were analysed for total phosphorus (i.e. dissolved plus particulate P forms) and dissolved inorganic phosphorus, i.e. orthophosphate (PO_4-P). This was done using a flow injection FIAstarTM 5000 analyser (FOSS – Tecator). Prior to analysis, 50 mL subsamples for determining PO_4-P concentrations were filtered with 0.45 μm Millipore© membrane filters. Subsamples (50 mL) for analysing TP, on the other hand, were first subjected to an oxidative digestion, using peroxodisulphate/alkali (Oxisolv®, Merck), and then filtered. The concentration of total suspended solids (TSS) of the overland flow samples was quantified gravimetrically through filtration of 50-150 mL of runoff by a glass fibre filter, followed by drying to a constant weight at 105 ºC (APHA, 1998).

4.2.4 *Data analysis*

Available phosphorus (P_{av}) contents of ash and topsoil samples were compared for the sites with contrasting forest types (BES vs. BPS) and for the sites with contrasting parent materials (BEG vs. BES) by means of a one-way ANOVA followed by a multi-comparison Tukey's test. The underlying assumptions of normality (Shapiro-Wilk test) and homogeneity of variance (Levene's test) were explicitly tested and, if one or both were rejected, data were logarithmically transformed prior to the analysis (Zar, 1999).

Phosphorus exports by overland flow were also analysed by a one-way ANOVA followed by a Tukey's test, and the same was true for overland flow amounts as well as for sediment losses. The influence of environmental variables (rainfall amount and intensity, overland flow and sediment losses) on P losses by overland flow was assessed by the Pearson's correlation coefficient (Zar, 1999). In the case of the variables that had not met the normality assumption, these coefficients were computed for logarithmically transformed data.

All statistical analyses were performed with SigmaPlot 11.0 package software, while testing was done at a significance level of 0.05.

4.3 *Results*

4.3.1 *Phosphorus contents in ash and topsoil*

The average contents of P_{av} in the ash and topsoil layers of the three study sites are shown in Table 4.2. No significant differences (ANOVA: $F = 0.531$, $p = 0.594$) were observed between the ashes collected at sites with contrasting forest types (BES *vs.* BPS) or with contrasting parent materials (BEG *vs.* BES). The P_{av} contents of ash at the two eucalypt sites (BEG: 0.5 mg g^{-1}, BES: 0.4 mg g^{-1}; Table 2), however, were on average 3 to 6 times lower than those of the topsoil (BEG: 1.7 mg g^{-1}, BES: 2.6 mg g^{-1}; Table 4.2). In contrast at the pine site (BPS), P_{av} contents were similar for ash (0.3 mg g^{-1}) and soils (0.2 mg g^{-1}).

Unlike for the ash layer, the topsoil of the two types of tree plantations on schist (BES and BPS) differed significantly in P_{av} contents (Table 2). This was true immediately after the fire, in August 2010 (ANOVA: $F = 4.980$, $p = 0.027$; Tukey's test: $p = 0.022$) as well as six months later, in February 2011 (ANOVA: $F = 20.181$, $p < 0.001$; Tukey's test: $p < 0.001$). In contrast, topsoil P_{av} contents, did not differ significantly between the two types of parent material at both sampling occasions (August 2010 – ANOVA: $F = 4.980$, $p = 0.027$; Tukey's test, $p = 0.485$; February 2011 – ANOVA: $F = 20.181$, $p < 0.001$; Tukey's test, $p = 0.922$).

With time since fire, a strong decline (ca. 95%) in soil P_{av} contents was observed at the two eucalypt sites (Table 4.2), while at the pine site P_{av} contents were more than two times higher in February 2011 (0.5 mg g^{-1}) than in August 2010 (0.2 mg g^{-1}).

Table 4.2 - Average (± standard deviation; n = 5) available phosphorus (P_{av}) concentrations in the ash and topsoil layers of the study sites, immediately (August 2010) and sixth months after fire (February 2011). Different letters within rows (a, b) correspond to significant differences (p < 0.05) among slopes with different types of parent material (BEG vs. BES). Different symbols (*, +) within rows correspond to significant differences (p < 0.05) among slopes with different types of vegetation (BES vs. BPS). BEG — burnt eucalypt-granite site; BES — burnt eucalypt-schist site; and BPS — burnt pine-schist site.

	Sampling date	Layer	**BEG**	**BES**	**BPS**
P Concentrations	Aug 2010	Ash	0.5 ± 0.1^{a}	0.4 ± 0.2^{a,*}	0.3 ± 0.3*
(mg g^{-1})		Soil	1.7 ± 1.5^{a}	2.6 ± 1.5$^{a,+}$	0.2 ± 0.1*
	Feb 2011	Soil	0.1 ± 0.1^{a}	0.1 ± 0.1$^{a,+}$	0.5 ± 0.2*
P Stocks	Aug 2010	Soil	23.9 ± 21.4	40.8 ± 23.7	2.5 ± 1.0
(g m^{-2})	Feb 2011	Soil	1.0 ± 0.6	1.6 ± 1.7	7.1 ± 2.3

4.3.2 *Phosphorus exports by overland flow*

The average exports of PO_4-P and TP during the first 6 months after fire are presented in Figure 4.2. At all three study sites, peaks in PO_4-P and TP exports were generally associated with the major rainfall/overland flow events (Figure 4.2). On average, PO_4-P exports represented a considerable fraction of TP exports, amounting to 21 % in the case of the two eucalypt plantations and 35 % in the case of the pine site.

Global TP (ANOVA: F = 4.965, p = 0.011; Tukey's test, p = 0.017) and PO_4-P exports (ANOVA: F = 3.057, p = 0.057; Tukey's test, p = 0.046) in the first 6 months after fire differed significantly between the two sites with contrasting forest types (Table 4.3). Global TP losses were almost 6 times higher than at the eucalypt than at the pine site on schist (BES: 0.85 *vs.* BPS: 0.15 g m^{-2}; Table 4.3). Likewise, global PO_4-P losses were more than 5 times higher at the BES (0.17 g m^{-2}) than at the BPS site (0.03 g m^{-2}).

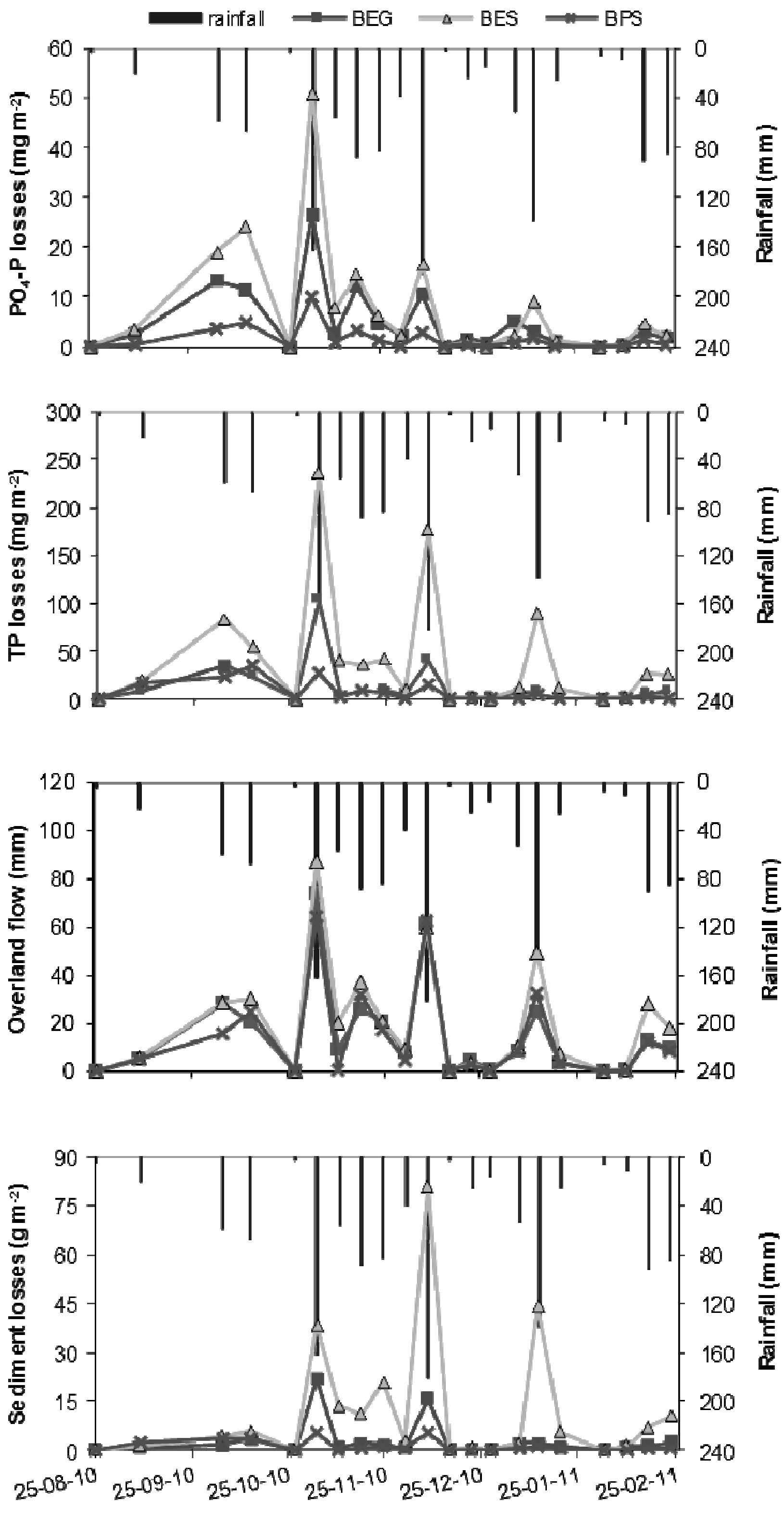

Figure 4.2 - Average orthophosphate (PO_4-P) and total phosphorus (TP) losses, overland flow amounts and sediment losses within the first 6 months after fire. BEG – eucalypt-granite site; BES – eucalypt-schist site and BPS – pine-schist site.

Table 4.3 - Average (± standard deviation) overall phosphorus losses (PO_4-P and TP), overland flow amounts, runoff coefficients and sediment losses at the three study sites for the first 6 months following fire (no. of plots per site = 3; no. of read-outs per plot = 21). Different letters within rows correspond to significant differences ($p < 0.05$) among slopes with different types of parent material (BEG vs. BES). Different symbols within rows correspond to significant differences ($p < 0.05$) among slopes with different types of vegetation (BES vs. BPS). BEG – eucalypt-granite site; BES – eucalypt-schist site and BPS – pine-schist site.

Variables	**BEG**	**BES**	**BPS**
Phosphorus export *(*g m^{-2}*)*			
PO_4-P	0.09 ± 0.06^{a}	$0.17 \pm 0.05^{a,*}$	$0.03 \pm 0.01^{+}$
TP	0.25 ± 0.15^{a}	$0.85 \pm 0.31^{b,*}$	$0.15 \pm 0.06^{+}$
Environmental variables			
Overland flow (mm)º	320 ± 245^{a}	$419 \pm 14^{a,*}$	$298 \pm 105^{*}$
Runoff coefficient (%)	26 ± 20^{a}	$34 \pm 1^{a,*}$	$25 \pm 9^{*}$
Sediment losses (g m^{-2})	54 ± 45^{a}	$249 \pm 113^{b,*}$	$26 \pm 13^{c,+}$

º Total rainfall associated = 1218 mm

Parent material also played a significant role in P exports but only in the case of TP and not in that of PO_4-P exports (Figure 4.2). Global TP exports were significantly different (ANOVA: $F = 4.965$, $p = 0.011$; Tukey's test, $p = 0.049$) between the BEG and BES sites, being more than 3 times higher at the schist (0.85 g m^{-2}) than at the granite site (0.25 g m^{-2}). As regards to PO_4-P, global losses were also clearly higher at the BES (0.17 g m^{-2}) than at the BEG site (0.09 g m^{-2}) but, as referred before, this difference was not statistically significant (ANOVA: $F = 4.965$, $p = 0.011$; Tukey's test, $p = 0.507$).

