



Wildland fire ash: Production, composition and eco-hydro-geomorphic effects



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ABSTRACT

Fire transforms fuels (i.e. biomass, necromass, soil organic matter) into materials with different chemical and physical properties. One of these materials is ash, which is the particulate residue remaining or deposited on the ground that consists of mineral materials and charred organic components. The quantity and characteristics of ash produced during a wildland fire depend mainly on (1) the total burned fuel (i.e. fuel load), (2) fuel type and (3) its combustion completeness. For a given fuel load and type, a higher combustion completeness will reduce the ash organic carbon content, increasing the relative mineral content, and hence reducing total mass of ash produced. The homogeneity and thickness of the ash layer can vary substantially in space and time and reported average thicknesses range from close to 0 to 50 mm. Ash is a highly mobile material that, after its deposition, may be incorporated into the soil profile, redistributed or removed from a burned site within days or weeks by wind and water erosion to surface depressions, footslopes, streams, lakes, reservoirs and, potentially, into marine deposits.

Research on the composition, properties and effects of ash on the burned ecosystem has been conducted on material collected in the field after wildland and prescribed fires as well as on material produced in the laboratory. At low combustion completeness (typically $T < 450$ °C), ash is organic-rich, with organic carbon as the main component. At high combustion completeness ($T > 450$ °C), most organic carbon is volatized and the remaining mineral ash has elevated pH when in solution. It is composed mainly of calcium, magnesium, sodium, potassium, silicon and phosphorous in the form of inorganic carbonates, whereas at $T > 580$ °C the most common forms are oxides. Ash produced under lower combustion completeness is usually darker, coarser, and less dense and has a higher saturated hydraulic conductivity than ash with higher combustion completeness, although physical reactions with CO_2 and when moistened produce further changes in ash characteristics.

As a new material present after a wildland fire, ash can have profound effects on ecosystems. It affects biogeochemical cycles, including the C cycle, not only within the burned area, but also globally. Ash incorporated into the soil increases temporarily soil pH and nutrient pools and changes physical properties such as albedo, soil texture and hydraulic properties including water repellency. Ash modifies soil hydrologic behavior by creating a two-layer system: the soil and the ash layer, which can function in different ways depending on (1) ash depth and type, (2) soil type and (3) rainfall characteristics. Key parameters are the ash's water holding capacity, hydraulic conductivity and its potential to clog soil pores. Runoff from burned areas carries soluble nutrients contained in ash, which can lead to problems for potable water supplies. Ash deposition also stimulates soil microbial activity and vegetation growth.

Further work is needed to (1) standardize methods for investigating ash and its effects on the ecosystem, (2) characterize ash properties for specific ecosystems and wildland fire types, (3) determine the effects of ash on human and ecosystem health, especially when transported by wind or water, (4) investigate ash's controls on water and soil losses at slope and catchment scales, (5) examine its role in the C cycle, and (6) study its redistribution and fate in the environment.

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1. Ash in the Earth system

Vegetation fires have been an important natural process since the Late Silurian Period (420 Myr) when vascular plants first began to cover the land surface (Scott and Glasspool, 2006; Scott, 2010; Scott et al., 2014). Currently wildland fires affect 330–430 Mha of the global land surface every year (Giglio et al., 2010), which equates to over 3% of the Earth's vegetated land surface. They affect a wide range of land cover types across the globe including boreal, temperate and tropical forests, peatlands, shrublands and grasslands. Wildland fires are ignited naturally by lightning and also by humans both accidentally and to accomplish management objectives such as clearing, reduction of fuel loads or the reintroduction of fire into areas where fire has been suppressed (Pyne et al., 1996). Fire can be seen as an important factor in soil formation, and heat and ash production are the main drivers of the changes that fire exerts on soils (Certini, 2013).

Fire transforms fuels (i.e. biomass, necromass, soil organic matter) into materials with different chemical and physical properties. Following fire, a layer of ash from residues of this transformation covers the landscape either in patches (Fig. 1a) or by blanketing the soil (Fig. 1b). This particulate residual material is the focus of this review. Ash can have profound ecological, hydrological and geomorphological effects. For example, ash is of importance in several biogeochemical cycles, including the carbon (C) cycle (Santín et al., 2012), it modifies soil infiltration and runoff generation, and it affects erosion rates (Woods and Balfour, 2010; Bodí et al., 2012). Even after being removed from the soil surface by slope wash, wind erosion or dissolution, ash can be incorporated into the soil and can modify the physical and chemical soil properties that at the same time exert an influence on the soil microorganisms and vegetation germination and growth (Raison, 1979).

Research on the effects of fire on the landscape has paid relatively little attention to ash until recently. Ash is often rapidly (re)distributed and removed from burnt sites by wind and water erosion (Mataix-Solera, 1999; Cerdà and Doerr, 2008; Pereira et al., 2013a), which frequently occur before the commencement of post-fire field studies, so that the potential importance of ash can be overlooked. Studies regarding wildfires and prescribed fires have focused mainly on the effects of fire on vegetation recovery, soil properties such as water repellency, or runoff generation and erosion, all of which tend to be more readily evident and accessible to quantify and characterize than ash. Another reason for the limited attention to date may be the

multi-disciplinarity required for the study of ash. Ash is usually considered separately from soil, vegetation, charcoal or from the biogeochemical cycles of some nutrients. However, it is now recognized that ash is relevant to all of these aspects and should therefore be considered. Much of the scientific information available to date is gleaned from prescribed fires (e.g. Alexis et al., 2007, 2010; Arkle and Pilliod, 2010; Stoof et al., 2012) because scientists have the opportunity to instrument the area before it is burned and collect samples before and after the fire. Increasingly laboratory experiments (Raison et al., 1985a; Úbeda et al., 2009; Bodí et al., 2011a; Gabet and Bookter, 2011) are used to collect data under controlled conditions.

This review aims to provide a synthesis of the knowledge about ash from wildland fires (i.e. fires that affect managed and unmanaged areas), and the ash from prescribed or experimental fires and laboratory experiments where relevant. We first provide a definition of wildland fire ash and describe how it is produced and deposited on the ground. Then ash constituents are described, paying special attention to the organic fraction, which has seen little attention to date, followed by the physical properties of ash. Subsequently, we outline ash effects on different ecosystem components: nutrient cycles and soil chemical properties, the C cycle, soil hydrology and erosion, as well as water quality. We also briefly cover ash effects on plant germination and growth; however, a comprehensive review of this broad topic is beyond the scope of this present endeavor. Finally, we identify research gaps and highlight future directions regarding the study of ash produced during wildland fires.

2. Ash definition

In this review we define wildland fire ash as *the particulate residue remaining, or deposited on the ground, from the burning of wildland fuels and consisting of mineral materials and charred organic components*. Thus, we include the following components in our definition of wildland fire ash:

- (1) An organic fraction derived from the combustion of the aboveground vegetation and/or the surface organic-rich layer of soils, often called necromass or plant litter and duff, on top of mineral soil, or organic soils like peat. Sometimes, organic matter in the underlying mineral soil is also combusted and the interface between the original organic layer and underlying soil become indistinguishable (see Section 4 on ash sampling).



Fig. 1. a) Ash covering the soil only beneath *Pinus halepensis* trees after a wildfire in Spain (inset, Scott Woods measuring the diameter of an ash patch); b) a thick ash layer blanketing the soil surface following a conifer forest wildfire in Montana, U.S.A.

Most of the organic components of ash are part of the “pyrogenic C continuum” which includes the whole range of organic materials transformed to some extent by charring, from slightly charred vegetation to charcoal or soot (Goldberg, 1985; Masiello, 2004). In some cases the organic fraction of ash can also contain unburnt organic materials, which have not been chemically modified by the effect of fire, but have become part of the ash layer.

(2) An inorganic fraction consisting of silicates, oxides, phosphates, carbonates, sulfates, and amorphous phases that either exist as primary minerals in the plant materials or undergo a transformation as a result of the heating during fire (Ulery et al., 1993; Quintana et al., 2007; Vassilev et al., 2010). The silicate portion can include phytoliths, which are siliceous structures found in many species of plants (Albert and Cabanes, 2007; Morris et al., 2010). This fraction is often called “mineral ash” in the literature on wildland fire or heating (Smith et al., 2010).

(3) Mineral soil particles that originate from aeolian deposition to plant canopies and the soil organic layer or that are introduced into the organic layer by bioturbation or freeze/thaw cycles prior to fire (Frandsen, 1987). In addition, soil particles can be incorporated into the ash layer after post-fire rainstorm events (Woods and Balfour, 2010; Pérez-Cabello et al., 2012) or by bioturbation (Topoliantz et al., 2006).

(4) Exogenous chemicals such as mercury (Caldwell et al., 2000; Biswas et al., 2008) and radionuclides (Palouris et al., 1995; Gallaher et al., 2002) that were originally deposited from the atmosphere onto the vegetation canopy and soil organic layer and that survived volatilization during the fire. Though these chemicals are not derived directly from the original organic matter, and may only represent a very small fraction of ash, they can impart a distinct chemical signature to the ash (Smith et al., 2010).

Other definitions of ash have been provided by a range of disciplines such as sedimentology, ecology, coal studies or industries that produce combustion residues (Jones et al., 1997; Schmidt and Noack, 2000; Scott and Glasspool, 2007). It should be noted that in some cases these residues are not derived from vegetation, but from volcanic, waste or coal mining and processing activities.¹ Within the wildland fire research community a range of definitions is used. For instance Quill et al. (2010) defined ash as “a category of Thermally Altered Plant Matter (TAPM) that has been submitted to intense temperatures in the presence of oxygen, and has whitish color and relatively greater inorganic mineral content than the original matter.” Brewer et al. (2013) use the terms “charred residues” and “post-fire residues” to include all of the resultant products from combustion. Others have also defined ash as a vegetation combustion by-product, e.g. Raison (1979), Giovannini (1994), Forbes et al. (2006), Kinner and Moody (2010), Scott (2010) and Santín et al. (2012). The main difference between our definition and some of the other definitions of ash is the consideration of ash as consisting of more than residual mineral material left over from the combustion of organic matter.

3. Ash production, deposition and redistribution

The processes leading to ash generation by progressive heating and burning of fuel are complex (Pyne et al., 1996; Théry-Parisot et al., 2010). Complete combustion of organic fuels results in production and oxidation of volatiles or gases such as carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄) or nitrogen dioxide (NO₂), with only mineral residue remaining (i.e. “mineral ash”; DeBano et al., 1998). However, under most wildland fire conditions, where oxygen availability can be locally limited, combustion is incomplete and some of the fuel is charred. This incomplete combustion generates pyrogenic organic compounds. The term “pyrogenic organic matter” comprises all organic compounds formed, or transformed during fire, and includes a continuum of C-rich solid organic materials, from partially charred vegetal biomass through charcoal to soot (Goldberg, 1985; Schmidt and Noack, 2000). For instance, charcoal comprises larger particles that retain enough physical and chemical properties to identify its biomass source. On the other extreme of the pyrogenic continuum is soot, submicron particles that settle out in the atmosphere, formed by condensation as a secondary product from the hot gases present in flames (Masiello, 2004).

Wildland fires can burn under a combined set of conditions. During initial heating, thermal degradation (pyrolysis) releases volatile gases that promote combustion. In the presence of oxygen there is a flaming phase, where temperatures can be between 450 and 1400 °C and fire can spread rapidly, yielding a mixture of charred particles and mineral ash (Ormeño et al., 2009; Saura-Mas et al., 2009). Under conditions where oxygen is limited, smoldering combustion takes place at temperatures of 250–450 °C. The combustion process is more prolonged during this phase, typically consuming “stumps, logs, downed branches, and “belowground biomass” (duff, roots, and organic soils)” (Bertschi et al., 2003). In smoldering combustion, oxidation is more complete, more particulates and gas are released, and the end product is predominantly mineral ash (DeBano et al., 1998; Ormeño et al., 2009).

The quantity of ash produced in a wildland fire depends mainly on (1) the total burned fuel (i.e. fuel load), (2) fuel type and (3) its

combustion completeness.² For a given fuel load, a higher combustion completeness will reduce the ash C content, which will increase the relative mineral content, and reduce the total mass of ash produced (Úbeda et al., 2009). Within a fire, these parameters tend to vary spatially. In addition, biophysical conditions, such as soil microtopography, terrain topography, and exposure affect ash accumulation during and after the fire. Winds during and after burning can, for example, move ash from the production zone to other areas within or outside the fire perimeter (Spencer et al., 2003; Pereira et al., 2013a).

The thickness of the ash layer covering the ground can thus vary substantially in space and time, from discontinuous small quantities of ash in wildland fires with low fuel loads and high combustion completeness (e.g. surface grassland fires) to thick layers of ash following fires in, for example, forests with substantial forest floor fuel layers. Reported average ash thicknesses range from 0 to 50 mm (Table 1). Even within a single fire, the blanket of ash can be very heterogeneous, not only in depth but also in continuity. For example, a continuous ash cover (100%) has been reported by Cerdà and Doerr (2008), Woods and Balfour (2008) and Balfour and Woods (2013); Fig. 1b), whereas Lavee et al. (1995) reported a 30% cover and De Luis et al. (2003) found variable ash covers, from 30 to 64% increasing with fire severity (Fig. 1a).

The non-homogeneity of ash deposition and ash characteristics are not only reflected in the spatial coverage of ash, but also in the range of the ash color. Patches may consist of white, gray and black ash, depending on the combustion completeness. When white ash (the result of more complete combustion) forms, it is usually on top of a layer of black ash (Blank and Zamudio, 1998; Carvalho Jr. et al., 2001; Carvalho et al., 2002).

