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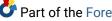
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Variations in wildfire ash properties and implications for post-fire hydrological response within Western North American ecosystems

Victoria Balfour The University of Montana

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1 2	VARIATIONS IN WILDFIRE ASH PROPERTIES AND IMPLICATIONS FOR POST- FIRE HYDROLOGICAL RESPONSE WITHIN WESTERN NORTH AMERICAN
3	ECOSYSTEMS.
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5	
6	By
7	VICTORIA NAIRN BALFOUR
8	
9	B.S., College of Charleston, Charleston, SC, 2002
10	M.S., University of Montana, Missoula, MT, 2007
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15	for the degree of
16	
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19	The University of Montana
20	Missoula, Montana
21	
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23	
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ProQuest LLC. 789 East Eisenhower Parkway P.O. Box 1346 Ann Arbor, MI 48106 - 1346 Variations in wildfire ash properties and implications for alterations in post-fire hydrological response within western North American ecosystems.

Chairperson: Dr. Ron Wakimoto

Abstract:

Within the Rocky Mountain region of the Western U.S.A the average number of wildfires over 40 hectares have quadrupled and the frequency of large wildfires (> 4,000 hectares) have increased seven times since the 1970's. The effect of this increase on resource management and ecosystem function is of increased interest to agencies and land managers within the region. The research presented in this dissertation aimed to contribute to the growing knowledge of post-fire hydrology, specifically with regards to the role of wildfire ash within recently burned ecosystems. Ash should not be considered a generic term, as it is an important element of post-fire landscapes, and should be categorized and taken into consideration when assessing post-fire ecosystems and hazards.

The main findings of this research were that saturated hydraulic conductivity of ash spans three orders of magnitude with some ash capable of decreasing an order of magnitude following initial hydration. More specifically, the hydrologic response of low- and high-combustion ash can prompt the formation of surface seals in post-fire systems by either creating a low conductive ash layer or a chemical ash crust layer. Mid-combustion ash, on the other hand, acts as a capillary barrier storing water thus explaining reported hydrologic buffering effects of ash layers. While numerous authors have previously reported the presence of an ash crust within post-fire ecosystems, this work is the first to document the formation of an *in-situ* ash crust within a month after wildfire activity. The formation of an ash crust decreased ash hydraulic conductivity by an order of magnitude, as well as significantly decrease ash layer bulk density and porosity. While raindrop impact increased the strength of an ash crust, raindrop impact alone is not sufficient to form an ash crust, instead mineralogical transformations must occur to produce a hydrologically important ash crust. Therefore, initial ash composition, the presence of oxides and a hydrating rainfall event are all necessary precursors for crust formation. The variations in initial ash characteristics as well as temporal alterations indicate that ash layers should be considered in modeling systems aimed at predicting post-fire infiltration response.

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134	Dedicated to Dr. Scott William Woods
135	(October 4, 1966 - April 7, 2012)
136	` , , , , , , , , , , , , , , , , , , ,
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139	From one Glaswegian to another,
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141	"Farewell to the mountains, high-cover'd with snow,
142	Farewell to the straths and green vallies below;
143	Farewell to the forests and wild-hanging woods,
144	Farewell to the torrents and loud-pouring floods.
145	My heart's in the Highlands, wherever I go"
146	–Robert Burns
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170	"Try to learn something about everything and everything about something"
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172	- Thomas H. Huxley (English Biologist 1825-1895)
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227	Table of Contents	
228		
229		Page
230	TITLE DAGE	•
231	TITLE PAGE	i
232 233	ABSTRACT	ii
233 234	ADSTRACT	ıı
235	COPYRIGHT PAGE	iii
236	COLINGIN TAGE	•••
237	DEDICATION	iv
238		
239	QUOTATION	v
240		
241	ACKNOWLEDEMENTS	vi - vii
242		
243	TABLE OF CONTENTS	viii - ix
244		
245	COMPLETE LIST OF TABLES AND FIGURES	x - xv
246	CHARTER 1 C 11 / 1 /	1 (1
247	CHAPTER 1: General Introduction	1 - 64
248	SECTION 1.0: What is a natural disturbance; is it detrimental or beneficial to	
249 250	ecosystems?	
250 251	1.1 Wildfire effects on long and short-term carbon cycling	
251 252	1.2 Wildfire effects on habitat variability1.3 Wildfire effects on aquatic ecosystems	
252 253	1.4 Wildfire effects on runoff and erosion	
254	1.4.1 The role of ash in post-wildfire runoff response	
255	1.4.2 The role of ash in post-wildfire erosion response	
256	1.4.3 The role of ash in post-wildfire management	
257	The The Total of Wall in pool with the management	
258	SECTION 2.0: What is ash and how is it formed?	
259	2.1 The source of ash	
260	2.2 Ash chemical properties: alterations associated with thermal	
261	decomposition and hydration	
262	2.3 Physical properties of ash	
263		
264	SECTION 3.0: Ecosystem effects of ash	
265	3.1 Effect of ash on soil properties	
266	3.1.1 Effect of ash on soil chemistry	
267	3.1.2 Effect of ash on soil physical properties	
268	3.1.3 Effect of ash leachate on soil characteristics	
269	3.2 Effect of ash on soil microbial activity and plant growth	
270	3.3 Effect of ash on water quality	
271 272	CHAPTER 2: Main Objectives of the Dissertation	65 – 67
, , ,	CLIAFIEN / IVIAII CHIECHVES OF THE LASSEHAHOH	n 3 — n /