4.3.3 *Environmental variables and post-fire phosphorus exports*

In general, the average TP and PO_4-P exports of the individual read-outs were strongly correlated with both rainfall amounts and intensities as well as with overland flow volumes and sediment losses (Table 4.4).

Table 4.4 - Pearson correlations between environmental variables (i.e. rainfall amount, maximum rainfall intensity during 30 min – I_{30}, overland flow and suspended sediments) and phosphorus losses (PO_4-P and TP) by overland flow (averages per read out). Significant values ($p \leq 0.05$) are presented in bold.

Slope	P form	**Rainfall** (mm)	**I_{30}** ($mm\ h^{-1}$)	**Overland flow** (mm)	**Sediments** ($g\ m^{-2}$)
BEG	PO_4-P	**0.63**	**0.82**	**0.87**	**0.80**
	TP	**0.91**	**0.66**	**0.81**	**0.91**
BES	PO_4-P	**0.69**	**0.82**	**0.86**	0.42
	TP	**0.85**	**0.89**	**0.95**	**0.79**
BPS	PO_4-P	**0.58**	**0.80**	**0.77**	**0.78**
	TP	0.32	**0.67**	**0.77**	**0.84**

Nevertheless, these relations were not identical for the three study sites. Forest type appeared to play a differential role in TP exports, as they were strongly correlated with rainfall amount at the eucalypt site (BES: r = 0.85) but not at the pine site (BPS: r = 0.32). The importance of forest type was also suggested in the case of PO4-P exports but in the opposite sense. PO4-P exports were strongly correlated to sediment losses at the pine site (BPS: r = 0.78) but not at the eucalypt site (BES: r = 0.42). The relation of PO4-P exports with sediment losses also differed for the two eucalypt sites with contrasting parent materials. At the eucalypt site on granite, PO4-P exports were strongly correlated to sediment losses (BEG: r = 0.80), unlike at the schist site (BES: r = 0.42).

4.3.4 *Environmental variables and post-fire phosphorus exports*

The temporal patterns of orthophosphate (PO_4-P) and total phosphorus (TP) concentrations in overland flow during the first 6 months after the wildfire are presented in Figure 4.3. A clear peak in TP concentrations was found for the first significant post-fire rainfall event at all three study sites. In the subsequent period, TP concentrations varied considerably and these variations agreed better with the temporal patterns in sediment concentrations than in rainfall amounts or runoff volumes (Figure 4.2 and Figure 4.3.). Differences in average TP concentrations between the three study sites were rather consistent throughout the study period. TP concentrations tended to be highest at the eucalypt site on schist (BES), lowest at the pine site on schist (BPS) and intermediate at the eucalypt site on granite (BEG), in agreement with the differences in global TP exports (Table 4.3).

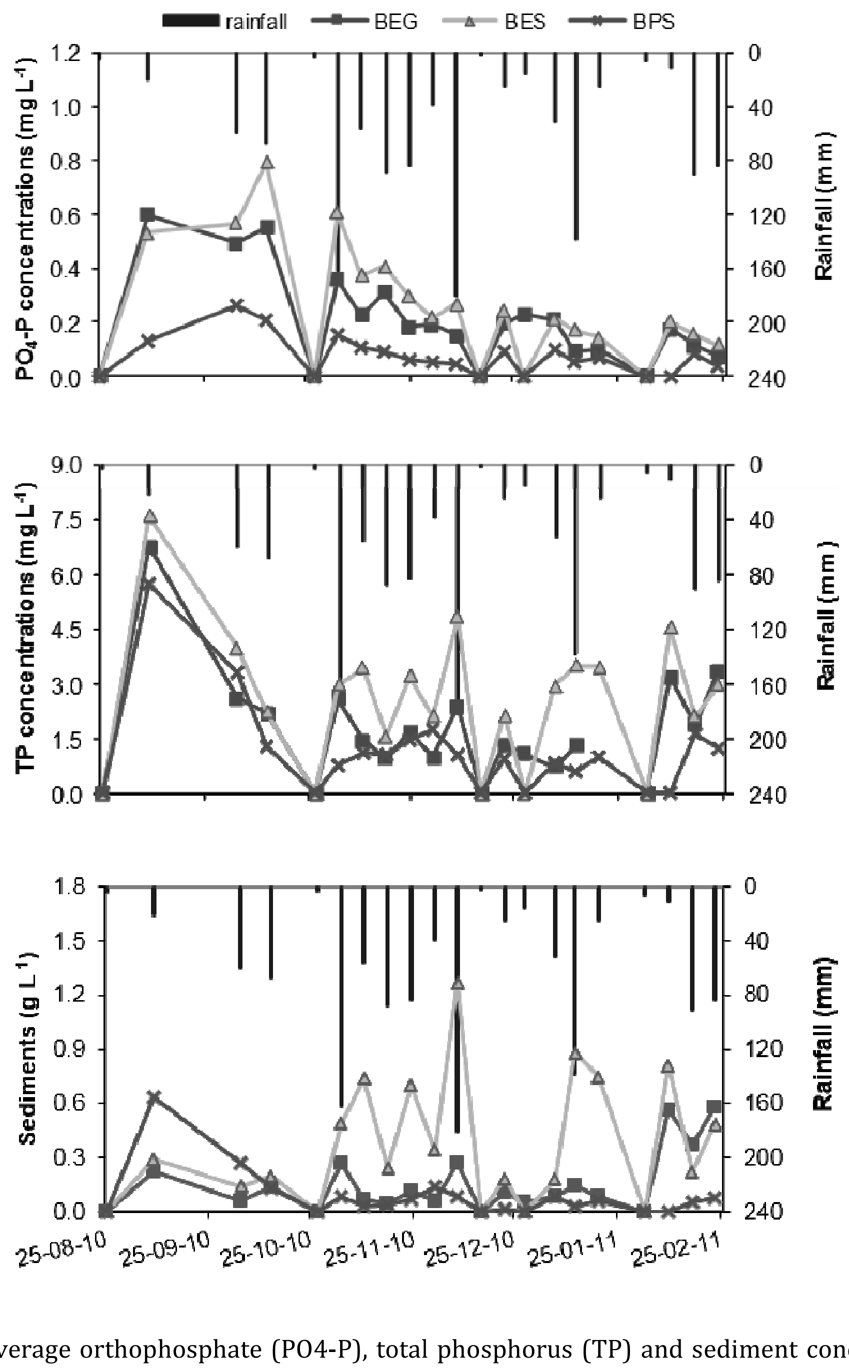

Figure 4.3 - Average orthophosphate (PO4-P), total phosphorus (TP) and sediment concentrations in overland flow, within the first 6 months after fire. BEG – eucalypt-granite site; BES – eucalypt-schist site and BPS – pine-schist site.

The average PO_4-P concentrations showed quite different temporal patterns than the average TP concentrations. Instead of revealing a single peak, PO_4-P concentrations at all three sites were highest for the first three significant rainfall events and after early November 2010 tended to decrease with time-since-fire (Figure 4.3). Therefore, PO_4-P concentrations seemed basically unrelated to the temporal patterns in rainfall amounts, runoff volumes or sediment concentrations (Figure 4.2 and Figure 4.3.). The PO_4-P concentrations at the pine site (BPS) tended to be clearly lower than those of the two eucalypt sites throughout the study period (Figure 4.3). The differences in PO_4-P concentrations between the two eucalypt sites were less straightforward, with a tendency for higher values at the site on schist (BES) than on granite (BES).

4.4 *Discussion*

4.4.1 *Phosphorus contents in ash and topsoil*

The ashes collected at sites with contrasting types of vegetation (BES *vs.* BPS) did not present significantly different P_{av} contents. As fire severity was classified as moderate at both sites (Table 4.1), the comparable ash contents could be explained by similar pre-fire P contents in vegetation and litter layers at both sites. This hypothesis is supported by the fact that similar P levels have indeed been found in northern Portugal, not just for eucalypt leaves and pine needles but also for litter and even for the organic matter-rich soil horizons of unburnt eucalypt and maritime pine stands (Magalhães et al., 2011; Nunes et al., 2010; Ribeiro et al., 2002).

Ash P_{av} contents also did not differ significantly between the two study sites with contrasting parent material (BEG vs. BES). This agreed with the similar P levels that Magalhães et al. (2011) reported for the organic horizons of unburnt soils on granite and schist in the study region.

The P_{av} contents of the ashes at the two eucalypt sites were, on average, lower than the contents of the topsoil (Table 4.2). This was to be expected as the soil tends to be the predominant P pool (94 – 98%) and not the litter or vegetation (Neary et al., 1999). At the pine site, however, the P_{av} content was slightly higher in the ashes than in the topsoil. This could be due to the dissolution of Ca^{2+} ions from the Ca^{2+} enriched pine ash (Machado et al., 2015), which most likely promoted the precipitation of P_{av} in the soil as calcium phosphate (Badía et al., 2014; Thomas et al., 2000b).

The P_{av} contents of the topsoil differed significantly between the two forest types immediately after the fire (Table 4.2). This difference presumably reflected a difference in the P topsoil content that existed before the wildfire, since fire severity was classified as moderate at both sites. An explanation for higher topsoil P_{av} content at the eucalypt site (BES) than at the pine site (BPS) would be a higher soil organic matter (SOM) content at the eucalypt site (22 *vs.* 19 %; Table 4.1). Fire-induced heating might have promoted SOM mineralization (Badía et al., 2014), thereby increasing P_{av} contents in the topsoil. On the other hand, SOM might have also influenced P adsorption and desorption processes (Kang et al., 2011; Otero et al., 2015). SOM can both enhance the amount of P sorbed by metal-chelate binding and inhibit P sorption, through competition of organic anions for P adsorption sites and also by increasing the negative charge of the topsoil (Kang et al., 2011).

The topsoil P_{av} contents immediately after the wildfire did not differ significantly with parent material (Table 4.2). This lack of a significant difference between the BEG and BES sites agreed with the similar P contents that were found for unburnt soils derived from granite and from schist in the study region (Magalhães et al., 2011). The P_{av} contents at the two eucalypt sites decreased dramatically (more than 90%) between August 2010 and February 2011 (Table 4.2), possibly as a result of P losses by runoff and soil erosion (Caon et al., 2014; Cerdà and Doerr, 2008; Certini, 2005; Khanna et al., 1994; Knoepp et al., 2005; Pausas et al., 2008; Shakesby, 2011; Thomas et al., 1999). In agreement with this explanation, TP exports were inversely related with decreases in topsoil P contents for the two eucalypt sites, with the site on schist exhibiting larger exports as well as decreases in topsoil content (TP exports: 0.85 g m^{-2}; Soil P_{av} losses: 2.5 mg g^{-1}) than the site on granite (TP exports: 0.25 g m^{-2}; Soil P_{av} losses: 1.6 mg g^{-1}). As P cycling is mainly ensured through the organic P pools, the removal of vegetation and litter by fire combined with soil erosion could have led to the exhaustion of above and belowground P pools at a pace higher than mineral weathering could replace it (DeBano and Klopatek, 1988; Neary et al., 1999).

In contrast to the two eucalypt sites, the pine site (BPS) revealed an increase in topsoil P_{av} content with time-since-fire (Table 4.2). This could be related to changes in soil pH that promoted the re-dissolution of calcium phosphate precipitates formed immediately after fire (Kutiel and Shaviv, 1992) as well as to the decomposition of the pine needle cast from the partially scorched tree crowns, since the breakdown of organic matter constitutes a major source of P_{av} (Ribeiro et al., 2007). Worth stressing in this respect were the lower TP exports and sediment losses at the pine site than at the two eucalypt sites.

At the end of this study, and in agreement to what was found immediately after the fire (Table 4.2), significant differences in topsoil P contents were found among sites with distinct types of vegetation (BES *vs.* BPS) but not among sites with distinct types of parent material (BEG *vs.* BES), which might suggest that soil processes were still under the influence of the “window of disturbance” (Ferreira et al., 2005, 2008; Shakesby and Doerr, 2006). Longer studies are therefore needed for a better knowledge of post-fire P cycling for the full duration of the “window of disturbance” (Ferreira et al., 2005, 2008; Shakesby and Doerr, 2006).