Ash may not remain on the soil surface for very long, since ash is highly mobile and in some cases ephemeral, depending on its properties (such as solubility, weight, particle size or density), terrain characteristics and meteorological conditions after the fire. Much of the ash might be redistributed or removed from a burned site within days or weeks after fire (Cerdà and Doerr, 2008; Pereira et al., 2013a). Ash can be incorporated into soils by downward migration (Pereira et al., 2013a). Woods and Balfour (2010) observed the presence of ash and charred material within soil pores by examining soil thin sections of experimentally burned plots of *Pinus ponderosa* and *Pseudotsuga menziesii* vegetation after rainfall simulations. Ash incorporation into soil can be enhanced by bioturbation, for example, by the action of organisms like earthworms (Topoliantz et al., 2006), and also by freeze–thaw cycles. We are not aware of any studies that have quantified ash movement in any detail, although Rumpel et al. (2009) made measurements from burned plots in Senegal to determine how much pyrogenic C gets incorporated into the mineral soil and how much is moved off-site in runoff. They found that 7–55% of pyrogenic C was subject to horizontal transport, and another 23–46% subject to vertical transport.

Some of the ash may be dispersed by wind, especially where high combustion completeness has resulted in small light particles of mineral ash. Mataix-Solera (1999) reported an almost complete removal of the ash layer after only one day when wind speeds reached 90 km h⁻¹ following an experimental fire in eastern Spain where shrubs and herbaceous species were burned. Pereira et al. (2013a) measured the evolution of the thickness of the ash layer at the hillslope scale over a 45-day period in a burned grassland area in Lithuania. Increases in ash thickness in some areas over time were attributed to ash redistribution by wind. After the first rains the ash was wetted, forming a crust on the soil surface (see Sections 5.1 and 7.4) and making the ash more resistant to entrainment by wind.

¹ References related to ash from the wood industry or fly ash from coal combustion (Ram and Masto, 2013) are not considered in this review unless indicated. Despite some similarities between ash from the wood industry and from wildland fires, the starting materials, combustion conditions, and temperatures are not sufficiently comparable (Someshwar, 1996; Augusto et al., 2008). Properties of wood ash are only considered here when the material has been burned under laboratory conditions that are similar to the field or laboratory conditions used in wildfire or prescribed fire research (e.g. Etiegny and Campbell, 1991; Someshwar, 1996; Demeyer et al., 2001).

² We have chosen the term “combustion completeness” to describe the degree of oxidation within a given fuel. The terms “fire severity” or “burn severity” are avoided here in as far as possible, because they do not necessarily relate closely to combustion completeness and describe the effect of a fire on ecosystem components, which includes, for example, not only the degree of fuel consumption, but also plant mortality or the changes to soil properties (Keeley, 2009).

Table 1

Reported average depths of various ash deposits in forested wildland fire sites and estimated pre-fire fuel loads.

Location	Average depth (mm)	Load (t ha ⁻¹)	Authors
New Mexico (USA)	50	— ^a	Cannon et al. (2001)
California (USA)	6–8	14–27	Goforth et al. (2005)
Eastern Spain	36	151	Cerdà and Doerr (2008)
Montana (USA)	19	71	Woods and Balfour (2008)
Colorado (USA)	12	63	Larsen et al. (2009)
Colorado (USA)	18	192.6	Ebel et al. (2012)
Victoria, AU	20	82	Santín et al. (2012)
Portugal	5	— ^a	Pereira et al. (2013a)

^a Bulk density not available.

Some ash is moved by surface runoff to surface depressions or footslopes (Novara et al., 2011; Santín et al., 2012; Pereira et al., 2013a; Fig. 2), to streams (Minshall et al., 1997; Ryan et al., 2011) and to lakes or reservoirs (Blake et al., 2006; Reneau et al., 2007), where it has the potential to affect water quality and aquatic organisms. Flood plain or debris flow deposits often contain ash (Agnew et al., 1997; Lindell et al., 2010), which might persist over thousands of years in depositional features like alluvial fans (Meyer and Wells, 1997; Elliott and Parker, 2001; Bigio et al., 2010). Ultimately, ash or some of its constituents can be incorporated into marine deposits (Herring, 1985; Shin et al., 2002).

4. Ash sampling and analysis procedures

Ash samples can be collected after wildland fires (e.g. Goforth et al., 2005; Bodí et al., 2011a; Balfour, in press), after prescribed or experimental burns (e.g. Ulery et al., 1993; Woods and Balfour, 2010; Pereira et al., 2011) or produced in the laboratory (e.g. Gray and Dighton, 2006; Balfour et al., 2009; Quill et al., 2010; Stoop et al., 2010).

Ash sampling following wildland fires or prescribed burns has usually been done as soon as it is feasible using transects (Hoefen et al., 2009), grids (Ebel et al., 2012; Pereira et al., 2013a), spokes (Hoefen et al., 2009) or a random approach (Bodí et al., 2011a), depending on the field conditions. A small trench can be created to assess the ash–soil profile to identify the ash layer and then the ash collection can be carried out using a sharp trowel, spoon (Brye et al., 2002;

Pereira et al., 2010; Balfour, in press) or a small vacuum device (Hughes et al., 2000). However, the ash–soil interface is sometimes difficult to identify and inclusion of mineral soil may occur during sampling, particularly where soils have a similar texture to ash or are organic rich (see also Section 2).

In the laboratory, ash has been produced in muffle furnaces (Úbeda et al., 2009; Bodí et al., 2011a; Hogue and Inglett, 2012; Balfour and Woods, 2013), or directly in aluminum pans (Soto and Diaz-Fierros, 1993; Stoop et al., 2010; Hogue and Inglett, 2012). These approaches have not followed a common methodology, using different heating durations e.g. 2 h (Gray and Dighton, 2006; Úbeda et al., 2009) or 20 min (Arcenegui et al., 2008; Bodí et al., 2011a); different initial moisture contents e.g. air-dried vegetation (Arcenegui et al., 2008) or oven-dried vegetation (24 h at 40 °C, Gabet and Bookter, 2011); and different fuel sizes e.g. ground vegetation (Gray and Dighton, 2006; Bodí et al., 2011a) or whole leaves (Úbeda et al., 2009; Quill et al., 2010). These different variables affect the ignition, combustion, and maximum temperature reached during heating, and therefore the characteristics of the resulting ash are not directly comparable between studies and may or may not be similar to ash from wildland fires. Therefore, caution is advised when comparing results from ash produced in the laboratory with ash produced in the field (Raison, 1979; Gray and Dighton, 2006; Bodí et al., 2011a; Hogue and Inglett, 2012). The study of ash produced in the laboratory using muffle furnaces is nevertheless thought to be valuable since production conditions can be controlled, with Pereira et al. (2010) suggesting some methodological standardization. For instance the fuel (leaves and small branches) should be cleaned with distilled water, dried at 24 h at room temperature and combusted for 2 h. Another method that creates combustion residues more similar to wildland fire ash appears to be laboratory fire in individual aluminum pans (Hogue and Inglett, 2012).

Once the ash is collected (or created), the methods used to analyze ash properties are largely the same as used for soil (Table 2), although some methods are more appropriate than others considering the nature of ash (see Sections 6 and 7). In addition, the chemical instability of some ash precludes samples from being reused following hydrological analysis, as the original characteristics may have been altered by hydration (Balfour and Woods, 2013).

Several imaging techniques have been used to study ash production and properties. High spatial resolution photography (HSRP) has proved to be very useful in monitoring ash evolution after a wildland fire



Fig. 2. Ash and sediments accumulated on a lower slope in the Sierra de Enguera (Spain) after a rain storm of 15 mm in 10 min, 2.5 months after a *Pinus halepensis* forest fire.

Table 2

Outline of the different methods used to analyze chemical and physical properties of ash.

Property	Method	References
Color	Chromameter (expressed in Munsell and in International Commission on Illumination notations) Munsell color chart ASD Field Spec Pro Portable field spectroradiometer Conventional gray scale chart with 20 scales (Tiffen Q-13)	Goforth et al. (2005) Úbeda et al. (2009), Bodí et al. (2011a, 2012), Pereira et al. (2010, 2012) Llovería et al. (2009), Roy et al. (2010) Roy et al. (2010)
CaCO ₃	Precipitation with barium chloride Manometer Bernard calcimeter Titration with NaOH to assess HCl that reacted with the carbonates Dry combustion in a TC analyzer (with prior heating 4 h at 450 °C to eliminate TOC)	Etiegny and Campbell (1991) Ulery et al. (1993), Goforth et al. (2005) Úbeda et al. (2009), Bodí et al. (2011b), Pereira et al. (2010, 2012) Bodí et al. (2011a,b) Santín et al. (2012), Dlapa et al. (2013) Etiegny and Campbell (1991)
pH and Electrical conductivity	Ratio 1:10 hydrochloric acid. Agitated on an orbital shaker at 300 rpm for one week until a constant pH was reached Ratio 1:1 and 2:1 (ash: dH ₂ O)	Goforth et al. (2005), Woods and Balfour (2008) Úbeda et al. (2009), Bodí et al. (2011b, 2012), Pereira et al. (2010, 2012, 2013b)
Cations	Ratio 1:6 (ash: dH ₂ O), agitated 6 h, filtered Leachate 25 g ash/100 mL distilled water; agitated 48 h; centrifuged; filtered; spectrometry analysis Solution 5 g ash/25 g of 0.1 M BaCl ₂ ; centrifuged 2 h; decanted; spectrometry analysis Digestion in HNO ₃ –HCl solution; spectrometry analysis	Etiegny and Campbell (1991) Etiegny and Campbell (1991), Woods and Balfour (2008) Etiegny and Campbell (1991), Gabet and Bookter (2011) Úbeda et al. (2009), Bodí et al. (2011b), Pereira et al. (2010, 2012, 2013b) Bodí et al. (2011a,b), Gabet and Bookter (2011), Goforth et al. (2005), Santín et al. (2012) Pereira et al. (2010, 2012)
Total N and C	Leachate 1 g ash/40 mL distilled water; settled 24 h; filtered; spectrometry analysis Elemental analyzer	Etiegny and Campbell (1991), Gabet and Bookter (2011), Goforth et al. (2005), Balfour and Woods (2013)
Total organic carbon (TOC)	Combustion-reduction by gas chromatography with a thermic conductivity detector	Etiegny and Campbell (1991), Gabet and Bookter (2011), Goforth et al. (2005), Balfour and Woods (2013)
Mineralogy	See Table 3 X-ray diffraction	Moody et al. (2009), Ebel (2012) Bodí et al. (2011b) Stoof et al. (2010), Bodí et al. (2011a,b), Gabet and Bookter (2011), Bodí et al. (2012), Balfour and Woods (2013)
Particle size	Scanning electron microscopy Sieving and shaking 15 min Gravimetry Laser diffractometry	Kinner and Moody (2008), Massman et al. (2008), Cerdà and Doerr (2008), Moody et al. (2009), Gabet and Bookter (2011), Bodí et al. (2012), Balfour and Woods (2013)
Density	Core samples (in some cases repacked in the laboratory)	Balfour and Woods (2007), Woods and Balfour (2010)
Particle Density	Pycnometer	Bodí et al. (2012), Balfour and Woods (2013)
Porosity	Thin section analysis From bulk density and particle density Vacuum saturation method	Balfour (in press)
Hydraulic conductivity	Rainfall simulation Minidisk Infiltrometer Falling head permeameter Constant head permeameter Air permeameter	Cerdà and Doerr (2008), Kinner and Moody (2008) Moody et al. (2009), Balfour (in press), Balfour et al. (in review) Bodí et al. (2012), Balfour and Woods (2013) Ebel et al., 2012 Balfour (in press)
Water retention	Pressure plate: 0.01, 0.02, 0.03, 0.04 and 0.05, 0.2, 0.3, 1.0, 2.0 and 5.0 bar Hanging column Dew-point potentiometer Relative-humidity-controlled chamber	Stoof et al. (2010), Balfour and Woods (2013), Ebel (2012) Ebel (2012), Balfour and Woods (2013), Ebel (2012) Ebel (2012)
Sorptivity	Sorptivity probe Tension infiltrometer	Balfour (in press), Balfour and Woods (2013) Balfour and Woods (2013)

(Pérez-Cabello et al., 2012). Remotely-sensed imaging (Smith and Hudak, 2005; Lentile et al., 2006; Smith et al., 2010), which detects spectral or color characteristics of the ash surface, provides the opportunity to assess changes that result from fire over larger spatial extents and allows trends to be monitored with time (Eidenshink et al., 2007). Since the reflectance or spectral values of ash, including pyrogenic C, are measured using these techniques, the quantity of ash production and degree of soil cover could be either measured directly or indirectly in a variety of ecosystems (Landmann, 2003; Smith et al., 2007; Lewis et al., 2011). Robichaud et al. (2007) discussed the advantages of hyperspectral remote-sensing techniques to help identify discrete ground cover components including ash. However, Kokaly et al. (2007) using Airborne Visible and Infrared Imaging Spectrometer (AVRIS) data to identify certain surface cover materials, pointed out the difficulty in distinguishing white ash from carbonate in underlying soils. Furthermore, as a layer of white ash is often found on top of black ash, the spectral properties of the ash surface layer may not necessarily be representative. Despite the extensive body of literature on remote sensing of the surface of burned areas (French et al., 2008; Holden et al., 2010; Picotte and Robertson, 2011), few explicit measurements of ash production exist across a range of ecosystems.

5. Ash chemical and mineralogical properties

There is currently no standard for the characterization of ash produced by wildland fires. In the laboratory, only a few studies have analyzed ash and the focus of these studies has been very diverse. Most studies that examine ash have focused on its chemical composition, especially on the composition of aqueous extracts of ash (e.g. Demeyer et al., 2001; Bennett et al., 2004; Pereira et al., 2012). The mineralogical composition of ash has been studied to a lesser extent (e.g. Ulery et al., 1993; Quintana et al., 2007; Balfour and Woods, 2013) and only recently has attention been directed to the organic component of ash (Scott, 2010; Quill et al., 2010; Santín et al., 2012) and its physical and hydrological properties (e.g. Kinner and Moody, 2008; Gabet and Bookter, 2011; Balfour and Woods, 2013). The current knowledge of the organic and inorganic constituents of ash is summarized in the following sections.