4.4.2 *Phosphorus exports by overland flow*

At all three forest sites, clear peaks in P exports – both PO_4-P and TP – occurred mainly associated to the major rainfall events, as would be expected since these events generated the largest amounts of runoff and sediment losses (Figure 4.2; Table 4.4). These findings are in line with what has been reported by various authors for other recently burnt areas in the Mediterranean region (Badía et al., 2014; Soto et al., 1997; Thomas et al., 1999, 2000b).

When comparing the two sites with different types of vegetation, global PO_4-P and TP exports were found to be significantly higher at the eucalypt than at the pine site on schist (Table 4.3). This could be explained by the typically stronger soil water repellency in eucalypt stands than in pine stands in the study region (Doerr et al., 1998; Keizer et al., 2005a, b; Santos et al., 2013), which was likely to have promoted overland flow and the associated sediment and P losses at the BES site. The possible existence of a water repellent ash layer overlying a strongly to extremely repellent topsoil at the BES site could have enhanced the differences in runoff and erosion between the eucalypt and pine sites (Bodí et al., 2011, 2014; Dlapa et al., 2013; Malvar et al., 2015b). An alternative explanation would be the needle cast cover, due to spontaneous mulching from the partially scorched pine crowns, reducing overland flow and erosion at the BPS site (Table 4.3) as also reported by prior post-fire erosion studies (Cerdà and Doerr, 2008; Knoepp et al., 2005; Kutiel and Shaviv, 1992). This pine needle cast was also held responsible for limiting the export of other nutrients such as nitrogen (Ferreira et al., 2015) and base cations (Machado et al., 2015) at the same study site, attesting to the importance of an effective mulch cover against soil fertility losses. The effectiveness of needle cast has mainly been attributed to the increases in interception storage and resistance to flow and the reduction in splash erosion (Martins et al., 2013; Prats et al., 2012, 2013; Shakesby et al., 1996; Thomas et al., 2000a, b). The resulting decreases in exports of particulate P forms as well as soil particles in general might explain the weak correlation that was observed between TP losses and rainfall amounts at the pine site ($r = 0.32$) as opposed to at the eucalypt site ($r = 0.85$).

When comparing the two eucalypt plantations with contrasting types of parent material, significant lower TP losses were found at the site on granite than on schist (Table 4.3). As the composition of the ash layer was similar at the two sites (Table 4.1 ; Ferreira et al., 2015; Machado et al., 2015) on one hand, and on the other, as its thickness was twice as great at the

BES (1 cm) than at the BEG site (0.5 cm), which would expectedly reduce overland flow and sediment yields (Bodí et al., 2011; Bodí et al., 2014; León et al., 2013), it is unlikely that the ash layer was responsible for the differences in P exports between the two eucalypt plantations. An alternative explanation, would be the coarser texture of the granite soils (Table 4.1), since a coarse texture has been reported to increase infiltration and, thus, reduce runoff (Wahren et al., 2016), particularly at the micro-plot scale (Boix-Fayos et al., 2006; Shakesby, 2011). In fact, the plots at the eucalypt site on granite did generate lower amounts of overland flow and associated sediment losses than those at the eucalypt site of schist (Table 4.3). These lower runoff and erosion rates were not only associated with lower exports of TP but also with significantly lower exports of total N (Ferreira et al., 2015) and base cations, namely Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} (Machado et al., 2015). PO_4-P exports were also lower at the eucalypt site on granite than on schist but not in a significant manner (Table 4.3). This contrast between TP and PO_4-P results might reflect a prevailing role of sediment losses in TP exports as opposed to a predominant role of runoff volumes in PO_4-P exports, since significant differences in sediment losses but not in overland flow were found between the BEG and BES site (Table 4.3). Such findings are also in line with the fact that inorganic P forms are mostly lost in solution rather than adsorbed to sediment particles (Thomas et al., 1999, 2000b).

The comparison of the present results with those of Ferreira et al. (2015) on nitrogen losses by overland flow at the same study sites showed that P solutes were preferentially lost over N solutes at all three sites, which suggests that P is more likely to become a limiting factor for vegetation recovery following fire than N. Moreover, global TP losses were higher than TN losses at one of the study sites (BES) but not at the other two sites (BEG and BPS), so the risk of decline in overall soil fertility would seem highest at the BES site. Besides the erosion risk per se, the risk of soil fertility decline at this site would seem relevant for defining post-fire erosion mitigation measures. However, further studies over longer time scales are required to confirm these results, especially since major changes to soil hydrology and erodibility can occur over the medium to long-term (Cerdà and Doerr, 2005; Cerdà and Lasanta, 2005), in turn influencing post-fire nutrient losses.

4.4.3 *Phosphorus concentrations in overland flow*

Phosphorus concentrations and exports by overland flow showed a distinctive variation pattern in time (Figure 4.2 and Figure 4.3). Unlike exports, peaks in PO_4-P and TP concentrations were not associated in a clear manner with the major rainfall or overland flow events. The first 3 significant post-fire rainfall events produced marked peaks in PO_4-P concentrations at the two eucalypt sites but clearly lower peaks at the pine site, suggesting that the pine needle cover provided effective protection against the transport of the solute-enriched ash layer which is typically easily erodible (Ferreira et al., 2005; Shakesby, 2011; Thomas et al., 1999). After the preferential erosion of the ash layer at the eucalypt sites (around November 2010), PO_4-P concentrations seemed unrelated to rainfall or overland flow events, possibly due to the complex biogeochemical processes involving this form of P (Certini, 2005; Kutiel and Shaviv, 1992; Murphy et al., 2006).

Peaks in TP concentrations also differed from the peaks in TP exports (Figure 4.2 and Figure 4.3). At all the study sites, TP concentrations were clearly highest during the first significant post-fire rainfall event, most likely as a consequence of the detachment and transport of the easily erodible ash layer and of the partially combusted organic material on the ground surface, as was also suggested by other authors for the study region (Ferreira et al., 2005, 2008; Thomas et al., 1999). After this first rainfall event, less pronounced peaks in TP concentrations seemed mainly associated to the largest erosion events (Figure 4.3), as would be expected since TP consists mostly of particulate P forms (Sharpey et al., 1992).

4.5 *Conclusions*

The present work evaluated post-fire P losses by overland flow at micro-plot scale in a recently burnt Mediterranean area, addressing a topic that has until now been investigated by a rather limited number of studies. The results of this study emphasized the importance of a protective soil layer (in this case, a spontaneous mulch layer of pine needle cast) for minimizing post-fire P exports. Parent material was also found to play an important role in post-fire TP losses and, ultimately, for implementing measures against soil fertility losses.

Nonetheless, the results of the current work must be regarded with some caution, especially as a basis for post-fire land management, since micro-plots may not be representative for post-fire hydrological and erosive processes at the field scale. Despite these limitations, the present findings are considered an important contribution to a better understanding of the effects of forest type and parent material on post-fire phosphorus export in the Mediterranean region. Studies at larger spatial scales (including catchment scale) as well as over longer periods are highly recommended for a more comprehensive knowledge of P cycling in recently burnt areas as well as in downstream aquatic systems.

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Chapter 5 - Nitrogen and phosphorus exports by overland flow in two recently burnt eucalypt stands with contrasting slope aspect, north-central Portugal

R.V. Ferreira[a], D. Serpa[a], M.A. Cerqueira[a], J.J. Keizer[a]
[a] University of Aveiro and CESAM

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ABSTRACT

Wildfires have affected vast areas in Mediterranean forests, triggering changes in geomorphological and hydrological processes that can lead to a variety of negative impacts on the ecosystems. Important research gaps, however, remain with respect to wildfire impacts on runoff, and especially on soil erosion and nutrient mobilization. To address this research gap on post-fire nutrient losses by overland flow, a recently burnt forest area in north-central Portugal was selected and instrumented immediately after a wildfire, to evaluate the export of dissolved (NO_3-N and PO_4-P) and total (TN and TP) nitrogen and phosphorus forms. Two recently burnt eucalypt plantations were selected for their contrasting slope aspect (north vs. south orientation). The selection of only eucalypt slopes was mainly influenced by the fact that eucalypt is one of the most important and, at the same time, most fire-prone forest type in north-central Portugal. Plots were monitored over a period of twenty months, in which overland flow samples were collected on a 1- to 2-weekly basis, depending on rainfall. The north west-facing slope (BE-NW) showed more nutrient losses than the one facing south east (BE-SE), probably reflecting the influence of a logging intervention taken place at the BE-NW slope, shortly before the fire. Nitrogen and phosphorus exports were particularly pronounced in the three months after fire. However, after this initial period, peaks in N and P exports were also observed in association to intense rainfall events. The present work provided estimates of the range of N and P exports by overland flow in a recently burnt area at micro-plot scale in a fire-prone landscape of the Mediterranean Basin. It represents an important addition to the studies on post-fire nutrient losses by overland flow conducted in this region, with a further insight into the comprehension of the processes involved, and particularly useful for anticipating the impacts of recurrent fires on soil productivity.

Keywords

Wildfire; Overland flow; Nitrogen loss; Phosphorus loss; Micro-plot; Eucalypt stand; Slope Aspect

5.1 *Introduction*

Forests in the Mediterranean basin are frequently subject to severe wildfires. As it is commonly known, wildfires can change geo-morphological and hydrological processes through their direct effects on vegetation, litter layer and topsoil, as comprehensively reviewed by Cerdà and Bodí (2007), Moody et al. (2013) and Shakesby (2011). Important research gaps remain, however, with respect to wildfire impacts on runoff, soil erosion, and especially on post-fire nutrient mobilization (Shakesby, 2011).

Given the complexity of soil dynamics under the influence of fire, a better understanding of spatial and temporal mechanisms occurring in the immediate post-fire period is important for defining priorities in post-fire land management to mitigate soil erosion hazards in burnt sites (Shakesby, 2011).

Slope aspect has been reported to be a determinant factor for the hydrological and erosive response of forest ecosystems, mainly because it influences the amount of radiation received by the slope, which in turn affects the soil and vegetation properties (Cerdà, 1998; Kutiel and Lavee, 1999; Sternberg and Shoshany, 2001; Gabarrón-Galeote et al., 2013).

Forestry practices can also strongly influence overland flow and erosion in recently burnt areas. Various studies on post-fire management operations showed that logging and salvage harvesting (Thomas et al., 2000b; Fernández et al., 2007; Smith et al., 2011b) can increase the risk of soil erosion.

The importance of nutrient dynamics in overland flow in burnt forest environments is often disregarded, in spite of their significance for fertility losses at the ecosystem level. In burnt areas, nutrient loss in solution and adsorbed to eroded sediments were found to be considerably higher than in mature forest stands, as a result of increased overland flow and erosion amounts, and of the increased nutrient concentrations at the topsoil, as a result of organic matter combustion during fire (Ferreira et al., 2005; Thomas et al., 1999, 2000a, 2000b). High nutrient availability in overland flow has direct consequences on the ecosystems, either due to the decrease in soil fertility (Caon et al., 2014; Certini, 2005; Pausas et al., 2008; Shakesby, 2011) as well as the eutrophication of downstream aquatic systems (Bowman and Boggs, 2006; Correll, 1998; Smith et al., 2011a).

In wet Mediterranean regions, such as the study area, those nutrient losses strongly affect soil productivity and the environmental sustainability, since they coincide with mountain areas where the soils are often weakly developed and nutrient-poor, regardless of vegetation abundance. The latter is also true in Portugal, where the schist mountain is generally characterized by poorly developed Humic Cambisols where the only nutrient pool is located at the organic layers, which are burned down by forest fires (Ferreira et al., 2005).