5.1. Organic constituents

Incomplete combustion, which typically occurs at temperatures below 450 °C, and thermal degradation of the organic matter in the absence of oxygen results in organic-rich ash (Quill et al., 2010; Santín et al., 2012). Organic C concentrations in ash range widely, from <1% (e.g., white ash from complete combustion of California vegetation, Goforth et al., 2005) up to more than half of the total ash mass (Table 3). Several wildland fire and wood combustion studies have equated total C content in ash to total, or pyrogenic, organic C (see for example review by Forbes et al., 2006). However, this simplification should be avoided because inorganic C, mainly in the form of carbonates, can be also an important contributor to the total C in ash (Ulery et al., 1993; Goforth et al., 2005; Úbeda et al., 2009).

A visual approximation can be made to estimate high or low organic content of ash. Charred organic compounds are dark colored (the term “black C” is usually used to describe pyrogenic C), whereas mineral ash tends to be light in color (White et al., 1973). Bodí et al. (2011a) found a positive relationship between these two properties in wildland fire ash from different Mediterranean forests: the darker the color, the higher the organic C content. Hence, fires with low combustion completeness will produce ash with higher organic C contents and darker colors. In contrast, in fires with very high combustion completeness, most organic C will be volatized with little C remaining in lighter-colored ash (Kuhlbusch and Crutzen, 1995; Pereira et al., 2012).

Much of the organic component of ash consists mainly of pyrogenic compounds, i.e. C-enriched (Dlapa et al., 2013), which are highly

aromatic and with hydrophobic nature although it may also contain some uncharred material (Scott, 2010). C is the major organic element in ash but other elements are also present in smaller proportions despite that during charring, organic nitrogen (N) is lost first then oxygen and hydrogen and lastly C (Almendros et al., 2003). Even if part of the organic N is lost (i.e. transformed into inorganic forms) some remains in the ash, mainly as heterocyclic compounds (Knicker, 2011). Regarding the characterization of the organic component of ash, the only study we are aware of to date has been that of Dlapa et al. (2013), who characterized ash produced in Mediterranean wildland fires of different fire severities using Fourier Transform-Infrared spectroscopy. They reported a predominance of hydrophobic chemical groups, both aromatic and aliphatic, within the organic fraction. Their study focused on the variability of the organic/inorganic ratio with fire severity and the variability within the organic fraction was not addressed. However, if we consider the general changes sustained by organic fuels during charring, we expect a decrease of O-alkyl C structures (i.e. polysaccharidic components such as cellulose) and an increase of aryl and O-aryl structures (aromatic hydrocarbons) with increasing charring temperatures (Baldock and Sermik, 2002). During wildland fires, this newly-formed pyrogenic aromatic fraction will be mainly composed of small aromatic units rather than polycyclic aromatic graphitic-type structures (Knicker et al., 2008). The inherent chemical recalcitrance of pyrogenic organic matter confers on it a long residence time in the environment, with important implications for the C cycle (see Section 7.2). Moreover, pyrogenic N has been proposed as a potentially recalcitrant form of organic N in soil environments that affects the C cycle (Knicker, 2011).

The solubility of the organic component of ash is generally low (Quill et al., 2010; Zhao et al., 2010). For example, water soluble organic C in ash was <1% of total organic C after moderate to severe Australian forest fires (Santín et al., 2012). Even if the water-soluble fraction is quantitatively small in wildland fire ash, it can be a source of important organic pollutants in waters, such as small-sized polycyclic aromatic hydrocarbons (Smith et al., 2011b). In a study of ash produced from Australian tree species (*Eucalyptus tricarpa*, *Pinus pinaceae*, *Isolepis nodosa*, *Acacia pycnantha* and *Cassinia arcuata*) in the laboratory, Quill et al. (2010) found an increase of aromatic structures and a decrease of polysaccharides in the soluble organic fraction at higher formation temperatures. This is probably related to the overall lower solubility of the whole organic ash component produced at higher temperatures. It is important to bear in mind that the organic component in ash consists of a range of organic materials with different chemical and physical properties and, therefore, different fates and behaviors in the environment (Santín et al., 2012). Hence, for a full understanding of the hydro-geomorphic effects of wildland fire ash, consideration of this complex component is needed, particularly its quantification and characterization in relation to ash production conditions and other ash properties. For example, Dlapa et al. (2013) found that an organic/carbonate ratio >2 (usually found in ash from fires with low combustion completeness) is associated with a water repellent behavior of ash. They consider that the organic component is the main source of hydrophobic surfaces, which has implications for post-fire hydrogeomorphic responses related to ash hydrophobic behavior.

5.2. Inorganic constituents

As temperature increases from 350 °C to 450–500 °C, oxidation is more intense, organic compounds are reduced (Fig. 3, Table 3; Quill et al., 2010; Hogue and Inglett, 2012; Balfour and Woods, 2013) and ash color becomes lighter (Lentile et al., 2009; Hogue and Inglett, 2012; Pereira et al., 2012). The pH of ash water-extracts increases by two to three units and the electrical conductivity of this ash slurry also increases as a result of the solubilization of major elements contained in ash (Ulery et al., 1993; Pereira et al., 2012). Depending on the plant species and ecosystems affected, the inorganic constituents are mainly calcium (Ca), magnesium (Mg), potassium (K), silicon (Si), and, in

Table 3

Total organic carbon concentration (TOC %) and quantification methods used for wildland fire ash and laboratory-produced ash.

Fire description	TOC (%)	Method ^a	Reference
California (USA). Wildfire, <i>Adenostoma fasciculatum</i>	38	Loss on ignition (700 °C)	Christensen (1973)
Australia. Low intensity prescribed burn (gray ash), <i>Eucalyptus pauciflora</i> forest	17.3 (wood) 55.0 (twig) 11.7 (thick bark) 14.9 (thin bark)	Loss on ignition	Raison et al. (1985a)
California (USA)	0	TOC = TC – TIC ^b	Ulery et al. (1993)
Prescribed fire Oak grassland	0	TC = dry combustion	
Wildfire, Ponderosa Pine forest	2.08	TIC = Manometer	
Wildfire, Mixed Conifer forest			
Northeast Victoria (Australia)	21	Loss on ignition (800 °C, 18 h)	Bennett et al. (2004)
Wildfire			
California (USA)	0.69 (w) ^c	TOC = TC – TIC ^b	Goforth et al. (2005)
Mixed coniferous forest, high tree density	4.83 (b) ^c	TC = dry combustion (carbon analyzer)	
Pine Oak woodland, low tree density	0.39 (w) ^c 6.63 (b) ^c	TIC = Manometer	
Colorado (USA)	14.7	Loss on ignition	Larsen et al. (2009)
High severity wildfire			
<i>Ponderosa Pine forest</i>			
Montana (USA)	28.2	Loss on ignition (550 °C, 4 h)	Balfour and Woods (2007), Woods and Balfour (2010)
Controlled fire	43.4		
(fuel up to 5 cm diameter):			
<i>Pseudotsuga menziesii</i> , <i>Pinus ponderosa</i> and <i>Larix occidentalis</i>			
<i>Pinus contorta</i>			
Spain (4 wildfires), Israel (1 wildfire). Mediterranean forest	4.6–31.1	TOC = TC – TIC ^b	Bodí et al. (2011a)
(<i>Pinus halepensis</i> , <i>Quercus coccifera</i> , <i>Rosmarinus officinalis</i>)	10.8 (w) ^b 15.1 (g) ^b 23.8 (b) ^b	TC = TC analyzer TIC = titration method (MAPA, 1994).	
Victoria (Australia). Extreme severity wildfire, <i>Eucalyptus</i> forest of mixed species	6.0–8.5	TOC = TC – TIC ^b	Santín et al. (2012)
Victoria (Australia). Moderate to high severity wildfire, temperate rainforest	11.8–18.6	TC = dry combustion at 1050 °C. TIC = dry combustion at 1050 °C, with a prior heating 4 h at 450 °C to eliminate TOC	
Laboratory procedure	TOC (%)	Method	Reference
Open burned in large metal trays:			
<i>Bothriochloa ambigua</i> S. T. and <i>Danthonia</i> spp (straw from native pasture)	14	–	Raison and McGarity (1980a)
Wheat straw	2.5		
Burned in a barrel: <i>Pinus contorta</i> , <i>Pinus ponderosa</i> and <i>Pseudotsuga menziesii</i> wood	47–66	Loss on ignition (400 °C, 15 h)	Burns (2007)
Burned in an oven at 300 °C: <i>Eucalyptus tricarpa</i> bark and leaves	40–41	TOC analyzer	Quill et al. (2010)
Burned in an oven 400 °C: <i>Eucalyptus tricarpa</i> bark and leaves	0–0.2		
Burned in a muffle furnace: <i>Pinus halepensis</i> , <i>Quercus coccifera</i> and <i>Rosmarinus officinalis</i>	39–48 (250 °C) 27–62 (350 °C) 36–44 (500 °C) 38–44 (700 °C)	TOC = TC – TIC ^b TC = TC analyzer TIC = titration method (MAPA, 1994).	Bodí et al. (2011a)

^a Where burn temperature and time or analysis method are not given, they have not been stated in the original article.^b TC: Total Carbon, TIC: Total Inorganic Carbon.^c The letters represent the color of the ash. w: white, g: gray, b: black.

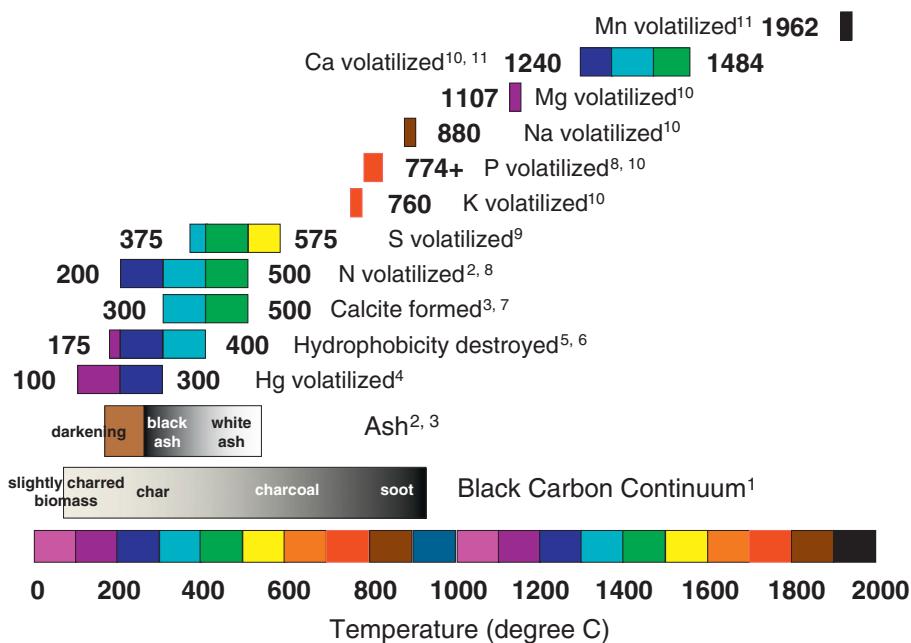


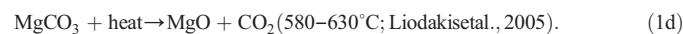
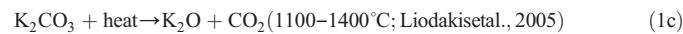
Fig. 3. Major temperature thresholds that affect ash and soil chemistry, based on Hungerford et al. (1991), with values from: ¹Kuo et al. (2008), inspired by Hammes et al. (2007); ²White et al. (1973); ³Úbeda et al. (2009); ⁴Biester and Scholz (1997), cited in Engle et al. (2006); ⁵DeBano and Krammes (1966); ⁶Dlapa et al. (2008); ⁷Wattez and Courty (1987); ⁸Hungerford et al. (1991); ⁹Tiedemann (1987); ¹⁰Wright and Bailey (1982); and ¹¹Weast (1980).

lower proportions, phosphorous (P), sodium (Na), sulfur (S), and other metals such as aluminum (Al), iron (Fe), manganese (Mn) and zinc (Zn) (Table 4; Qian et al., 2009; Pereira and Úbeda, 2010; Gabet and Booker, 2011). The relative proportion of some of these elements in ash increases as the temperature of combustion increases and the proportion of others decreases due to their lower temperatures of volatilization (Hogue and Inglett, 2012; Fig. 3).

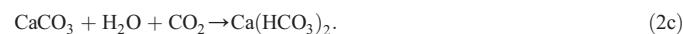
Between 500 °C and 1400 °C, provided that sufficient oxygen is available, organic compounds are almost completely combusted, leaving a light gray or white colored-ash (Ulery et al., 1993; Goforth et al., 2005; Qian et al., 2009). At these high temperatures, the ash from different plant species becomes chemically more similar as a result of thermal decomposition reactions. The main differences with temperature are the relative proportions of the minerals contained in the ash (Balfour and Woods, 2013).

The dominant constituents of ash produced at around 500 °C are silica and carbonate compounds, mainly calcium carbonate (CaCO_3), followed by magnesium (MgCO_3) and potassium carbonate (K_2CO_3). The high CaCO_3 levels result from the thermal decomposition (Eq. (1a)) of whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; Ulery et al., 1993), both calcium oxalates that naturally occur in the stems, roots and leaves of common plants (Misra et al., 1993; Monje and Baran, 2002; Liodakis et al., 2005), and lichens (Kloprogge et al., 2004).

Carbonate compounds will then dissociate (Eq. (1b)) to oxides at 580 to 1100 °C depending on the carbonate compound in question (Frost and Weier, 2004; Kloprogge et al., 2004; Echigo et al., 2005; Goforth et al., 2005; Plante et al., 2009; Quill et al., 2010; Pereira et al., 2012). While no distinct morphological changes occur for the thermal decomposition at temperatures lower than 580 °C, this transformation from carbonate to oxide (Eq. (1b)) is accompanied by a change in the crystal morphology from massive to sponge-like (Kloprogge et al., 2004).