Post-fire nutrient losses by overland flow have been poorly investigated in the Mediterranean (Cancelo-González et al., 2013; DeBano et al., 1998; Díaz-Fierros et al., 1990; Lasanta and Cerdà, 2005; Machado et al., 2015). In Portugal, in particular, only a small number of studies have measured post-fire nitrogen and phosphorus exports by overland flow (Coelho et al., 2004; Ferreira et al., 1997, 2005; Thomas et al., 1999, 2000a, 2000b; Walsh et al., 1992). Prior studies have also only evaluated solute losses and not total nitrogen losses (i.e. solute + particulate fraction) by overland flow. The present study aims to address this knowledge gap, by evaluating total nitrogen and total phosphorus exports by post-fire overland flow in a recently burnt area of the western Mediterranean Region.

The current work does not assess the effects of fire on nitrogen and phosphorus losses by overland flow since it does not present comparable data from unburnt plantations in the surroundings of the burnt area. In turn, the main aim of this study was to provide estimates of nitrogen and phosphorus exports by overland flow from recently burnt eucalypt plantations, one of the main and, at the same time, most fire-prone forest type in north-central Portugal. More specifically, this study wanted to quantify nitrogen and phosphorus exports by overland flow at the micro-plot scale: (i) for eucalypt plantations with contrasting slope aspects (north vs. south orientation); (ii) to determine the contributions of dissolved versus particulate fractions in nutrient exports; and (iii) to understand the spatial and temporal variation patterns in post-fire N and P losses. These losses were furthermore related to the N and P contents of the ash layer and the topsoil, for a better understanding of the N and P cycle following fire.

5.2 *Materials and Methods*

5.2.1 *Study area and study sites*

The study area was located within the Vouga River Basin, near the Ermida village in the Sever do Vouga municipality, north-central Portugal (Figure 5.1). The area was affected by a wildfire that took place between July 26 and July 28 2010 and that consumed, in total, some 300 ha of forest (DUDF, 2011). When the fire occurred, the area was predominantly covered by plantations of eucalypt (*Eucalyptus globulus* Labil.) but did also include some plantations of maritime pine (*Pinus pinaster* Ait.). Two contrasting burnt eucalypt (E. globulus) plantations in steep hill slopes with similar slope angle were selected for the present study by their contrasting aspects, i.e. South-East (BE-SE) and North-West (BE-NW) (Figure 5.1; Table 5.1)

The climate of the study area can be classified as humid meso-thermal (Csb, according to the Köppen classification), with moderate but prolonged dry summers (DRA-Centro, 2002). The mean annual temperature at the nearest climate station (Castelo-Burgães: 40°51′10″N, 8° 22′44″W at 306 m a.s.l.) was 14.9 °C (1991–2011; SNIRH, 2011), with average monthly temperatures ranging from 8.9 °C in January to 21 °C in July. Annual rainfall at the nearest rainfall station (Ribeiradio: 40°73′65″N, 8°30′08″W at 228 m a.s.l.) was, on average, 1655 mm, but varied markedly between dry (960 mm) and wet (2530 mm) years (1991–2011; SNIRH, 2011).

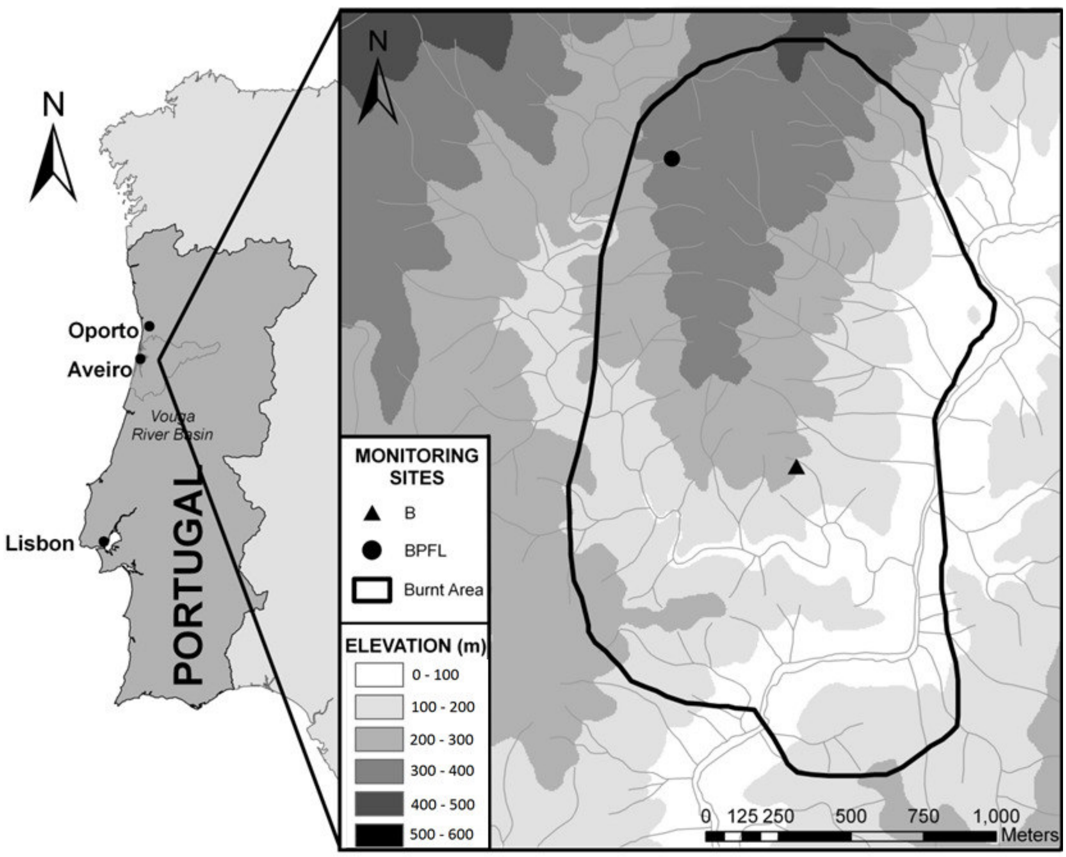

Figure 5.1 - Location of the Ermida study area within the Vouga River basin, north-central Portugal. Location of the study sites: BE-NW — burnt eucalypt site facing North-West; and BE-SE — burnt eucalypt site facing South-East. The bold line represents the burnt area.

Table 5.1 - General slope description. BE-NW — burnt eucalypt site facing North-West; and BE-SE — burnt eucalypt site facing South-East.

Slope	**BE-SE**	**BE-NW**
General characteristics		
Forest type	*Eucalyptus globulus*	*Eucalyptus globulus*
Parent material	Schist	Schist
Exposure	South-East	North-West
Geographical coordinates	40º43'23'' N	40º44'04'' N
	8º20'57'' W	8º21'16'' W
Elevation (*m.a.s.l.)*	180	200
Slope angle (º)	20.0 ± 2.0	19.0 ± 3.0
Slope length (m)	60	90
Fire severity	moderate	moderate
Topsoil properties		
[0-2] cm depth		
Texture	Sandy clay loam	Sandy loam
Sand fraction (%)	67	71
Silt fraction (%)	9	10
Clay fraction (%)	24	18
Organic matter (%)	25 ± 5	24 ± 4
[0-5] cm depth		
Bulk density ($g.cm^{-3}$)	1.15 ± 0.19	0.88 ± 0.13

The area belongs to the Hesperic Massif, one of the major physiographic units in the region (Ferreira, 1978). The parent material in the study area mainly consisted of pre-Ordovician schists but included Hercynian granites at some locations, as is typical for the Hesperic Massif (Pereira and FitzPatrick, 1995). The soils were mapped, at a scale of 1:1 000 000, as predominantly Humic Cambisols (Cardoso et al., 1973), but field descriptions of soil profiles at the study sites revealed that soils are mainly Umbric Leptosols (IUSS, 2006).

The topsoil (0–2 cm) at the study sites was rather coarse, with a sandy-loam to sandy-clay loam texture and high organic matter content (24–25%) (Table 5.1). The bulk density in the topsoil (0-5cm depth) tend to be higher at the south-facing slope (BE-SE: 1.15 ± 0.19 $g.cm^{-3}$) than at the north-facing slope (BE-NW: 0.88 ± 0.13 $g.cm^{-3}$) but not in a substantial manner.

At both sites, fire severity was classified as moderate (Shakesby and Doerr, 2006). Ash colour (predominantly black), as well as the degree of tree crown scorching (only partially combusted) and litter layer consumption (completely consumed by fire) were used as indicators.

Ground cover descriptions right after the fire revealed that the BE-NW site had 87% of ashes covering the ground whereas the BE-SE showed some 61%. Also stones and litter cover showed some discrepancy between the two sites: 1 and 2%, respectively at the BE-NW site and 22 and 17%, respectively at the BE-SE site. Before the fire, the BE-NW site had a commercial logging operation, with clear-cutting of the eucalypt plantation on this slope, with the purpose of harvesting wood and maintaining the roots for eucalypt re-sprouting. Possibly, the harvesting remains left on the ground (see Prats et al., 2014) were burnt by the fire which can explain the differences in ash cover between sites.

5.2.2 *Experimental design, field data and sample collection*

Both study sites within the burnt area were divided into two adjacent strips running from the base to the top of the slope section. In one of these strips, two pairs of bounded micro-plots (0.25–0.30 m^2) were installed before the occurrence of post-fire rainfall, one pair at the base and the other pair halfway up the slope, for monitoring overland flow. The other strip was used for repeated collection of soil samples. Samples and plots at each study site were treated as independent observations, despite the reduced distances between them, since the samples/plots from each of the present study sites exhibit considerable variability.

Only samples of the topsoil (0-2 cm depth) were collected because moderate fires are widely known for affecting mainly the upper 2 cm of soil (Badía et al., 2014; Cerdà, 2000; Mataix-Solera et al., 2011; Zavala, 2014). Soil sampling was done first on August 2010, roughly two weeks after the wildfire and before the occurrence of any rainfall; and then sampled with a regular interval of six months from that date onward, until after the end of the monitoring period (August 2012). At the first sampling event, ash samples were collected along with soil samples. Sampling was done at five equally-distant points along a transect that was laid out from the base to the top of the slope section, and shifted approximately 1-2 m across the slope in the subsequent sampling occasion. At each point of the transect ashes were collected over an area of 0.25 m^2 (0.5 m × 0.5 m) and topsoil (0-2 cm depth) over an area of 0.06 m^2 (0.25 m × 0.25 m).

The overland flow from the micro-plots was collected in barrels of 30 to 70 L. In each field trip, overland flow volumes were measured and, whenever the volume in each barrel exceeded 250 mL, samples were collected, following intensive stirring of the water in the barrels. Sampling was done during 20 months after the wildfire, at 1–2-weekly intervals, depending on rainfall. During this period, overland flow samples were collected in 500 mL polyethylene bottles that had been previously rinsed with hydrochloric acid (pH < 2.0) and distilled and dionized water. Overland flow samples were then transported to the laboratory in cool boxes and stored at 4ºC for no longer than 24 h.

The 1- to 2-weekly field trips also involved measurement of rainfall accumulated in 4 storage gauges (in-house design) that had been installed across the study area by the middle of August 2010. Their main purpose, however, was to validate the automatic recordings of two tipping-bucket rainfall gauges (Pronamic Professional Rain Gauge with 0.2 mm resolution) that had been installed in close proximity to two of the storage gauges.

5.2.3 *Laboratory work*

Upon arrival to the laboratory, the ash and soil samples were air dried and sieved manually with a 2 mm sieve. Total nitrogen content (TKN) in ashes and soils was determined using the Kjeldahl method (Bremner, 1979). Available phosphorus (P_{av}) content in ashes and soils was determined by the Bray method (Bray and Kurtz, 1945), using a mixture of ammonium fluoride (0.03 M) and hydrochloric acid (0.025 M) as extractant. The extracted P was analyzed spectrophotometrically as ortophosphate by the molybdenum blue method (APHA, 1998).

Aside from nitrogen and phosphorus, soil samples were also analysed for: i) bulk density, using the core method as described by Porta et al. (2003); ii) soil particle size, following the international method of mechanical analysis as defined by Guitián and Carballas (1976); and iii) organic matter, determined by loss on ignition at 550ºC for 4 h, as described by Botelho da Costa (2004).