Once ash is produced, chemical alterations associated with hydration have been documented via thermal gravimetric and X-ray diffraction analysis, especially for ash with a high degree of combustion completeness (Fig. 4) (Balfour and Woods, 2013). New carbonates can be formed by ash interacting with atmospheric moisture and CO_2 . For example calcium oxide (CaO) can be hydrated to form (Eq. (2a)) portlandite ($\text{Ca}(\text{OH})_2$), a process known in the cement industry (Dweck et al., 2000; Kantiranis, 2003; Sakai et al., 2004), which can subsequently absorb CO_2 to form (Eq. (2b)) carbonate (CaCO_3) or (Eq. (2c)) bicarbonates ($\text{Ca}(\text{HCO}_3)_2$ depending upon environmental conditions (Etiigni and Campbell, 1991; Demeyer et al., 2001).



These chemical reactions result in physical changes with an increase in particle size due to agglomeration (Steenari et al., 1999) or swelling of ash particles (Etiigni and Campbell, 1991; Demeyer et al., 2001; Stoof et al., 2010) and in other cases in the formation of an ash crust

Table 4
Chemical composition of various types of ash.

Species	Type of combustion	Elements (mg kg ⁻¹)						Reference				
		Ca	K	Mg	S	P	Na	Mn	Zn	Fe	Si	Al
<i>Quercus engelmannii</i>	Prescribed fire	385,000	42,000	9000	–	1000	1000	–	–	1000	1000	Trace
<i>Pinus ponderosa</i>	Wildfire	313,000	4000	7000	–	2000	1000	–	1000	3000	5000	Ulery et al. (1993)
<i>Pinus ponderosa</i> and <i>Pseudotsuga menziesii</i>	Wildfire	94,000	1000	1000	–	2000	Trace	6000	–	6000	4000	Ulery et al. (1993)
<i>Eucalyptus pauciflora</i> and <i>Eucalyptus dives</i> litter (leaves, bark and twigs)	Laboratory burn	104,000	19,000	20,000	3900	6000	1000	17,000	241	9800	–	Khanna et al. (1994)
<i>Pinus halepensis</i>	Muffle: 600 °C >2 h	192,000	130,000	88,400	36,100	31,300	17,800	11,200	2800	9100	25,500	–
<i>Pistacia lentiscus</i>	Muffle: 600 °C >2 h	261,000	133,000	64,000	30,300	23,900	22,900	14,600	3800	12,400	5700	–
<i>Quercus coccifera</i>	Muffle: 600 °C >2 h	259,000	107,100	77,900	26,200	17,300	5100	14,500	3700	12,300	11,300	–
Native grass (Montana)	Muffle: 450 °C, 3 h	16,940	101,203	3262	3285	10,498	291	1056	142	710	950	Gabet and Bookter (2011)
<i>Pinus ponderosa</i> limb	Muffle: 450 °C, 3 h	34,110	18,370	8724	1490	4642	Trace	1699	269	1562	198	2012
<i>Pinus ponderosa</i> limb	Muffle: 950 °C, 3 h	118,107	30,435	28,971	3399	18,855	2701	6631	143	3070	460	12,097

(with subsequent hydrological consequences, Sections 7.3 and 7.4) or wood-ash stone (Humphreys et al., 2004).

6. Physical properties of ash

Ash color is one of the most visible and diagnostic features of the combustion completeness of the fuel (Smith et al., 2005, 2007; Úbeda et al., 2009; Roy et al., 2010). Úbeda et al. (2009) using laboratory-generated ash from Mediterranean plant species and Goforth et al. (2005) using wildland fire ash from mixed-conifer forest in California, found that a positive correlation exists between chroma measured using a Munsell color chart (Munsell Color Company, 1950) and combustion completeness, which may be related to temperatures reached, duration of the fire and O₂ availability. Úbeda et al. (2009) highlight the fact that not all ash color falls within the gray scale spectrum. At low temperatures, the organic matter remaining is brownish as a result of dehydration and ash is reddish due to the oxidation of iron components. In general, the lighter (shades of light gray and white) the color of ash, the more complete the combustion of the original material.

Greater combustion completeness is also associated with a reduction of the mass of the fuel. At temperatures lower than 350 °C mass loss, mainly due to volatilization of water and elements, is as high as 50–60% (Úbeda et al., 2009). This loss progresses at different rates depending on the plant species and its flammability (Mutch and Philpot, 1970; Dimitrakopoulos and Panov, 2001), a trait that is characterized by ignitability, flame sustainability, combustibility, and consumability of fuel (White and Zipperer, 2010; Curt et al., 2011).

The particle size of ash also appears to depend on combustion temperature (Fig. 5, Table 5), based on laboratory burning experiments conducted by Balfour and Woods (2013), with fuel from *Pinus contorta*, *P. ponderosa* and *P. menziesii*, as well as controlled barrel burns conducted by Bodí et al. (2011b) with *Eucalyptus radiata* fuel. Between 350 and 700 °C, ash particle size becomes finer with increasing temperature due to more complete combustion and there is a transition from primarily organic fragments to primarily crystalline fragments of calcite and other minerals (Fig. 6, Table 5). However, at 900 °C, a further increase of particle size is detected and is related to crystal growth within ash particles after hydration (Balfour and Woods, 2013).

Measurements of the particle size distribution of ash from wildland fires are scarce and, therefore, it is difficult to reach definitive conclusions. Gabet and Bookter (2011) found that the wildland fire ash had a larger median particle size (D₅₀) than the ash produced in the laboratory, which is also evident from the available data compiled in Table 5. The lower temperatures in prescribed and low severity fires result in larger particle sizes, and within a specific fire there are differences in size according to the ash combustion completeness (Smith et al., 2005; Table 5). In addition, this trend in particle size with temperature is obscured by differences in the ash produced by different plant species. For example, in a moderate severity forest fire in Colorado, Kinner and Moody (2008) found that the particle size of the ash was finer in north-facing plots than in the south-facing plots (Table 6). They attributed the differences to the type of plant. Vegetation on the south-facing slope had larger needles and branches and combustion produced coarser ash on this aspect.

A recent study by Balfour and Woods (2013) indicated that changes in ash particle densities, which ranged from 1.27 to 2.88 g cm⁻³ (Table 5) reflected thermal alterations in ash composition. In their experiment, samples of *P. contorta*, *P. ponderosa* and *P. menziesii* were burned in a muffle furnace at different temperatures. Ash produced at 300 °C consisted primarily of low-density char particles (1.0–2.0 g cm⁻³), which are able to float in water (Mulleneers et al., 1999; Rumpel et al., 2006). Temperatures between 500 and 700 °C resulted in ash composed primarily of silica and carbonates (with densities of 2.56 and 2.71 g cm⁻³, respectively), while ash produced at temperatures >900 °C contained mainly silica and oxides with the greatest

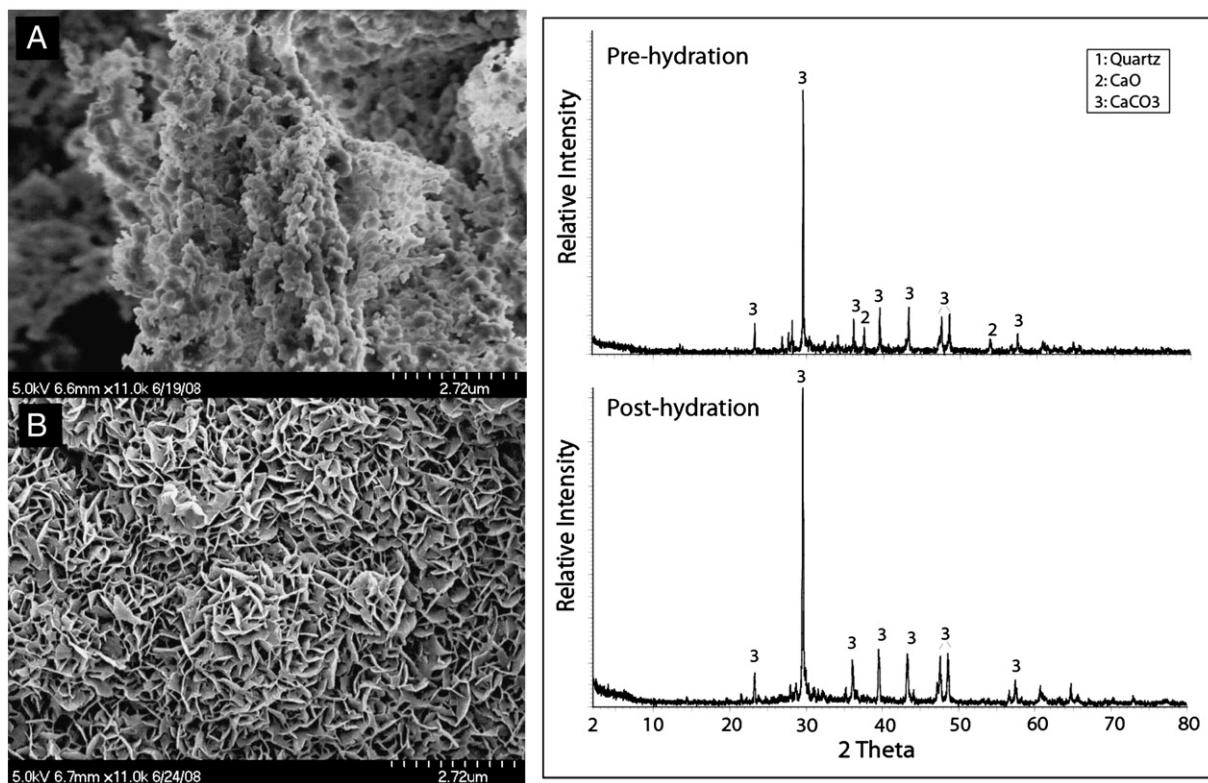


Fig. 4. Scanning electron microscope pictographs (left) and corresponding X-ray diffraction (XRD) peaks (right) of wildfire ash samples (a) before hydration and (b) after hydration respectively (Balfour and Woods, 2013). Note the loss of CaO peaks.

density (2.80 g cm^{-3}). Particle density of ash has also been shown to increase as the ash particles become smaller (Kinner and Moody, 2008).

The bulk density of ash is difficult to determine in the field due to the thinness and changeability of the ash layer with time. Reported bulk densities range from 0.18 to 0.62 g cm^{-3} , with higher values associated with thicker layers (Cerdà and Doerr, 2008; Goforth et al., 2005; Moody et al., 2009). Bulk density values for ash are in some cases considerably lower than the typical range of values for mineral soils, reflecting the high porosity of ash (60–90%) and its associated high capacity to store

water. A layer of ash can store a depth of water approximately equal to half its thickness before the initiation of runoff (Cerdà and Doerr, 2008; Woods and Balfour, 2010; Ebel, 2012); this has hydrological implications as discussed in Sections 7.3 and 7.4. Scanning electron microscope analysis conducted by Balfour and Woods (2013) indicated that the formation of surface micro-pores on ash particles, as well as other physical and chemical alterations associated with variations in temperature, may account for the exceptionally high porosity of some ash (Fig. 7).

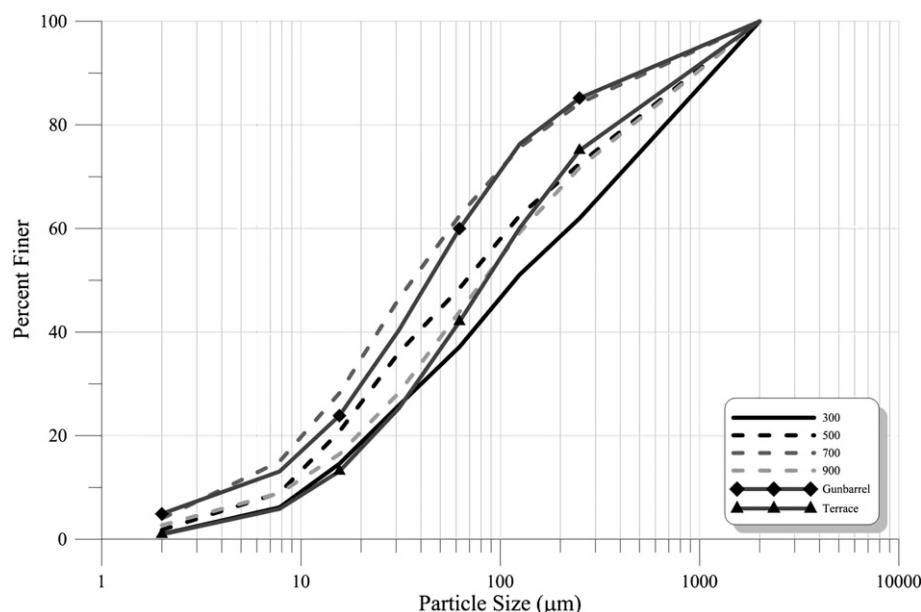


Fig. 5. Particle size distribution results for ash produced in the laboratory at varying temperatures ($^{\circ}\text{C}$) and ash from two wildfires (Balfour and Woods, 2013).

Field-based saturated hydraulic conductivity (K_{sat}) of ash is also difficult to measure; therefore the available data have been derived mainly from laboratory experiments on repacked ash cores. Saturated hydraulic conductivity of ash samples can vary by an order of magnitude (Table 5). Coarse ash produced at lower temperatures has the highest saturated hydraulic conductivity due to the higher quantity of charred material in the matrix (Balfour and Woods, 2013). However, there is no direct correlation between increasing combustion temperature and decreasing hydraulic conductivity; ash produced at higher temperatures (900 °C) in the laboratory and white ash containing oxides within wildland fire samples, show an order of magnitude increase in hydraulic conductivity compared to ash combusted in the 500–700 °C range.