Overland flow samples were analysed for total (i.e. dissolved plus particulate forms) nitrogen and phosphorus (i.e. dissolved plus particulate P forms), nitrate (NO_3-N) and orthophosphate (PO_4-P), using a flow injection FIAstarTM 5000 analyser (FOSS-Tecator). Prior to analysis, overland flow subsamples (50 mL) for determining NO_3-N and PO_4-P concentrations were filtered with 0.45 µm Millipore© membrane filters. Subsamples (50 mL) for analysing TN and TP were subjected to an oxidative digestion, using peroxodisulphate/alkali (Oxisolv®, Merck) and then filtered.

Sediments in overland flow samples were analyzed in the form of total suspended solids (TSS) and were quantified gravimetrically through filtration of 50 to 150 mL of water by a glass fibre filter, followed by drying to a constant weight at 105 ºC (APHA, 1998).

5.2.4 *Data analysis*

Differences in total Kjedahl nitrogen (TKN) and available phosphorus (P_{av}) contents in ash and topsoil, between study sites, were evaluated by a one-way ANOVA, if the assumptions of normality (checked by the Shapiro-Wilk test) and homogeneity of variance (checked by the Levene's test) were not rejected. If one or both of them were rejected, logarithmic transformations of the data were performed to comply with the assumptions of the ANOVA (Zar, 1999). For each study site, differences in ash and soil TKN and P_{av} contents between sampling dates were evaluated by a one-way ANOVA followed by a multi comparison Tukey's test, after checking for the ANOVA assumptions.

Regarding NO_3-N, TN, PO_4-P and TP exports in overland flow and their respective concentrations, a one-way ANOVA was performed to test differences between sites, after checking for data normality and homogeneity of variance. If one or both of them were rejected, logarithmic transformations of the data were tried first and, if unsuccessful, the non-parametric Kruskal-Wallis one-way ANOVA test was applied (Zar, 1999). Between-sites differences in overland flow and sediment losses were also evaluated by a one-way ANOVA. The influence of environmental variables (rainfall amount and intensity, overland flow and sediment losses), on nitrogen and phosphorus losses by overland flow, were assessed by the Pearson's correlation coefficient. In the case of the variables that had not met the normality assumption by the above-mentioned Shapiro-Wilk test, the coefficients were computed for the transformed data.

The significance level was set at 0.05, and all statistical analyses were performed using SigmaPlot 11.0 package software.

5.3 *Results and discussion*

5.3.1 *Nitrogen and phosphorus contents in ash and topsoil*

The average total Kjeldahl nitrogen (TKN) and available phosphorus (P_{av}) contents in the ash and topsoil layers of the two study sites are shown in Table 5.2. No significant differences were observed between the ashes collected at both study sites in terms of TKN (ANOVA: $F = 3.200$, $p = 0.111$) or P_{av} (ANOVA: $F = 0.226$, $p = 0.648$) contents. As fire severity was similar at the two study sites (Table 5.1), these results most likely reflected the pre-fire N and P contents in topsoil organic matter and vegetation.

Table 5.2 – Average (±standard deviation) nitrogen (TKN) and available phosphorus (P_{av}) concentrations/stocks in the ash and topsoil layers of the two study sites, throughout the study period BE-NW — burnt eucalypt site facing North-West; and BE-SE — burnt eucalypt site facing South-East. For each variable, different letters and symbols within columns correspond to significant differences ($p<0.05$) among sampling dates at the BE-SE and at the BE-NW sites, respectively.

	Nutrient	Sampling date	Layer	Site	
				BE-SE	**BE-NW**
***Concentrations* (mg g^{-1})**	**TKN**	Aug 2010	Ash	1.50 ± 0.42	1.96 ± 0.40
			Soil	0.70 ± 0.23^{a}	0.79 ± 0.23^{x}
		Feb 2011	Soil	0.27 ± 0.13^{b}	0.46 ± 0.19*
		Aug 2011	Soil	0.38 ± 0.15^{b}	0.37 ± 0.12*
		Feb 2012	Soil	0.39 ± 0.13^{b}	0.30 ± 0.11*
		Aug 2012	Soil	0.23 ± 0.06^{b}	0.24 ± 0.08*
	P_{av}	Aug 2010	Ash	0.30 ± 0.15	0.25 ± 0.19
			Soil	0.13 ± 0.10^{a}	0.13 ± 0.05^{x}
		Feb 2011	Soil	0.05 ± 0.02^{b}	0.03 ± 0.02*
		Aug 2011	Soil	0.05 ± 0.04^{b}	0.03 ± 0.03*
		Feb 2012	Soil	0.05 ± 0.04^{b}	0.007 ± 0.004*
		Aug 2012	Soil	0.02 ± 0.02^{b}	0.01 ± 0.006*
***Stocks* (g m^{-2})**	**TKN**	Aug 2010	Soil	16.2 ± 5.2	14.0 ± 4.0
		Feb 2011	Soil	6.3 ± 3.1	7.9 ± 3.3
		Aug 2011	Soil	8.8 ± 3.5	6.5 ± 2.2
		Feb 2012	Soil	9.0 ± 3.0	5.2 ± 1.9
		Aug 2012	Soil	5.3 ± 1.4	4.2 ± 1.5
	P_{av}	Aug 2010	Soil	3.0 ± 2.2	2.2 ± 0.9
		Feb 2011	Soil	1.2 ± 0.4	0.5 ± 0.3
		Aug 2011	Soil	1.2 ± 0.8	0.4 ± 0.6
		Feb 2012	Soil	1.1 ± 0.9	0.1 ± 0.07
		Aug 2012	Soil	0.5 ± 0.5	0.2 ± 0.1

For both study sites, TKN ash contents immediately after the wildfire were on average two-fold higher than in the topsoil (Table 5.2). An explanation behind these findings is probably related to the natural composition of plant biomass and litter layers, as they are typically richer in N than soils (Busse and Debano, 2005; Nunes et al., 2010; Ribeiro et al., 2002). P_{av} ash contents were on average 3 to 4 times higher than those of the topsoil at both study sites (Table 5.2).

Topsoil TKN contents did not differ significantly between the two study sites (ANOVA: $F = 0.389$, $p = 0.536$), in agreement with the results of the ash layer. In contrast, topsoil P_{av} contents differed significantly (ANOVA: $F = 4.812$, $p = 0.033$) between the two study sites (Table 5.2),), probably due to pre-fire differences in topsoil organic matter content, which were maintained after the fire (Table 5.1). On one hand, the slightly higher soil organic matter contents at the BE-SE site were likely to have been responsible for the somewhat higher P_{av} contents in the topsoil, since fire-induced heating promotes the mineralization of soil organic matter (Badía et al., 2014). On the other hand, soil organic matter might have also influenced P adsorption and desorption processes (Kang et al., 2011; Otero et al., 2015). Soil organic matter can both enhance P sorption by metals and inhibit P sorption, through competition of organic anions for P adsorption sites and also by increasing the negative charge of the topsoil (Kang et al., 2011).

The comparison of topsoil TKN contents between sampling dates (Table 5.2) revealed a significant decrease in soil nitrogen availability within the first 6 months after fire at both the BE-NW (ANOVA: $F = 9.502$, $p < 0.001$) and BE-SE site (ANOVA: $F = 7.593$, $p < 0.001$). After this initially sharp decrease, a consistent but slight reduction in TKN contents was observed at the BE-NW site till the end of the monitoring period (Table 5.2). At the BE-SE site, on the other hand, an overall decline was observed after the first 6 months after fire but this was not consistent over time since an increase in TKN contents was observed from February 2011 to August 2011, possibly as a result of litter decomposition (McIntosh et al., 2005), which was substantially higher at this site than at the BE-NW site (cf. section 5.2.1).

According to the later author, as litter decomposes, nutrients can return to the soil surface, where they will be susceptible to leaching and erosion processes by runoff (McIntosh et al., 2005) after intense rainfall events. Inconsistencies between sampling sites over time could also be related to the multitude of factors influencing nitrogen pools, such as leaching processes, soil erosion, plant uptake and microbial immobilization as well as to the spatial heterogeneity of nutrient losses after fire (Hamman et al., 2008).

Either way, the marked decrease (42% to 70%) in average topsoil contents observed at both study sites from the beginning to the end of the monitoring period (Table 5.2), most likely resulted from N leaching into deeper soil layers as well as N losses (Table 5.3) by runoff and soil erosion (Bodí et al., 2014; Caon et al., 2014; Cerdà and Doerr, 2008; Certini et al., 2005; Khanna et al., 1994; Knoepp et al., 2005; Pausas et al., 2008; Shakesby, 2011; Thomas et al., 1999).

Table 5.3 – Total average (±standard deviation) nitrogen (NO_3-N and TN) and phosphorus losses (PO_4-P and TP), overland flow amounts, runoff coefficients and sediment losses for the 20 months following fire. BE-NW — burnt eucalypt site facing North-West; and BE-SE — burnt eucalypt plantation site South-East. For each variable, different letters within lines correspond to significant differences (p<0.05) among sites.

Variables	**BE-SE**	**BE-NW**
Nutrients export *(*g m^{-2})		
NO_3-N	0.04 ± 0.03 ^{a}	0.08 ± 0.06 ^{b}
TN	0.8 ± 0.4 ^{a}	1.4 ± 0.7 ^{b}
PO_4-P	0.00002 ± 0.00001 ^{a}	0.0002 ± 0.0002 ^{b}
TP	0.2 ± 0.1 ^{a}	0.7 ± 0.6 ^{b}
Environmental variables		
Overland flow (mm)°	577 ± 257^a	577 ± 292 ^{a}
Runoff coefficient (%)	27 ± 12^a	27 ± 13^a
Sediment losses (g m^{-2})	86 ± 54^a	266 ± 178^b

° Total rainfall associated = 2101 mm

As regards to topsoil P_{av} contents (Table 5.2), a sharp decrease in the first 6 months after fire (ANOVA: F = 11.950, p < 0.001) followed by a slow decrease in the remaining study period was observed at the BE-NW site). At the BE-SE site, on the other hand, topsoil P_{av} contents did not differ significantly during the study period (ANOVA: F = 2.349, p = 0.089), despite the overall decline trend. This more pronounced decline in average topsoil P_{av} contents at the BE-NW site (80% to 94%) than at the BE-SE site (60% to 83%), was most likely a result of the higher P losses by runoff and soil erosion observed at this slope (Table 5.3).

5.3.2 *Spatial variation patterns of nitrogen and phosphorus exports by overland flow*

The first two years after fire were considered regular hydrological years since rainfall amounts (year 1 - 1416; year 2 – 1175) were within the range of the long-term average annual rainfall at the nearby rainfall station (Ribeiradio). In the entire study period (August 2010 to April 2012) roughly 2101 mm of rainfall have fell in the study area. Overall, runoff generated during the study period produced, on average, significantly higher nitrogen (ANOVA: F = 5.149, p = 0.027) and phosphorus losses by overland flow at the BE-NW site than at the BE-SE site (Table 5.3; Figure 5.2 andFigure 5.3).

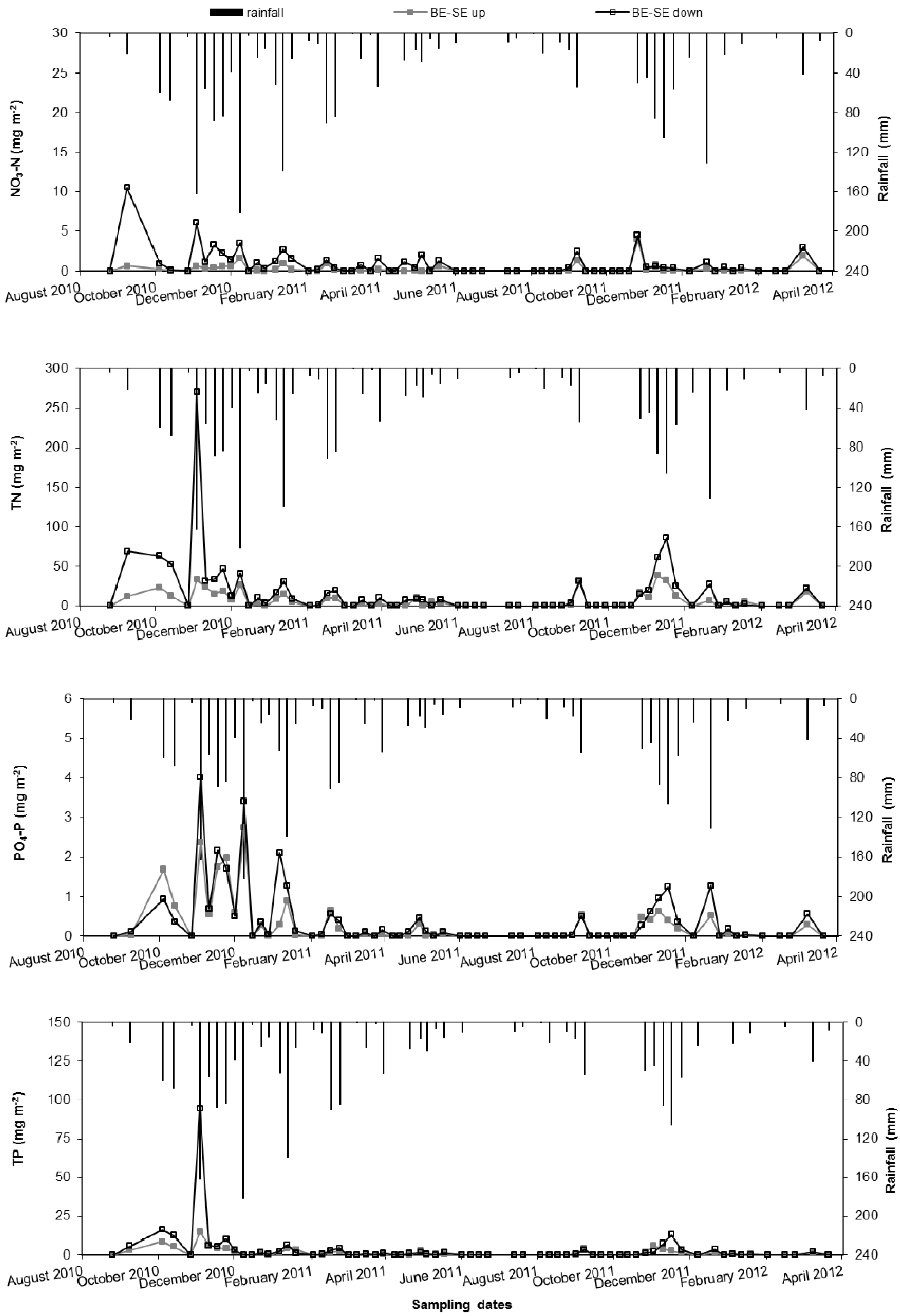

Figure 5.2 - Nitrate (NO_3-N), total nitrogen (TN), orthophosphate (PO_4-P) and total phosphorus (TP) losses by overland flow within the first 20 months after fire, at the burnt eucalypt site facing South-East (BE-SE). BE-SEup – data from plots located on an upper part of the slope; BE-SEdown – data from plots located at the base of the slope.

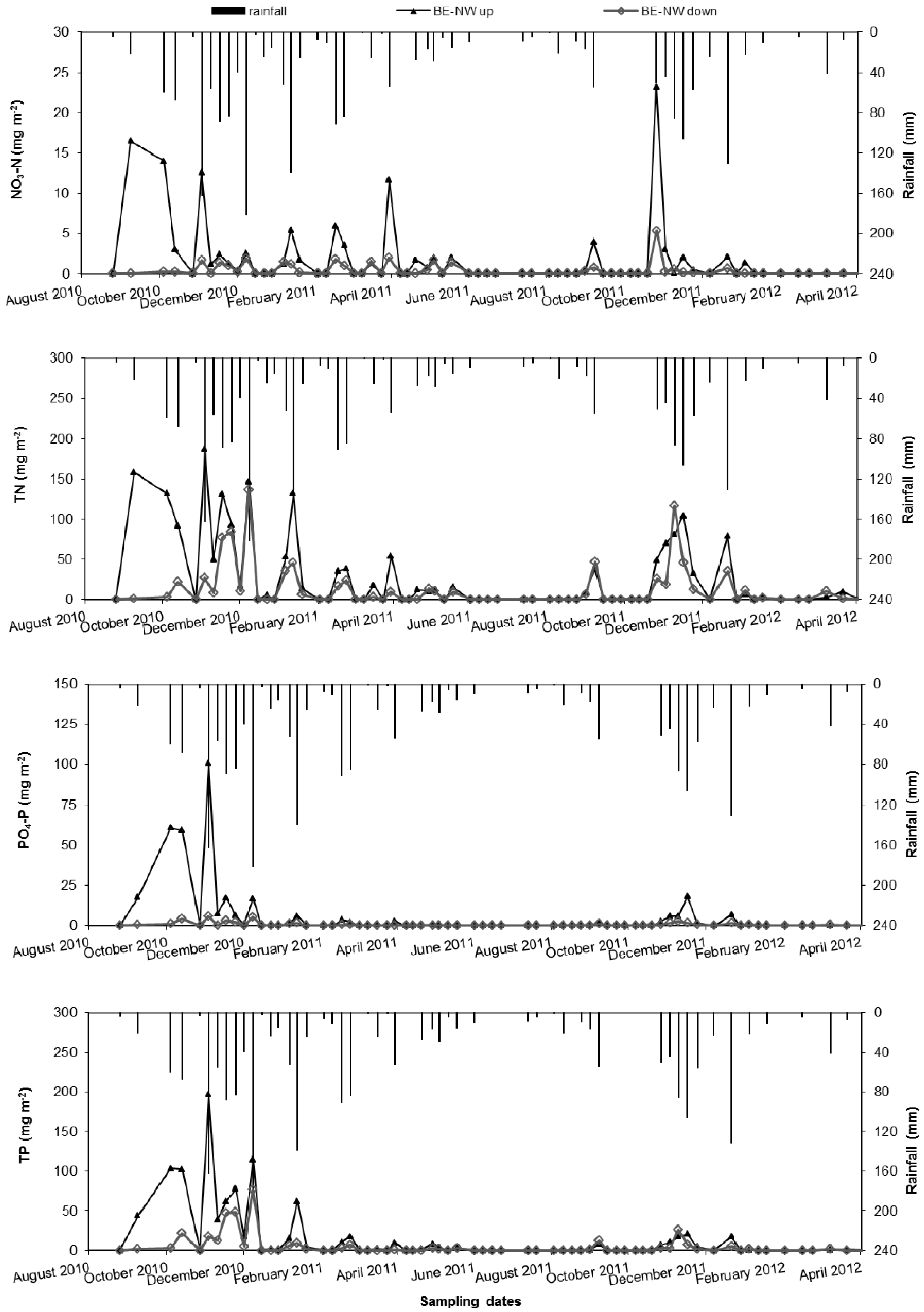

Figure 5.3 - Nitrate (NO_3-N), total nitrogen (TN), orthophosphate (PO_4-P) and total phosphorus (TP) losses by overland flow within the first 20 months after fire, at the burnt eucalypt site facing North-West (BE-NW).BE-NWup – data from plots located on an upper part of the slope; BE-NWdown – data from plots located at the base of the slope.

Global TN losses over the entire study period (Table 5.3) were almost two times higher at the BE-NW site (1.4 g m^{-2}) than at the BE-SE site (0.8 g m^{-2}). Also for dissolved N forms, i.e. NO_3-N (Table 5.3), losses were about 2 times higher at the BE-NW site (0.08 g m^{-2}) than at the BE-SE site (0.04 g m^{-2}). However, NO_3-N exports accounted only for less than 5% of the overall N exports at both sites, as N is mainly lost in its particulate forms (Soto et al., 1997) (Table 5.3).

The predominance of particulate forms in overland flow was even more pronounced for P, as the contribution of PO_4-P losses represented only 0.02 to 0.03% of the overall P losses (Table 5.3). As regards to this nutrient, and similarly to what was found for N, significant losses (TP – ANOVA: $F = 11.116$, $p = 0.001$; PO_4-P – ANOVA: $F = 15.554$, $p < 0.001$) were found between the two sites. At the BE-NW site, global TP losses were almost 4 times higher than at the BE-SE site (0.7 vs. 0.2 g m^{-2}; Table 3). The differences in global PO_4-P losses between these two sites were even more pronounced, being about 10 times higher at the BE-NW (0.0002 g m^{-2}) than at the BE-SE site (0.00002 g m^{-2}).Between-site differences in N and P exports were most likely related to the higher sediment losses (ANOVA: $F = 6.149$, $p = 0.016$) at the BE-NW than at the BE-SE site (Table 5.3; Figure 5.4 and Figure 5.5), since similar (ANOVA: $F = 0.000721$, $p = 0.979$) overland flow amounts were generated at each site.

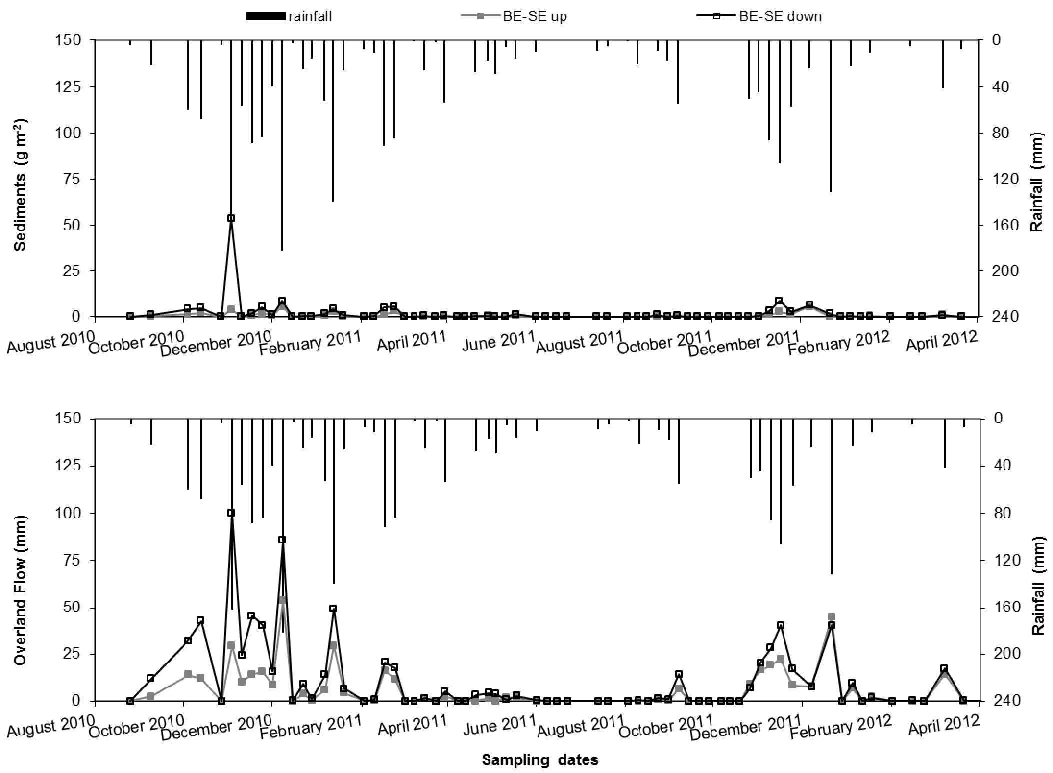

Figure 5.4 - Overland flow amount and sediment losses by overland flow within the first 20 months after fire, at the burnt eucalypt site facing South-East (BE-SE). BE-SEup – data from plots located on an upper part of the slope; BE-SEdown – data from plots located at the base of the slope.