The hydraulic conductivity and the high water storage capacity of ash indicate that ash has hydrophilic nature (Leighton-Boyce et al., 2007; Balfour and Woods, 2013). This wettability nature of ash has only been specifically reported on a few occasions based on wettability (water repellency) measurements (Cerdà and Doerr, 2008; Balfour et al., in review). There have been reports of ash being difficult to wet from Californian chaparral (Gabet and Sternberg, 2008), *Eucalyptus* sp. forest in Australia (Khanna et al., 1996) and *P. menziesii* forest in Montana (Stark, 1977). The existence of water repellent behavior (see review by Doerr et al., 2000) for certain types of ash was subsequently tested and confirmed by Bodí et al. (2011a). It was found in samples produced in a muffle furnace at temperatures lower than 350 °C with higher values of repellency found for ash from *Quercus coccinea* and *Pinus halepensis* than *Rosmarinus officinalis*. Water repellency was also found in 33% of the samples collected in 5 wildland fires in the Mediterranean forest, and appears to be mainly present in ash from fires of low severity. This water repellency was correlated with total organic C content of the samples ($r = 0.80$). Dlapa et al. (2013), using infrared spectroscopy, found that water repellency of ash was related to organic hydrophobic compounds (aromatic, aliphatic and carboxylic). In this case repellency was inversely related to the CaCO_3 content of ash; water repellent samples had more than double the amount of organic C compared to inorganic C content.

The physical properties of ash can also change when the ash is moistened. Ash produced at temperatures greater than 500 °C swells after wetting (Stoof et al., 2010). Other common physical and chemical transformations from ash wetting are crusting and hardening, especially for ash with high combustion completeness, due to the mineralogical

transformation of calcium oxide (CaO) (Balfour and Woods, 2013; see Section 5.1). This ash has a substantially lower hydraulic conductivity and infiltration capacity than unhardened ash (Cerdà, 1998a; Onda et al., 2008; Balfour et al., in review; Fig. 8).

7. Ash effects on ecosystem components

This section examines the effects of ash on different parts of the ecosystem, including effects on the physical and chemical properties of the soil, the nutrient cycles, the C cycle, hydrological processes, water quality, microbial activity and plant growth. Heterogeneity of ash properties and spatial distribution, along with post-fire ash evolution, increase the complexity of ash effects in space and time (Pereira et al., 2013b), and results in high variability of ash effects between and even within burned areas. The effects of ash are also difficult to separate from other effects related to fire, such as heat-induced changes to soil or loss of vegetation, although attempts have been made to examine the effects of heat and ash separately as well as their interactions (e.g. Raison and McGarity, 1980a,b; Khanna et al., 1996; Badía and Martí, 2003).

7.1. Nutrient cycles and soil chemical properties

Nutrients in vegetated terrain are stored in rocks, soil, necromass and living organisms, and can be transferred between these compartments along a variety of pathways (i.e. weathering, decomposition, and mineralization, or through the food chain) at different rates, depending on climate and ecosystem properties (Attiwill and Leeper, 1990; DeBano et al., 1998). After a wildland fire these elements are released much faster than would occur from biological decomposition, due to the intense mineralization induced by fire. Some may be rendered volatile or subject to particulate transfer in smoke. Raison et al. (1985b) measured losses after a low severity prescribed burn in *Eucalyptus* litter ranging from 25% of the total Mg to 75% of the total N (see also Section 5.2). The remaining elements will be released onto the ground in the form of ash (DeBano and Conrad, 1978; Raison et al., 2009). These elements in ash may be available for incorporation into the soil and uptake by plants, although some might be redistributed horizontally by wind or surface erosion or downwards by leaching into the soil (Boerner, 1982; Khanna et al., 1994; Cerdà and Doerr, 2008).

Table 5
Median particle size (D_{50} , μm), particle density (g cm^{-3}) and hydraulic conductivity (K_{sat} , mm h^{-1}) measurements of ash. The methodology used in each reference is provided in Table 2.

Type of fire	Plant species	Particle size D_{50} (μm)	Particle density (g cm^{-3})	Hydraulic conductivity ($K_{\text{sat}} = \text{mm h}^{-1}$)	Reference
Wildfire	<i>Populus tremuloides</i> , <i>Pseudotsuga menziesii</i>	750	1.7 (500–250 μm) 1.8 (250–63 μm)		Kinner and Moody (2008)
Intense wildfire	<i>Pinus ponderosa</i>	1020–1400		56	Woods and Balfour (2008)
Controlled fire	<i>Pinus ponderosa</i>				Woods and Balfour (2010)
Barrel: 491 °C, 5.8 h	<i>Pseudotsuga menziesii</i> , <i>Pinus ponderosa</i> , <i>Larix occidentalis</i> , <i>Pinus contorta</i>	147 and 244			
Barrel: 572 °C, 1.7 h	Duff	14		165	Gabet and Bookter (2011)
Barrel: 707 °C, 1.5 h	<i>Pinus ponderosa</i> needles	34			
Barrel: 1160 °C, 2.8 h	Grass	136			
Wildfire, white ash	<i>Pinus ponderosa</i> branches	34			
Furnace: 300 °C	Mainly <i>Pinus ponderosa</i>	46–64	2.5		
Furnace: 500 °C	<i>Pinus contorta</i> , <i>Pinus ponderosa</i> , <i>Pseudotsuga</i>	90		3600	Balfour and Woods, 2013
Furnace: 700 °C	<i>menziesii</i>	20		126	
Furnace: 900 °C		18		90	
Wildfire Spain	<i>Pinus pinaster</i> , <i>Quercus suber</i>	40		720	
Wildfire Spain	<i>Pinus halepensis</i> , <i>Quercus ilex</i>	18–134	2.05–2.36		
Prescribed fire	<i>Eucalyptus radiata</i>	17–123	2.41–2.52		
Barrel: 300 °C, max = 600 °C	<i>Eucalyptus radiata</i>	72	1.42		Bodí et al. (2011b)
Barrel: 500 °C, max = 1234 °C	<i>Eucalyptus radiata</i>	57	1.35		
Medium severity wildfire	<i>Pinus halepensis</i>	30	2.04		
Low severity wildfire	<i>Pinus halepensis</i>	70	2.6		
		180	1.47	137.75	Bodí et al. (2012)

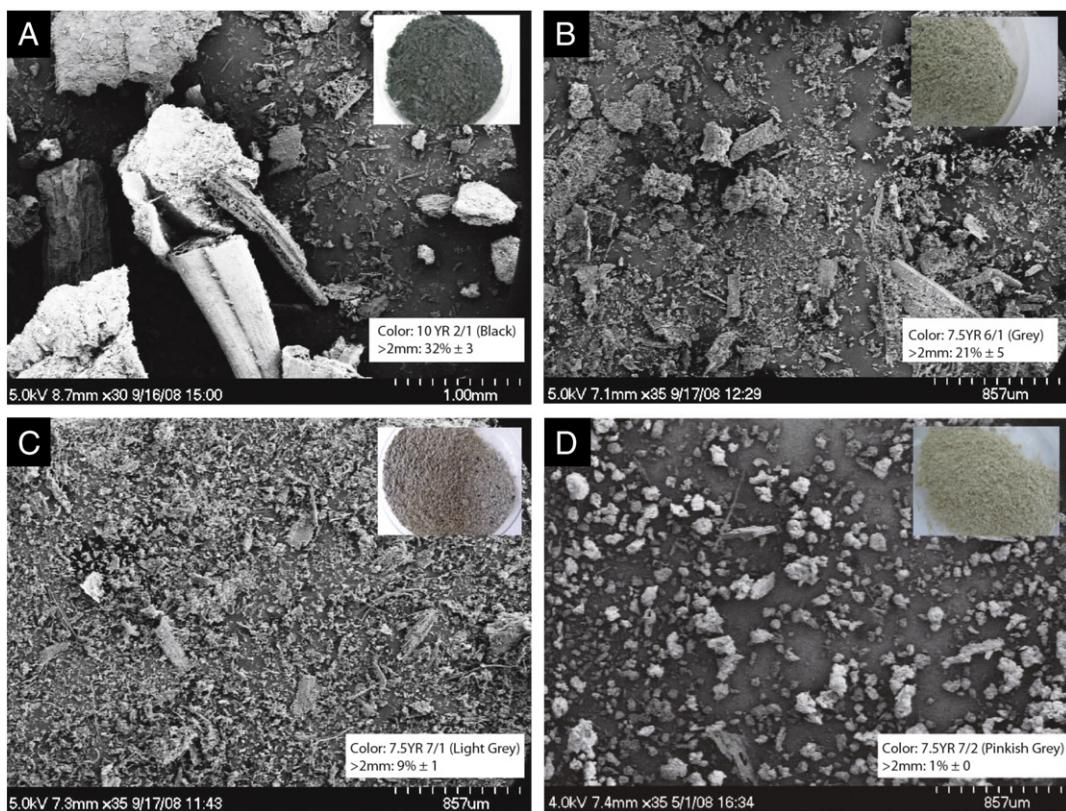


Fig. 6. Scanning electron microscope pictographs indicating relative particle shape and size for ash samples created in the laboratory, combusted at A) 300 °C, B) 500 °C, C) 700 °C and D) 900 °C. An image of the actual ash color is shown in the upper right corner of each pictograph. The Munsell classification and percentage of sample >2 mm is given in the lower right corner (Balfour and Woods, 2013).

In the case of ash produced at temperatures below 500 °C, a considerable amount of pyrogenic C might be incorporated into the soil by biological or physical mechanisms and become part of the soil organic matter (Carcaillet and Talon, 2001; Hammond et al., 2007; Eckmeier et al., 2010). Once the pyrogenic C is incorporated into the deeper mineral soil, it may be protected to some degree from further oxidation by microbiological decomposition and off-site losses by erosion (Rumpel et al., 2009). As a consequence of this pyrogenic C input from ash, the soil organic matter may change in its quality (for example, increasing its aromaticity). This alteration should not be confused with the in situ formation of pyrogenic organic compounds within the soil by burning of soil organic matter (González-Pérez et al., 2004). In addition, due to its porosity and high adsorption capacity, pyrogenic C can bind soil chemicals, which can influence microbial processes, the rate of decomposition of native soil organic matter and plant growth

(Keech et al., 2005; DeLuca et al., 2006; Ball et al., 2010). Elements or compounds such as chloride (Cl), phosphorous (P) and ammonium (NH_4^+) have also been found to increase after low severity wildland fires due to ash incorporation into the soil (Khanna and Raison, 1986; Marion et al., 1991; Khanna et al., 1994).

The incorporation of ash produced at temperatures above 500 °C is more likely to affect the inorganic component of the soil. Mineral ash may increase soil pH by up to 3 units, depending on the initial soil pH (Blank and Zamudio, 1998; Badía and Martí, 2003; Alauziz et al., 2004), with the magnitude of change being dependent on the type and quantity of ash added and the soil buffering capacity (Raison and McGarity, 1980b; Molina et al., 2007; Marcos et al., 2009). After ash deposition, substantial increases in Ca, Mg and K have been reported in numerous locations (Khanna and Raison, 1986; Andreu et al., 1996; Pereira et al., 2013b), with lower quantities of Na, Al, Fe, Mn, Zn and Si (Kutiel and Naveh, 1987; Thomas and Wein, 1990; Khanna et al., 1994). These increases have been detected particularly in the first 2.5–5 cm of soil (Marion et al., 1991; Ludwig et al., 1998; Molina et al., 2007).

Depending on the solubility of the ash, however, only some of the total ash incorporated into the soil will become part of the soil solution and thus available for plant uptake. The solubilization of nutrients in ash depends on: (1) the availability of water and moisture conditions after the wildland fire, with the first substantial storm releasing a major part of the nutrients (Grier, 1975; Soto et al., 1997; Lasanta and Cerdà, 2005) and on (2) the mineral components and pH of ash extracts, as oxides and bicarbonates are easier to dissolve than carbonates, and can persist three years after fire (Soto and Diaz-Fierros, 1993; Ulery et al., 1993; Pereira et al., 2012). Therefore, major cations such as Ca, Mg, Na and K are more soluble from ash produced at mean temperatures between 350 and 450 °C and S is more soluble from ash produced at temperatures higher than 450 °C (although this is strongly dependent on the burned plant species, especially at high temperatures; Úbeda

Table 6

Particle size distribution (%) of ash collected after wildfire in Colorado. Left: North aspect with *Populus tremuloides* and *Pseudotsuga menziesii*. Right: South aspect with *Pinus ponderosa*. The latter was produced from larger needles and branches, which resulted in coarser ash.

After Kinner and Moody (2008).

Particle size (mm)	Particle size distribution (%)	
	North aspect	South aspect
8–4	3.6	8
4–2	6	16.1
2–1	13.4	20.4
1–0.500	16.8	19.2
0.500–0.250	19.9	16.4
0.250–0.125	25.9	13
0.125–0.063	10.5	4.2
<0.063	4	2.5

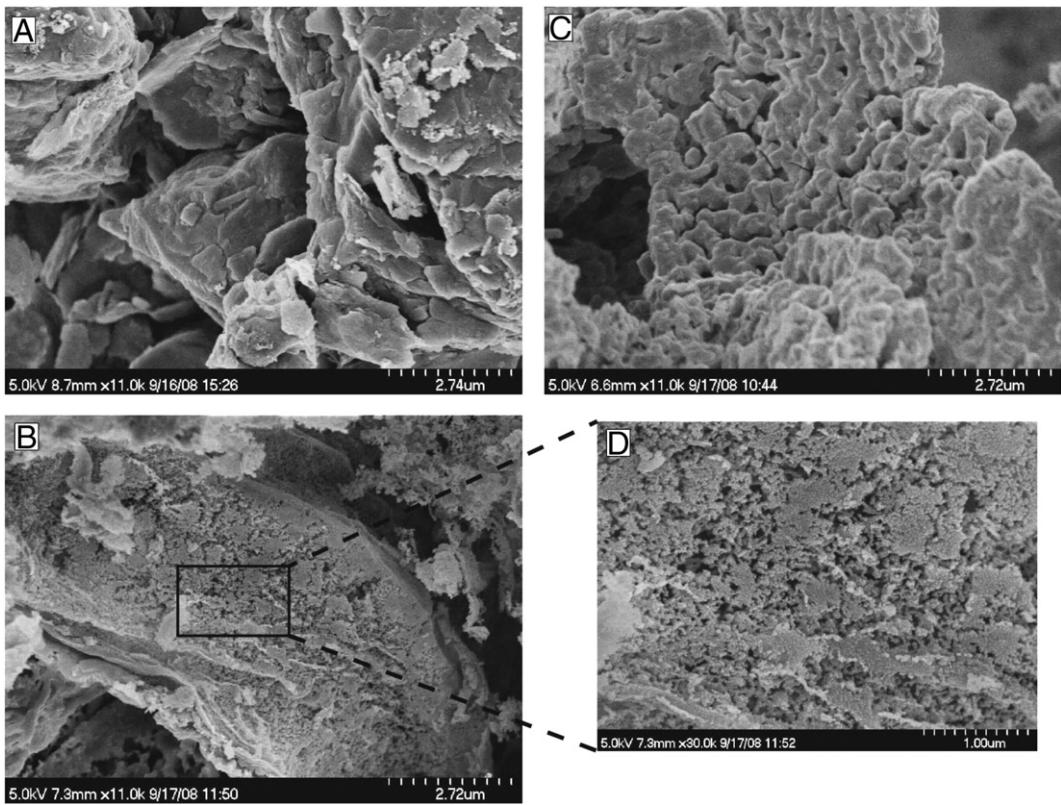


Fig. 7. Scanning electron microscope pictographs of surface porosity for laboratory ash combusted at A) 300 °C, B) 700 °C, C) 900 °C and D) magnification of the 700 °C sample highlighting intricate pore structure (Balfour and Woods, 2013).

et al., 2009; Pereira et al., 2012). Independent of the combustion completeness, Khanna et al. (1994) grouped ash elements into three categories according to their solubility: (1) most of the K, S and B (boron) were water soluble in part, while about 30% of the amount remained insoluble; (2) much Ca, Mg, Si and Fe dissolved progressively as more water was added to the ash; and (3) P was

mostly insoluble in water and required protons for dissolution, making it more available in acidic soils.

Once certain elements in ash are dissolved, their retention in soil depends on the type of soil, particularly its texture, pH, cation exchange capacity (CEC) and microbial activity (Marion et al., 1991; Khanna et al., 1996; Ketterings and Bighman, 2000) and these effects can vary with



Fig. 8. Left: Crusted ash produced in the laboratory at temperatures >900 °C. Right: Ash crust formed during high severity wildfire in Montana, USA (Balfour et al., in review).

time. Johnson et al. (2005) found greater exchangeable K^+ , Ca^{2+} , and Mg^{2+} in the soil after fire, which they attributed to the effect of ash after as much as 20 years. Higher pH values have been reported in burnt plots compared to unburned ones seven (Úbeda et al., 2005) and nine years (Humphreys and Lambert, 1965) after fire. In contrast, soil chemical changes only during the first year have been detected by Kutié and Naveh (1987), Soto et al. (1997) and Marcos et al. (1999) and within only 12 weeks by Ketterings and Bighman (2000) in a slash and burn fire.

The ash losses off-site by wind or water contribute to a reduction of the total nutrients in the ecosystem (Neary et al., 1999; Boerner, 2006; Raison et al., 2009) including soluble and non-soluble nutrients and also pyrogenic C (DeBano and Conrad, 1978; Thomas et al., 1999; Rumpel et al., 2009). Burned landscapes are particularly exposed to the agents of erosion due to the loss of protective vegetation and litter cover. Nutrient losses will depend on the wildland fire severity, the steepness of the terrain and the weather (wind and rainfall) during and immediately following the fire. Losses of nutrients due to ash erosion by water were estimated to be 3–4 orders of magnitude in a eucalypt forest in Portugal during the first three years after the wildland fire (Thomas et al., 1999), one order of magnitude higher from a burned plot compared to a control plot in a gorse scrubland in southern Spain two months after a prescribed fire (Carreira and Niell, 1995), and 22–25% (total C and N) and 5–12% (NH_4^+ -N, Ca, P and Mg) of the available nutrients in ash in an experimental fire in a shrubland in north-west Spain over a period of the first 13 months after the fire (Gómez-Rey et al., 2013).

Losses by percolation or lixiviation through the soil are limited compared with erosion, except in sandy soils that have little cation exchange capacity and insignificant runoff production (Khanna and Raison, 1986; Raison et al., 2009). Most of the nutrient losses after a fire were due to lixiviation in a *Pinus banksiana* forest in Canada (Smith, 1970), in a South Carolina pine forest (Lewis, 1974), and in a *Pinus radiata* forest in Spain (Marcos et al., 1999).

7.2. Carbon cycle

Wildland fires strongly influence C cycling and storage in a wide range of ecosystems (Turner et al., 1995; Schimel and Baker, 2002; Scott, 2009). Fires emit C stored in biomass, litter and soil into the atmosphere as well as convert C into pyrogenic C (see Section 5.1). Part of the material within the pyrogenic C continuum has an enhanced residence time in soils and sediments due to its intrinsically high resistance to environmental degradation. It is thus generally seen as a long-term C sink with important implications for the global C cycle (Masiello, 2004; Forbes et al., 2006), although abiotic and biotic decomposition of pyrogenic C have been documented (Abiven et al., 2011; Zimmermann et al., 2012).

Pyrogenic C represents a continuum of organic materials transformed by different degrees of charring and, hence, can be found in different post-fire pools, such as standing and down wood, soils or the ash layer (Scott, 2010). Despite the fact that ash can contain significant amounts of pyrogenic C (Section 5.1), the role of ash has rarely been considered in studies examining C budgets and fluxes from wildland fires (Forbes et al., 2006). For example, Santín et al. (2012) calculated a deposition of 4–10 Mg organic C ha^{-1} within the ash layer produced in moderate- and high-severity eucalypt forest fires. This is in the range of current applications of biochar (i.e. man-made 'pyrogenic C') to soils for soil amelioration and C sequestration (Blackwell et al., 2009).

To fully ascertain the potential role of wildland fire in C sequestration through the production of pyrogenic C, the mobilization and long term fate of the C contained in ash (and other pyrogenic components) need to be determined (see Section 3). In all these cases, where pyrogenic C accumulates in the soil, is eroded and buried in off-site sediments, or forms part of the recalcitrant pool of dissolved organic C in the ocean, wildland fire could act as a mechanism for long-term C

sequestration (Forbes et al., 2006; Santín et al., 2012; Jaffé et al., 2013). This has certainly been the case in the geological past, as demonstrated by the high charcoal content in bedrock strata (Scott, 2010; Belcher et al., 2013). In addition to pyrogenic organic C, the inorganic C component in ash could also contribute to C storage, however, little is known about its quantities and residence times.

7.3. Soil physical properties

The soil darkening by the addition of incomplete combusted ash (Badía and Martí, 2003) may affect significantly the thermal properties of the soil by decreasing its albedo. Massman et al. (2008), after measuring soil and ash thermal properties in a slash experimental burn, suggested that the presence of an ash layer (of non-reported color) insulates the soil proportional to the ash layer depth, thereby reducing extreme temperature that would otherwise occur in the soil.

Soil texture is not altered by the addition of ash to the soil, as reported by Badía and Martí (2003), who incorporated 1% and 0.5% of black ash by weight to soil (5 g kg^{-1} and 10 g kg^{-1}), and Stoof et al. (2010), who added 15.5% ash by weight (equivalent to 1 cm of ash over the soil). However, Durgin (1985) observed that ash leachate was able to disperse soil particles, but only for the most well-developed soils, which had more hydroxides and pH-dependent charge than less-developed soils. Similar effects of ash on soil particle size were reported by Giovannini (1994) in the hours immediately following the application of ash leachates to the soil; however, as the contact time with water increased, aggregation of finer clay particles into silt-sized fraction increased. This aggregation was also reported by Holcomb and Durgin (1979), who sprayed a plot with white ash leachates and observed that flocculation of clays reduced soil erosion. Pereira et al. (2013b) observed that the Sodium and Potassium Adsorption Ratio (SPAR) was high in ash produced at high combustion completeness, which means that the potential of ash solutions to induce soil clay dispersion and increase the vulnerability to soil erosion is high for that ash.

Ash incorporation can also modify soil hydraulic properties. Stoof et al. (2010), Ebel (2012), and Ebel et al. (2012) observed an increase in soil water retention due to the ash addition to the soil. Ebel (2012) hypothesized that ash incorporation into the soil could be a factor that produces an "homogenization" of soil–water retention across the landscape for high to moderate burn severities. The increase in soil water retention is also suggested to relate to the swelling nature of ash (Stoof et al., 2010). For a soil containing ash, the volume of water stored at saturation includes water stored in pores (i.e. soil porosity) and the volume of water absorbed by ash particles. However, ash is also reported to clog soil pores, thus reducing soil porosity and infiltration capacity (Mallik et al., 1984; Balfour and Woods, 2007; Woods and Balfour, 2008). Soil water repellency can be also modified by ash (Bodí et al., 2012). If ash covers the soil, a layer of wettable ash more than 5 mm thick was shown in laboratory experiments to reduce soil water repellency by increasing the hydraulic pressure and the contact between water and soil, and hence promoting fingered subsurface flow, especially during the first rain event after the fire. After the first rainfall event, and where the soil was still wet, ash did not produce a significant reduction on soil water repellency compared with bare soil. When ash is incorporated into the soil, it can increase or reduce soil water repellency depending on its wettable or water repellent nature (Bodí et al., 2011a). In the case of water repellent ash, the increase is likely to be especially important if ash is incorporated by dry mechanisms such as wind erosion and deposition, or bioturbation.

7.4. Soil hydrology and erosion

There have been few studies to date examining the effects of ash on overland and subsurface flow processes or on soil erosion compared to those focusing on ash effects on soil chemistry and nutrient cycles. This

may be a result of the difficulty in examining soil hydrological processes immediately after a wildland fire, when ash still covers the soil.

The layer of ash on the top of the soil is considered to act as a two-layer system and some authors have suggested that assumptions about soil and infiltration theories may need reconsideration because of the presence of a layer of ash (Kinner and Moody, 2010; Ebel and Moody, 2013; Moody et al., 2013). However, the effects of ash on soil hydrological responses are not straightforward and a variable response

of ash has been measured (Table 7). In some cases ash was found to reduce overland flow rates and in other cases the opposite.

Ash has been described to act as a storage reservoir for rainfall, preventing runoff (Cerdà, 1998b; Martin and Moody, 2001; Gimeno-García et al., 2007). This result has been confirmed by rainfall simulation experiments that specifically compare runoff and erosion rates obtained from ash-covered and control plots in a paired-plot strategy approach. Woods and Balfour (2008) demonstrated in western Montana that

Table 7
Results of rainfall simulation experiments that compare ash-covered soil to bare soil: time of the onset of overland flow (min), overland flow coefficient (%) and total sediment yield (g cm^{-2}).

Reference	Fire and forest information	Rainfall intensity (mm h^{-1} / min of duration)	Plot size (m^2)	Soil texture and type	Mean ash depth (cm)	Delay of the onset of overland flow compared to bare soil (min)	Overland flow coefficient (%)		Total sediment yield (gm^{-2})		
							Ash covered soil	Bare soil	Ash covered soil	Bare soil	
Leighton-Boyce et al. (2007)	Wildfire, Eucalyptus plantations (Portugal)	100/30	0.36	Loamy sand to sand, <i>Umbric Leptosols</i> and <i>Humic Cambisols</i>	Wettable soil Water repellent soil (WDPT > 5h)	3.9	10 ± 3	0	13.2 ± 5.7	0	10.5 ± 5.8
							18 Seconds	69.9 ± 9.3	99.7 ± 7.1	31.4 ± 5.8	114.7 ± 18.6
Woods and Balfour (2008)	High severity Wildfire, western Montana (USA)	1 month after the fire 9 months after the fire 12 months after the fire	75/60	0.5	Loam, <i>Typic Ustochrepts</i> from metasedimentary rocks	2.25	12 ± 10	16 ± 10	44 ± 12	274 ± 196	1040 ± 450
							-1.3 ± 1.8	28 ± 20	21 ± 8	414 ± 494	116 ± 80
							-2.2 ± 3.1	37 ± 14	37 ± 17	66 ± 66	<66
Cerdà and Doerr (2008)	High severity wildfire, <i>Pinus halepensis</i> forest (Spain)	55/60	0.25	Sandy loam, <i>Leptosols</i> and <i>Lithic Leptosols</i>	3.6	43	2.38	43.28	5	303.2	
Zavala et al. (2009)	Low severity prescribed fire, open heathland (Spain)	70/60	0.13	Loam	4.1	37 ± 13	4.2 ± 2	48 ± 18.8	2.6 ± 0.9	162.8 ± 200.3	
Larsen et al. (2009)	High severity wildfire, <i>Pinus ponderosa</i> forest (USA). Laboratory experiments	40/45	0.15	Granitic soil Micaceous soil	0.5	3 ± 2	17 ± 3.1	35 ± 5.8	106	160	
					1.2	6 ± 5	7.2 ± 0.8		73		
					0.5	2 ± 7	3.7 ± 0.7	7.8 ± 1.3	80	160	
					1.2	6 ± 5	3.2 ± 1.4		66		
Woods and Balfour (2010) ^a and Pseudotsuga menziesii (USA)	High severity controlled burns, <i>Pinus ponderosa</i> and <i>Pseudotsuga menziesii</i> (USA). 10 months after the controlled fire	Immediately after the controlled fire	80/60	0.5	Sandy loam soil Silt loam Sandy loam soil Silt loam Sandy loam Loamy sand wettable Loamy sand water repellent Loamy sand wettable Loamy sand water repellent Loamy sand wettable	1 cm white and black ash	3.8 ± 4.2	58 ± 28	16 ± 15	–	
						1 cm black ash	10.3 ± 9.4	49 ± 30	58 ± 19		
						<0.1	3.5 ± 3.6	34 ± 16	16 ± 15		
						<0.1	4.9 ± 6.3	47 ± 23	58 ± 19		
						0.5	-0.3 ± 5.9	49 ± 22	31 ± 22		
						2.5	7 ± 6.3	28 ± 7	45 ± 16		
						5	12 ± 8.4	17 ± 5	30 ± 25		
						0.5	-4.75 ± 1.2	1 ± 1	0.01		
						1.5	-9.5 ± 2.5	2.19 ± 2	0	0.01	
						3	-15.8 ± 3.9	2.75 ± 2		0.01	
Bodí et al. (2012)	Medium severity wildfire, <i>Pinus halepensis</i> forest (Spain). Laboratory experiments	82.5/40 First rainfall simulation 82.5/40 Second rainfall simulation 24h after the first 82.5/40 Second rainfall simulation 4 days after the first and in the oven at 25 °C	0.09		Loamy sand wettable Loamy sand water repellent Loamy sand wettable Loamy sand water repellent	77.94 ± 5	78.29 ± 5	0.12	0.45		
						1.5	9.3 ± 1.16	49.55 ± 5			
						3	16.2 ± 0.70	26.74 ± 2	0.16		
						0.5	0	0	0		
						1.5	-3	15.75	0	0.03	
						3	-4.3	12.86		0.03	
						0.5	0	72.83	0.52		
						1.5	2.6	7.07	24.81	0.01	
						3	2.4	16.65		0.37	
						0.5	-9.8	17.23	0.03		
						1.5	-7.6	16.02	0	0.08	
						3	-11.8	18.01		0.06	
						0.5	6.6	18.34	0.10		
						1.5	2.6	28.93	15.95	0.03	
						3	9.3	20.12		0.002	