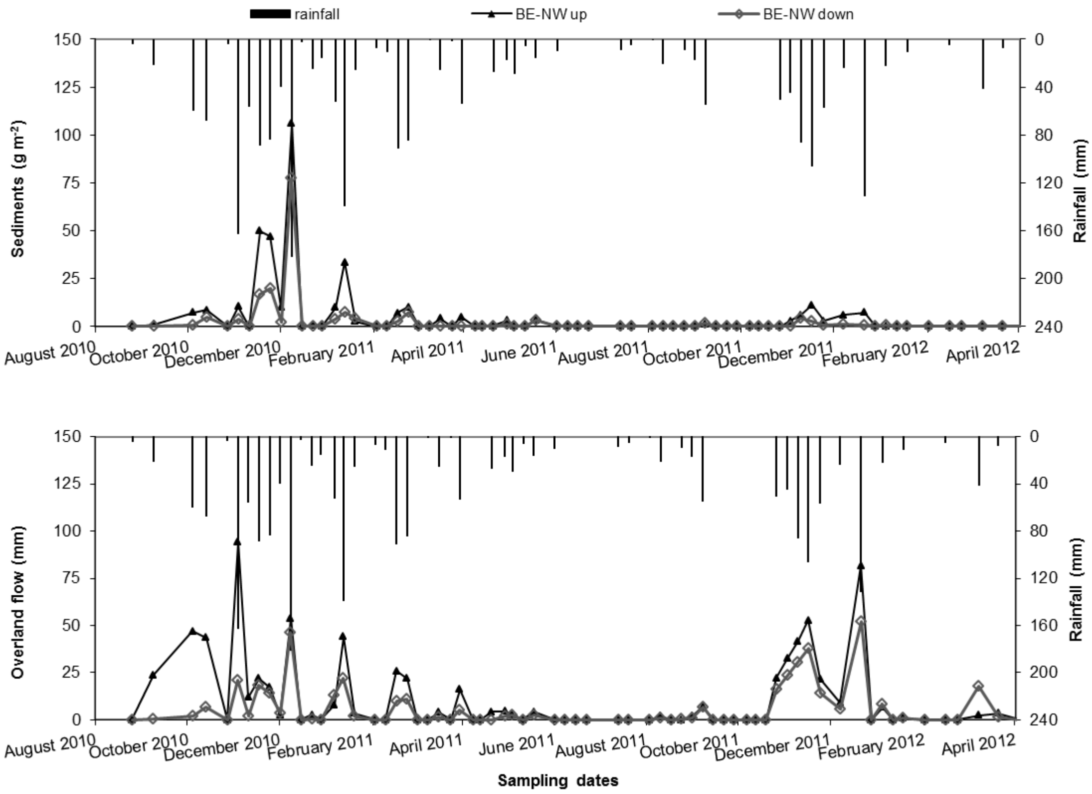

Figure 5.5 - Overland flow amount and sediment losses by overland flow within the first 20 months after fire, at the burnt eucalypt site facing North-West (BE-NW). BE-NWup – data from plots located on an upper part of the slope; BE-NWdown – data from plots located at the base of the slope.

As most N and P are exported in its particulate form, higher losses were found at the site with highest sediment losses (i.e. BE-NW). These results are also corroborated by the Pearson's correlations (Table 5.4), since no relationship was found between NO_3-N exports and the hydrological (I30: r = 0.44; Overland flow: r = 0.45) and erosion variables (r = 0.26) at the BE-SE site, unlike at the BE-NW site. As this dissolved N form has a higher contribution for overall exports than PO_4-P (Table 5.3), no correlation was found in the site with lower sediment losses. When comparing the overall TN losses in the first 20 months after fire with the changes in soil N contents from the beginning to the end of the study period, it was noticeable that TN losses by overland flow at the BE-NW site represented twice as much of the topsoil N losses (14 %) than at the BE-SE site (7%). The same was true for P, since overall TP losses by overland flow corresponded to a 35% reduction in soil P stocks at the BE-NW site (and only to an 8% reduction at the BE-SE site (8%) (Table 5.2 and Table 5.3).

Table 5.4 – Pearson correlations between environmental variables (*i.e.* rainfall amount, maximum rainfall intensity during 30 min -I_{30}, overland flow and suspended sediments) and nitrogen (NO_3-N and TN) and phosphorus losses (PO_4-P and TP) by overland flow (averages per read out). Significant values ($p \leq 0.05$) are in bold.

Site	**Variable**	**Nutrient losses** ($g.m^{-2}$)			
		NO_3-N	TN	PO_4-P	TP
BE-SE	Rainfall (mm)	**0.54**	**0.79**	**0.87**	**0.79**
	I30 ($mm\ h^{-1}$)	0.44	**0.66**	**0.66**	**0.65**
	Overland flow (mm)	0.45	**0.89**	**0.92**	**0.90**
	Sediments ($g\ m^{-2}$)	0.26	**0.75**	**0.72**	**0.80**
BE-NW	Rainfall (mm)	**0.53**	**0.81**	**0.78**	**0.79**
	I30 ($mm\ h^{-1}$)	**0.63**	**0.69**	**0.64**	**0.71**
	Overland flow (mm)	**0.57**	**0.89**	**0.88**	**0.77**
	Sediments ($g\ m^{-2}$)	**0.61**	**0.74**	**0.63**	**0.81**

The results of the present work seem to contradict those of other studies carried out in the Mediterranean basin (Cerdá, 1998; Kutiel and Lavee, 1999; Sternberg and Shoshany, 2001), since lower sediment losses were found at south-facing slopes rather than at north-facing slopes. According to the previous studies, as south-facing slopes receive higher solar radiation than those facing north, this affects soil moisture, and soil aggregation processes, which, in tum, affect vegetation growth that tends to be lower on these slopes (Kutiel and Lavee, 1999; Sternberg and Shoshany, 2001; Gabarrón-Galeote et al., 2013). As a result of its higher vegetation cover and therefore lower bare soil and rock outcrops, north-facing slopes typically present lower sediments losses than south-facing slopes (Cerdá, 1998; Kutiel and Lavee, 1999; Sternberg and Shoshany, 2001). As slope aspect is unlikely to have been responsible for the differences between sites, the alternative explanation would be the differences in pre-fire management operations, since the BE-NW site was under an intensive logging intervention of clear-cutting before the fire, which might have highly modified the soil surface and vegetation pattern. Clear-cutting is widely known not only to damage the ground and shrub layer but also to eliminate tree interception and promote soil compaction (Beasley and Granillo, 1985). The removal of vegetation, in particular, makes the soil more vulnerable to splash erosion, thereby promoting overland flow generation and the associated sediment and nutrient losses (Beasley and Granillo, 1985). Soil compaction by mechanical soil disturbance also influences the hydrological and erosive response of forest areas by decreasing macroporosity as well as the soil hydraulic connectivity and infiltration capacity

(Carr and Loague, 2012; Huang et al., 1996). Taking into account the findings of present study, one might therefore hypothesize that pre-fire management operations are crucial for post-fire soil fertility losses.

Within each site, overall nitrogen and phosphorus losses differed between plots with different locations along the slope, but the response was not consistent between sites site (Figure 5.2 andFigure 5.3). At the BE-SE site (Figure 2), NO_3-N (0.06 vs. 0.02 g m^{-2}) and TN exports (1.1 vs. 0.4 g m^{-2}), as well as PO_4-P (0.00003 vs. 0.00002 g m^{-2}) and TP exports (0.2 vs 0.09 g m^{-2}) were higher at plots located at the base of the slope than at those located in an upper part of the slope. Conversely, at the BE-NW site, higher nitrogen (NO_3-N: 0.13 vs. 0.03 g m^{-2}; TN: 1.9 vs. 0.9 g m^{-2}) and phosphorus (PO_4-P: 0.0004 vs. 0.00004 g m^{-2}; TP: 1.0 vs. 0.34 g m^{-2}) losses were found for plots with an upper slope position than those located at the base of the slope (Figure 5.3). These results are in agreement to prior studies in the region, which found contradictory results on the role of slope position on post-fire runoff and erosion at the micro-plot scale (Malvar et al., 2015; Prats et al., 2014).

5.3.3 *Temporal variation patterns of nitrogen and phosphorus exports by overland flow*

At both study sites, peaks of NO_3-N, TN, PO_4-P, TP and sediments exports were generally associated to the major rainfall events (Figure 5.2 andFigure 5.3), as expected since these events generated the highest amounts of runoff and sediment losses (Figure 5.4 and Figure 5.5), as also observed in other burnt areas of the Mediterranean region (Badía et al., 2014; Soto et al., 1997; Thomas et al., 1999, 2000b).

The highest nitrogen and phosphorus losses occurred in the third week after the fire (Figure 5.2 andFigure 5.3) most likely because the rainfall amounts (> 20 mm) were large enough to saturate the ash layer and trigger overland flow and erosion processes. Nitrogen and phosphorus exports varied markedly in the first six months after fire, showing a clear decline with time-since-fire (Figure 5.2 andFigure 5.3).

Subsequent peaks were lower and occurred in response to extreme rainfall events (>50 mm per week). An exception pattern was found at the eucalypt site facing north (BE-NW), where clear peaks in N exports were observed along the monitoring period (Figure 5.3),in response to extreme rainfall events. At the BE-SE site, on the other hand, N exports were unrelated to rainfall amounts, after the first four months after fire (Figure 5.2).

5.3.4 *Nitrogen and phosphorus concentrations in overland flow*

The temporal patterns of nitrate (NO_3-N), total nitrogen (TN), orthophosphate (PO_4-P) and total phosphorus (TP) concentrations in overland flow for the 20 months following fire are presented in Figure 5.6 and Figure 5.7.

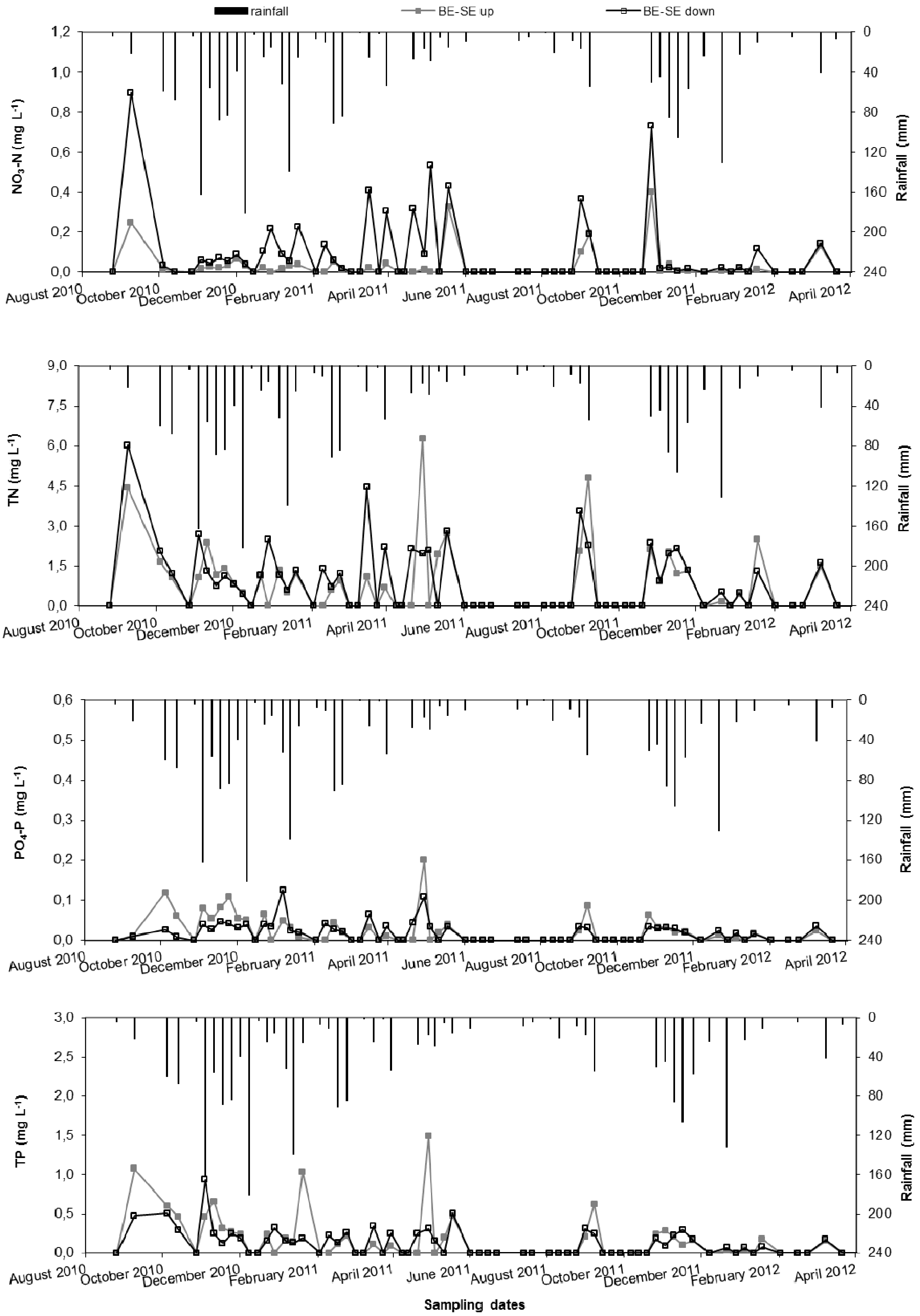

Figure 5.6 - Nitrate (NO_3-N), total nitrogen (TN), orthophosphate (PO_4-P) and total phosphorus (TP) concentrations in overland flow, within the first 20 months after fire, at the burnt eucalypt site facing South-East (BE-SE). BE-SEup – data from plots located on an upper part of the slope; BE-SEdown – data from plots installed on the base of the slope.