^a Instead of onset overland flow it is considered time to ponding and instead of bare soil is pre-fire conditions.

ash can temporarily, but substantially, reduce post-fire runoff and erosion rates in the period immediately following severe wildland fires. They attributed the reduction and delay of runoff to the storage of water in the highly porous ash layer and to the fact that the ash protects the underlying mineral soil from surface sealing via rain drop impact. The reduction in erosion from ash-covered soils was primarily due to this reduction in runoff caused by the ash layer, and to the rain splash detachment reduction by ash soil protection. The same effect of ash delaying overland flow by storing water and the reduction in sediment yields has been reported for other experiments: immediately after a wildland fire in an *Eucalyptus* forest in Portugal under wettable and water repellent conditions (Leighton-Boyce et al., 2007), in a *Populus tremuloides* and *P. ponderosa* wildland fire in Colorado (Kinner and Moody, 2008), in a wildland fire in *P. halepensis* forest in Spain (Cerdà and Doerr, 2008), in a heathland in the south of Spain (Zavala et al., 2009), in a *P. menziesii*–*P. ponderosa* forest in Colorado (Ebel et al., 2012), in unburned plots covered with ash from a low severity wildland fire of *P. halepensis* (León et al., 2013), and in laboratory rainfall simulations using two different soils (developed over granitic and micaceous lithologies) and ash collected in a *P. ponderosa* fire using two ash thickness (0.5 cm and 1.2 cm; Larsen et al., 2009). As ash thickness increased, runoff coefficients, final runoff rates, and sediment yields decreased.

The large water storage capacity of ash and the consequent reduction of overland flow are especially important when ash covers water repellent soils. Bodí et al. (2012) measured in laboratory experiments that a layer of ash collected from a low severity *P. halepensis* wildland fire reduced overland flow from 1% for 5 mm of ash thickness, 28% for 15 mm and 52% for 30 mm of ash thickness. This was a result of water stored in the ash, and because the saturated layer of ash promoted the wettability of the soil by increasing the hydraulic pressure and the contact between water and soil, leading to fingered flow through the profile (Onda et al., 2008).

However, other studies have demonstrated that ash can increase overland flow for ash-covered soils (Table 7). Woods and Balfour (2010) covered burned plots with ash of varying thicknesses and noted that if the ash layer was thinner than 1 cm there was a reduction in the infiltration rates while layers of 2 cm and 5 cm delayed and reduced total overland flow. This phenomenon only occurred in the plots with sandy loam soil as the fine-sand sized ash particles clogged macropores of this soil type, reducing the overall infiltration by 40%, even 10 months after ash application. Thicker ash layers altered the number of hydrologically-active macropores contributing to infiltration, with thicker ash layers increasing the number of active micropores offsetting the reduced flux along each macropore (Woods and Balfour, 2010). Soil pore clogging by ash was also detected after a previous rain in a repacked coarse soil during a laboratory experiment (Bodí et al., 2012) although the same ash, that was collected in a low severity wildland fire in Spain, did not clog the pores of the clayey soils of an unburned field used in another experiment (León et al., 2013). Gabet and Sternberg (2008) also attributed the reduction in coarse soil infiltrability to pore clogging during a laboratory study of progressive debris flow using a flume.

Onda et al. (2008) detected increases in the runoff response by a factor of four relative to the first post-fire storm in a *Pinus muricata* and *P. menziesii* forest in California. In this case they attributed the increases in surface sealing to a low conductivity ash layer formed by the raindrop impacts that compacted and crusted the ash after the first storm. The formation of a crust with low hydraulic conductivity was also observed in plots covered with ash created at high severity and rich in CaCO_3 (Fig. 8, right; León et al., 2013), by Woods and Balfour (2008) 10 months after a fire in Montana and by Balfour et al. (in review) following a high severity wildland fire within Montana. These authors attributed the crust formation to chemical transformations (see Section 5.1) and raindrop compaction of the ash layer, which in turn led to a decrease in ash hydraulic conductivity by an order of magnitude.

Fundamentally, the variability in the response can be attributed to three main factors: (1) ash depth and type (e.g. composition, particle size, hydrological properties); (2) soil type (e.g. particle size, porosity); and (3) rainfall characteristics (timing, duration and intensity).

In order to account for variations in this two-layer system following a fire, the runoff generation mechanisms have been outlined in Fig. 9. The high porosity and low bulk density of ash layers allow them to hold a substantial quantity of water; therefore, the hydraulic conductivity and infiltration capacity are often higher than the local rainfall intensity (see Section 5). The only reported exceptions occur when ash is water repellent (Gabet and Sternberg, 2008; Bodí et al., 2011a) or when it has formed a crust (Fig. 8) (Cerdà, 1998b; Onda et al., 2008; Woods and Balfour, 2008; Balfour and Woods, 2013). The latter has been shown to occur particularly for ash containing oxides, which are capable of hydrating and recrystallizing as carbonate crust (Section 5.1; Balfour et al., in review). Ash crusts also tend to form following the first rainfall event, indicating the importance of rainfall-induced compaction. Regardless, the formation of an ash crust layer and a subsequent decrease in ash layer hydraulic conductivity may explain a shift to Hortonian (infiltration excess) overland flow, as suggested by Onda et al. (2008).

These exceptions aside, the permeability of ash is generally greater than that of the underlying soil. Ponding is therefore more likely to occur at the soil/ash interface (Kinner and Moody, 2010; Ebel et al., 2012) and the ash layer can be expected to delay overland flow and runoff proportionally to its thickness (Cerdà and Doerr, 2008; Woods and Balfour, 2008; Larsen et al., 2009; Zavala et al., 2009; Bodí et al., 2011a, 2012). Once ash is saturated, overland flow by saturation excess over the ash layer may occur as well as subsurface flow between the ash and soil (Bodí et al., 2012; Ebel et al., 2012). A number of scenarios may subsequently occur (Fig. 9):

- (1) The infiltration rate of the two-layer system can become similar or even higher than would be the case for bare soil (Cerdà and Doerr, 2008; Woods and Balfour, 2008; Larsen et al., 2009; Bodí et al., 2012). Thus overland flow may be reduced in the cases where the soil is water repellent and becomes gradually wettable (Zavala et al., 2009; Bodí et al., 2012), or in all the cases where ash prevents soil from self crusting and compacting (Woods and Balfour, 2008; Bodí et al., 2011a; Ebel et al., 2012).
- (2) Depending on the texture, particle size and pore structure of soil and ash, ash may clog the soil pores, thereby reducing the soil infiltration rates and increasing overland flow (Balfour and Woods, 2007; Larsen et al., 2009; Woods and Balfour, 2010). Ash can swell when wet, and if it swells prior to the incorporation into the soil, the ash will be unable to block soil pores of fine soils (Gabet and Sternberg, 2008).
- (3) Following prolonged or successive rains, ash may lose its structure, but still protect the soil from compaction and self-crusting (Moody et al., 2009; Kinner and Moody, 2010; Bodí et al., 2012), or may be entirely removed from a burned site. This would reduce or eliminate any two-layer effects, whereas the effect of ash incorporation into the soil pore space could be expected to be longer-lived (Onda et al., 2008; Woods and Balfour, 2010).

Overall, as described earlier the deposition, properties and redistribution of ash may exhibit significant spatial variability. Indeed, our knowledge of the production, properties and effects of ash to date is currently too limited to allow detailed predictions about its net off-site hydrological or geomorphological effects at hillslope or catchment scales. Only for large erosional events following intense storms (Cannon et al., 2001) and in association with peak flow conditions (Smith et al., 2012) has ash been observed to contribute to post-fire mass movements such as progressive debris flows. The mechanisms put forward by Burns (2007) and Gabet and Sternberg (2008) suggest that when ash has delayed the onset of overland flow and is completely

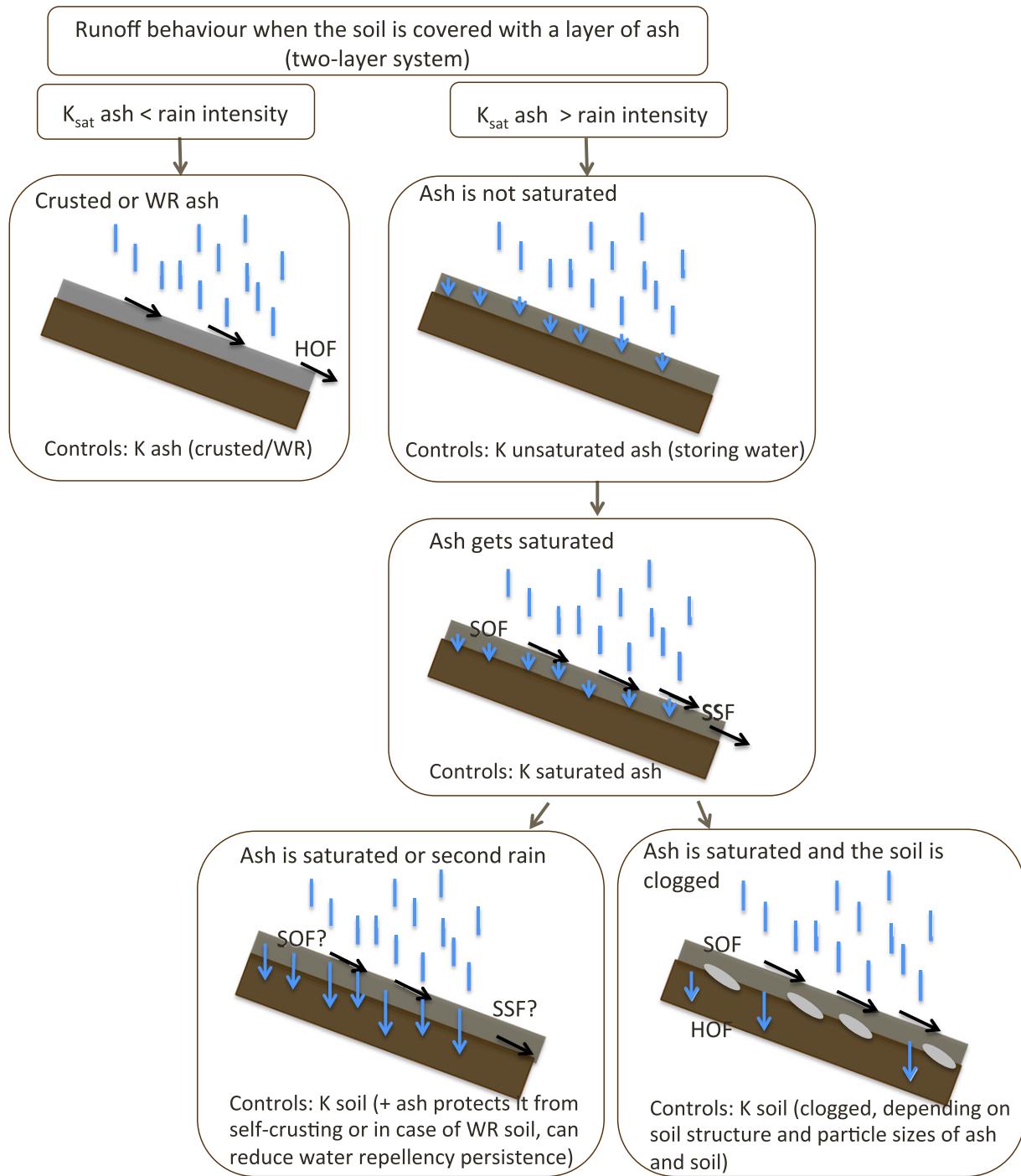


Fig. 9. Schematic diagram of the different runoff generation mechanisms for the ash-soil two layer system following wildland fire (K: hydraulic conductivity; HOF: Hortonian overland flow; SOF: saturation overland flow; SSF: subsurface flow; WR: Water repellent).

saturated, runoff can begin to flow downslope, incorporating additional ash and other fine particles. The fine particles increase the viscosity of the initial debris flow leading to a reduction in its settling velocity within the slurry, and causing the flow to become denser, exerting a greater shear stress on the hillslope. In turn, the addition of the fine material decreases the settling velocity of the coarser material, thus further increasing the density of the flow and its erosivity. This process, which evolves from an ash slurry into a debris flow, can deliver large volumes of sediment to valley floors. Massive movements of ash offsite have been reported by [Reneau et al. \(2007\)](#) where in a reservoir in New Mexico in a mixed conifer catchment of 16.6 km², the ash yield the first year after fire was 2.1 Mg ha⁻¹ (total 3567 Mg), which was 19%

of the fine sediment exported and accounted for more than 90% of total ash exports.

7.5. Water quality

The transport of ash and nutrients therein can affect downstream water quality. In many cases after an erosion event, the ash layer is only redistributed to the footslopes and in depressions, changing the water quality of the runoff. In other others cases ash and solutes will also reach streams, rivers, reservoirs or the sea ([Shin et al., 2002](#); [Ranalli, 2004](#); [Spencer et al., 2003](#)).

The specific effect of ash on stream or reservoir water quality is difficult to quantify, given that the contribution of ash is rarely distinguished from that of mineral sediment delivered to streams (Smith et al., 2011b). However, an increase in nutrients in streams and lakes due to ash after wildland fires has been documented. For example, Spencer et al. (2003) reported an increase from 5 to 60-fold in NO_3^- , NH_4^+ and PO_4^{3-} concentrations above background levels following wildland fire in Montana. Experimental evidence indicated that the early N pulses came mainly from diffusion of smoke gases into the stream waters while the phosphorus spikes originated largely from rapid leaching of ash deposited in the streams during the fire-storm (Spencer and Hauer, 1991; Gerla and Galloway, 1998). Cations and nitrates are carried to water bodies by overland flow or by leaching of ash and transport in subsurface flow to ground water (Hauer and Spencer, 1998; Lasanta and Cerdà, 2005; Ryan et al., 2011).

Even when only a small increase in post-fire sediment yield occurred during the first 15 months after a fire in the British Columbia, Petticrew et al. (2006) detected increases in the spatial and seasonal composition of the suspended sediments in the $<500\text{ }\mu\text{m}$ size fraction, which contained more organic matter. Ash enriched with cadmium from a wildland fire in *Pinus densiflora* was found to impact the growth and biochemical changes of the algal community in the eastern coastal waters of Korea (Shin et al., 2002).

Few studies have focused specifically on the effects of ash on water quality. A study by Earl and Blinn (2003) in New Mexico involved an experimental ash input (1140 L ash slurry delivered over a 1.25 h period) to a first order stream, and monitoring of streams in burned catchments. The experimental ash input resulted in an immediate increase in concentrations of major cations and ammonium, nitrate and soluble reactive phosphate, as well as turbidity, conductivity and pH, while dissolved oxygen decreased. Changes in water chemistry were short-lived and concentrations returned to pre-experiment levels within 24 h except for the soluble reactive phosphate, which lasted for one month. In the streams that drained burned catchments or adjacent catchments, concentrations returned to pre-fire levels within 4 months. In another study in New Mexico, Gallaher et al. (2002), Johansen et al. (2003) and Gallaher and Koch (2004) measured the chemistry of ash and streamflow containing ash after the 2000 Cerro Grande wildfire. This study found that post-fire stream flows had higher suspended sediment than pre-fire flows and that the suspended sediment consisted mainly of ash containing Ca, CN^- , K, NH_3 , PO_4^{3-} , Ba, Fe, Mn, ^{137}Cs , $^{239,240}\text{Pu}$ and ^{90}Sr . Levels of suspended sediment and associated chemicals declined to pre-fire levels by the fourth year of sampling after the wildfire. Some studies have found that nutrients returned to background concentrations within several weeks after the fire (Spencer et al., 2003; Lasanta and Cerdà, 2005), but other studies have reported that nutrient concentration continued increasing periodically in subsequent years, especially during spring runoff and snowmelt (Tiedemann et al., 1978; Prepas et al., 2003; Spencer et al., 2003; Allin et al., 2012).

Post-fire impacts on water quality can lead to problems with drinking water supplies, although in many cases this only occurs for one storm event and turbidity peaks rapidly return to baseline conditions (Smith et al., 2011b). However, this is one of the major issues affecting urban areas after wildland fires. Notable in this context are, for instance, the disruption to the supply of drinking water of major cities such as Canberra and others cities in Victoria (Australia) following multiple wildland fires in 2003 (White et al., 2006; Smith et al., 2011a). Municipal water supplies in the western United States and Canada have also been affected by ash and sediment from burned areas, leading to increased treatment costs and loss of reservoir capacity (Miller and Yates, 2006). A topic of current concern is the effect of post-fire runoff that contains ash on the treatability of drinking water, including effects on coagulation and disinfection (Emelko et al., 2011; Writer and Murphy, 2012; Sham et al., 2013).

7.6. Microorganisms, plant germination and growth

It is widely accepted that ash stimulates microbial activity due to the chemical changes produced when it is incorporated in the soil. According to the reviews of Raison (1979) and Mataix-Solera et al. (2009), this may be the cause of the post-fire increase in the bacteria/fungi ratio, given that a high pH favors bacteria. However, the changes seem to vary with soil type. Raison and McGarity (1980a) reported increases in respiration rates in sandy podzolic soils with any dose of ash addition, but for the more highly buffered Krasnozem soil, high rates of ash addition slightly decreased respiration rates while small amounts had no effect. In addition, ash did not stimulate the respiration rate in steam-sterilized podzolic soil, which indicates that ash exerts an influence on previously active soil biological populations.

The effects of wildland fire and laboratory-generated ash on plant germination have been studied for nearly a century; the earliest work seems to be that of Alway (1920) who carried out seed germination studies using burned peat. The majority of studies have been conducted on species from Mediterranean biomes, including those from the circum-Mediterranean region, and California. Many of the circum-Mediterranean studies are compiled in the on-line BROT database [Plant Trait Database for Mediterranean Basin Species] (Paula et al., 2009; Paula and Pausas, 2009). Those studies suggest that a thick layer of ash ($>2\text{ cm}$) has a negative effect on seed germination of a range of species, including *Pinus pinaster*, *P. radiata*, *Eucalyptus globulus* (González-Rabanal et al., 1994); *Avenula marginata*, *Calluna vulgaris*, *Erica umbellata* (González-Rabanal and Casal, 1995), *P. halepensis*, *Cistus salvifolius* (Ne'eman et al., 1993b; Izhaki et al., 2000) and *P. banksiana* (Thomas and Wein, 1990). However, ash solutions appear to have no effect (Ne'eman et al., 1993b; Escudero et al., 1997; Herrero et al., 2007). Hypotheses of the inhibition of germination by ash are that it may prevent water from reaching the seed given the high osmotic pressure in the medium to which some species are sensitive, or maybe the seed is poisoned by the toxic effects of certain ions (Ne'eman et al., 1993a) or by the alkaline pH of the solution (Thomas and Wein, 1990).

In contrast, regarding vegetation growth, experiments in greenhouses with different species (*Lactuca sativa*, Vlamis and Gowans, 1961; *Hordeum sativum* and *Medicago sativa*, Kutil and Naveh, 1987) have shown that plants are positively affected by the addition of ash nutrients such as Ca^{2+} , Mg^{2+} , K^+ , P and N fixation stimulated by fire during one year. This is especially important under ash beds because fertilization effects operate longer term, producing the 'ash bed effect' (Humphreys and Lambert, 1965; Raison, 1979; Chambers and Attiwill, 1994; Raison et al., 2009).

8. Concluding remarks and future research directions

Though the pace of research on the ash from wildland and prescribed or experimental fires has increased since the 1950s, and particularly over the last few years, many research questions and challenges still remain.

There is an ongoing challenge to develop standardized methods to define and characterize ash, including its color, physical properties, proportion of pyrogenic C, chemical and biological reactivity and persistence in the environment. At least three ocular methods have been used to classify the color of ash; visual inspection (e.g. Stronach and McNaughton, 1989; Parsons et al., 2010), use of a standardized gray scale (Roy et al., 2010), and use of the Munsell color chart (Úbeda et al., 2009; Bodí et al., 2011a; Pereira et al., 2012). All of these methods are subjective, therefore improvements in accuracy and precision are being realized through the use of spectroscopy (Goforth et al., 2005; Llovería et al., 2009), although this method can be time consuming when large numbers of samples are analyzed. There is also a further need to validate, calibrate and test measurements collected through

remote sensing (Landmann, 2003; Smith and Hudak, 2005; Kokaly et al., 2007) with on-the-ground measurements.

The ash research community needs to explore innovative techniques to characterize the particle size distribution of ash and the density of ash layers that cover the soil surface. Current methods to determine the particle size distribution of ash rely on sieving, and even when conducted gently, this approach can be expected to disrupt fragile particles that make up the ash matrix. Scientists are using different sieve sizes to process ash samples. Wanthonchai et al. (2008) sieved ash to 0.5 mm, Moreno and Oechel (1991) 1 mm and Stoof et al. (2010) to 2 mm, with char or charcoal considered to comprise the bigger organic particles. Settling techniques in aqueous solutions (used in the soil science field) have a distinct drawback because portions of the complex mixture that comprises ash are soluble, notably the oxides, hydroxides, and other meta-stable phases. It is critical to understand the production of ash by measuring its depth, density, and size fraction distribution compared to that of the underlying soil (Woods and Balfour, 2010).

It is necessary to develop standardized sampling techniques that allow cross comparison among sites and avoid inclusion of the underlying soil unless the burned surface soil forms part of the ash layer (e.g., Brye et al., 2002). Metrics also need to be standardized to understand the spatial variability of ash at the plot or hillslope scale (for example Pereira et al., 2013a). Significant variability can exist within an ash layer profile; for example, white ash can blanket underlying layers of black ash either as a result of the initial combustion process or by redistribution by wind. Also, individual pieces of charred material can exhibit a gradient of charring that leaves a fringe of white ash on the surface with blacker material underneath, or ash can lie atop uncombusted organic matter (Frandsen, 1987). Ash (re)distribution after the fire can have important and complex effects on soil hydrology that requires study in the future (Carvalho Jr. et al., 2001; Carvalho et al., 2002; Pereira et al., 2013a).

The effects of ash on soil erosion rates has been mainly studied by means of rainfall simulation experiments in small plots, and those measurements demonstrate that ash is a key factor at the 1 m² (pedon) scale, but it is unclear if ash exerts a similar control at hillslope or catchment scales (Woods and Balfour, 2010; Cerdà and Lasanta, 2005; León et al., 2013). Therefore, it is necessary to study the connectivity of patches of ash to make progress in understanding the role of ash in infiltration and the generation of runoff (Moody et al., 2013). This is why restoration, rehabilitation and erosion control measures need to take into account the role of ash in the fate of the ecosystem immediately after the fire, as well as the combination of ash and other cover, such as the needles, in the post-fire period (Pannkuk and Robichaud, 2003; Cerdà and Doerr, 2008). We have made progress in recent years in understanding the organic chemistry of pyrogenic organic C (Fernandes et al., 2003; Almendros and González-Vila, 2012), but studies that address the pyrogenic C in ash and its fate are scarce (Santín et al., 2012). Further research is needed regarding the amount and forms of C in ash, including studies characterizing its chemical and biological reactivity and degradability in soil and sedimentary environments.

The ash research community still needs to untangle the significance of the effects of maximum temperature reached during combustion (Gundale and DeLuca, 2006; Arcenegui et al., 2008) versus the duration of heating. Given the range of the volatilization temperatures of elements found in biomass, we might expect that the chemistry of ash from different plant species or plant tissues (i.e. bark, branches, and leaves or needles) in different underlying geologic substrates produced under high temperatures should be somewhat similar (Reimann et al., 2001; Balfour and Woods, 2013), although this is not always confirmed (Úbeda et al., 2009). We still lack sufficient data on the temperatures reached in the layer of organic matter on the soil surface during wildland fires and have even fewer data on the duration of heating. We also need to have a better understanding of the legacy of atmospherically-deposited elements and dust to fully understand the complex chemistry

of ash, and at the same time assess its effects on human health (e.g. Wolf et al., 2008). Though extensive studies have been conducted on the effects of wildland fire on N cycling, few studies have addressed the biogeochemical cycling of most elements as influenced by fire. This would be especially fruitful for elements like P, critical for the ecosystems functioning in many of the world ecosystems (Raison et al., 2009); Si (Blecker et al., 2006; Cornelis et al., 2011), which affects several soil processes and the long-term regulation of atmospheric CO₂; and Mn, common in plant tissues and surface soils and complexed with organic matter at temperatures >400 °C (Chambers and Attiwill, 1994), and which has been elevated in post-fire runoff in places like New Mexico and Colorado, U.S.A. (Gallaher and Koch, 2004; McCleskey et al., 2012), and has affected the treatability of water for municipal purposes.

While Balfour et al. (in review) have provided the first study documenting the evolution of ash characteristics in situ following the first month of post-fire activity, more ash studies are needed to address issues of how much ash stays on site after fire, especially how much is incorporated into underlying soil layers, compared to how much is eroded by wind and water and becomes incorporated into depositional environments located away from the site (Rumpel et al., 2009; Smith et al., 2011a; Gómez-Rey et al., 2013; Smith et al., 2013). Several activities, such as land and water supply management, risk reduction, and planning for societal and ecosystem resilience in the face of a changing climate, will benefit from the insights gained from the ash research community about topics such as nutrient cycling, C sequestration, and the generation of post-fire runoff and erosion.

Finally, though remarkable communication and collaboration among wildland fire scientists, including the subset of scientists who study ash, exist across the globe (Bento-Gonçalves et al., 2012), it is further recognized that research in large areas of the world that burn (e.g., Africa and Russia) is underrepresented. A future direction should be to enhance collaboration across the globe on the multidisciplinary topic of ash research.

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