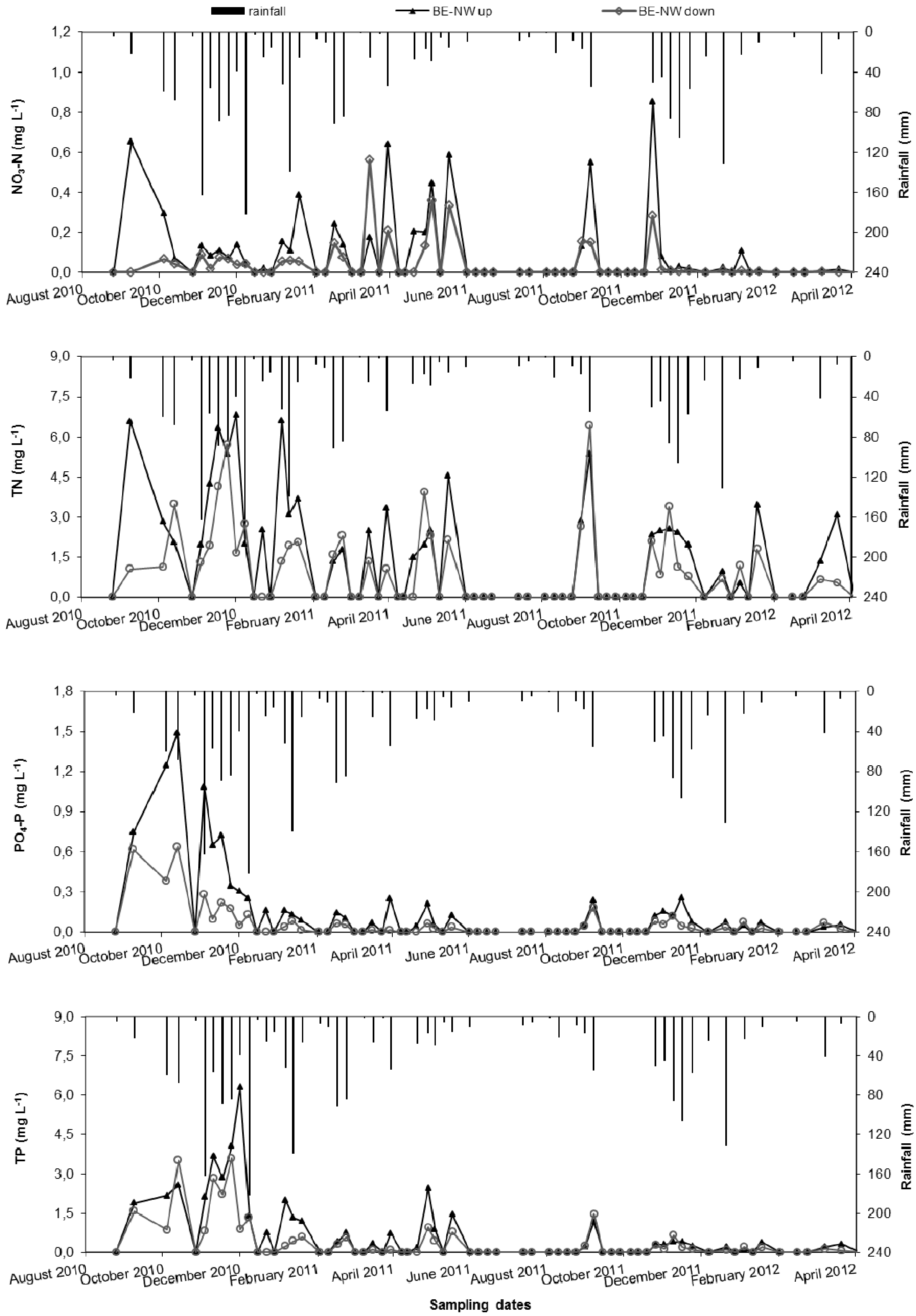

Figure 5.7 - Nitrate (NO_3-N), total nitrogen (TN), orthophosphate (PO_4-P) and total phosphorus (TP) concentrations in overland flow, within the first 20 months after fire, at the burnt eucalypt site facing North-West (BE-NW). BE-NWup – data from plots located on an upper part of the slope; BE-NWdown – data from plots located on the base of the slope.

Nitrogen and phosphorus concentrations in overland flow showed a distinctive variation pattern than N and P exports at both study sites (Figure 5.2 andFigure 5.3). Nitrogen and phosphorus concentration peaks were not directly related with the major overland flow events (Figure 5.6 and Figure 5.7),), in contrast to the N and P exports (Figure 5.2 andFigure 5.3). This was more evident immediately after the first significant post-fire rainfall event, when almost all the plots exhibited a major peak in dissolved and total nitrogen and phosphorus concentrations, most likely as a result of the detachment and transport of the nutrient enriched, easily erodible ash layer and of the partially combusted organic material on the ground surface (Ferreira et al., 2005, 2008; Thomas et al., 1999). After this first event, peaks in dissolved and total nutrient concentrations were often unrelated to rainfall/overland flow events, possibly because of the complex biogeochemical processes occurring in burnt forest areas (Caon et al., 2014; Murphy et al., 2006).

5.4 *Conclusions*

The present work evaluated post-fire nitrogen and phosphorus losses by overland flow at micro-plot scale in a recently burnt Mediterranean area, providing estimates of the range of N and P exports in a fire-prone landscape. It represents an important addition to the studies on post-fire nutrient losses by overland flow conducted in the Mediterranean region, which are crucial for anticipating the impacts of recurrent fires on soil productivity. Nitrogen and phosphorus exports were particularly pronounced in the three months after fire. However, after this initial period, peaks in N and P exports were also observed in association to intense rainfall events. These results thereby show that broader time scales are useful to gain insight into the soil fertility losses in burnt forest areas.

Although micro-plots can provide a rapid characterization of the hydrological and erosion response in burnt forest areas, the results of this study should be analysed with some caution as micro-plots usually have some limitations regarding the representativeness of post-fire hydrological and erosive processes at the field scale. Regardless of these constraints, the present study can be viewed as an important contribution for a better understanding of post-fire nitrogen and phosphorus exports in the Mediterranean region, where wildfires are expected to become more frequent as a result of climate changes. Studies at larger spatial scales are also recommended for a comprehensive understanding of nutrient dynamics after wildfires and assessment of post-fire erosion risks, which has important implications for the recovery process of burned Mediterranean forests as well as for post-fire land management.

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Chapter 6 - General conclusions

The present study focused on post-fire nutrient mobilization by overland flow, and in relation to soil nutrient stocks, focusing on several features, with different nutrients:

(i) Short-term variation of base cations losses in contrasting slopes in terms of vegetation (eucalypt vs. pine) and parent material (granite vs. schist), at micro-plot scale and slope scale, with comparison to unburnt slope only at slope scale; in a selection of some rainfall events over the six-months monitoring period (Chapter 2);

(ii) Short-term variation of nitrogen losses in contrasting slopes in terms of vegetation (eucalypt vs. pine) and parent material (granite vs. schist), at micro-plot scale, over a six-months monitoring period (Chapter 3);

(iii) Short-term variation of phosphorus losses in contrasting slopes in terms of vegetation (eucalypt vs. pine) and parent material (granite vs. schist), at micro-plot scale, over a six-months monitoring period (Chapter 4);

(iv) Temporal and spatial variation of nitrogen and phosphorus losses in contrasting slopes in terms of slope aspect, in eucalypt plantations, at micro-plot, over a twenty-months monitoring period (Chapter 5).

The fact that this work was carried out in the Mediterranean Basin is important since this region coincide with mountain areas where the soils are often weakly developed and poor in nutrients, regardless of their abundant vegetation. Also important for anticipating the impacts of recurrent fires on soil productivity because fire frequency is expected to increase in the future as a result of climate changes.

The main conclusions from the results obtained in Chapters 2 to 5 are summarized as follows:

i) the existence of a protective litter layer (i.e. of scorched pine needles) at the burnt pine site considerably reduced post-fire N export compared to the burnt eucalypt site, mainly by decreasing overland flow generation and the associated sediment losses. This information can be considered relevant for post-fire land management since it emphasizes that spontaneous mulching can be highly effective to reduce soil (fertility) losses and, thereby, will make further soil conservation measures superfluous.

ii) overland flow and soil (fertility) losses were markedly lower at the eucalypt site on granite than at that at the eucalypt site on schist, probably due to the coarser texture and, thus, higher infiltration capacity of the granite soils. This parent material-related difference in post-fire erosion risk is important for defining priorities in post-fire land management and, in particular, for the application of soil conservation measures such as mulching.

iii) overland flow and soil losses were also markedly lower at the site facing south than at that facing north. The pre-fire conditions could also have contributed to this difference, since the site facing north was having a logging operation at the time of the fire. This operation could have promoted forest soil disturbances, such as affecting soil infiltration capacity, and increased the amount of biomass available on the ground, enriching even more the nutrient-rich ash layer, contributing for the distinctly losses between sites;

iv) nutrients exports were particularly intense in the two months after fire but after this initial period, peaks in nutrients concentrations were also observed in association to intense rainfall events. These results suggest that wider time scales (i.e. wider than 6 months) are needed to evaluate the full extension of wildfires on forest lands. Nevertheless, it seems reasonable to recommend that post-fire management efforts should focus on the first 3 months after fire, to minimize the loss of soil fertility and degradation of burnt forest areas.

v) scale size is an important factor when studying the effects of wildfires on soil degradation, since different responses were observed at micro-plot and slope scale. At smaller scales, cation losses were higher than at larger scales, possibly because runoff and erosion decreases at larger scales as a result of changes in the soil infiltration patterns. These findings confirm the idea that although micro-plots may be suitable to quickly characterize the hydrological and erosion response in burnt forest areas, studies carried out at a larger scale are probably closer to reality due to a better representation of the natural connectivity within forest systems.

Studies at broader spatial scales, as well as wider time scales, are therefore recommended to assess the effective risk of post-fire soil fertility loss, which has important implications for the recovery process of burned Mediterranean forests as well as for post-fire land management.

The present findings are viewed as an important contribution to the current knowledge of post-fire nutrient mobilization and redistribution and of the resulting soil degradation in the Mediterranean Basin, especially since such information continues to be scarce for this region and since Mediterranean soils are typically nutrient poor. Future studies are, however, recommended to address broader spatial scales as well as wider time scales to fully understand post-fire nutrient dynamics and to assess the effective risk of post-fire soil fertility loss, which has important implications for the recovery process of burned Mediterranean forests as well as for post-fire land management.