273		
274	CHAPTER 3: Manuscript One 68 -	117
275		
276	Balfour, V.N. and S.W. Woods, 2013. The Hydrological Properties and the Effects of Hydra	tion
277	on Vegetative Ash from the Northern Rockies, USA. Catena 111: 9-24.	
278		
279	CHAPTER 4: Manuscript Two 118 -	- 154
280		
281	Balfour, V.N., in review. Determining ash saturated hydraulic conductivity and sorptivity wi	th
282	laboratory and field methods. Catena. Manuscript # 3065 submitted Sept., 2011	
283		
284	CHAPTER 5: Manuscript Three 155 -	- 200
285		
286	Balfour, V.N., S.H. Doerr and P.R. Robichaud, in review. The temporal evolution of wildfire	ash
287	and implications for post-fire infiltration. International Journal of Wildland Fire	·e.
288	Manuscript # WF13159 submitted Sept., 2011.	
289		
290	CHAPTER 6: Key Findings and Overall Conclusions of the Dissertation 201 –	207
291		
292	APPENDIX A: Publication List 207 -	- 210
293		
294	List of conference presentations and other co-author publications associated with	th
295	the presented dissertation research.	

TABLES AND FIGURES **CHAPTER ONE** Page Figure 1: A photograph showing the deposit of an alluvial fan following a punctuated sediment supply event from the Hayman Creek Wildfire, 2002. This PSS occurred shortly after the wildfire and obstructed flow for numerous years. This image was taken in 2010, and shows the active river (running left to right) has down cut the fan (Photo: Sierra Larson, USFS). Figure 2: Planview (upper) and longitudinal view (lower) of a typical channel response to the deposition of a PSS following a wildfire (Hoffman and Gabet, 2007). Figure 3: Conceptual sketches regarding the effect of ash thickness on macropore infiltration. In unburned areas macropore infiltration only occurs in ponded zones. With a thin ash layer the primary effect is pore clogging, and the infiltration flux is reduced. With a thicker ash layer pore clogging still occurs but the saturated ash layer increases the proportion of the plot area with macropore flow. This offsets the effects of clogging, increasing the overall infiltration flux (Balfour, 2007; Woods and Balfour, 2010). Figure 4: Schematic diagrams of runoff generation on forest-fire effected soil (HOF: Hortonian overland flow, SSSF: Subsurface storm flow, SOF: saturation overland flow; Onda et al., 2008). Figure 5: Polarized microscope images of burned thin sections taken within the upper 1-2 mm of the soil surface. Images A and B are of the same thin section, however, B was acquired under cross-polarized light to highlight the location of calcium carbonate ash. Image C is the magnification of another thin section emphasizing white ash filling spaces between black ash particles; the images was also acquired under cross-polarized light (Balfour, 2007). Figure 6: A replication of fire product terminology according to Jones et al. (1997). Figure 7: Ash samples ranging over a variety of colors (Bodi et al., 2012). Table 1: Ash particle density (P_p) , mean particle size (D_{50}) , total porosity (Θ_{total}) , bulk density (P_B), depth, field hydraulic conductivity (K_f), and laboratory saturated hydraulic conductivity (K) for wildfire ash samples. Only studies containing wildfire ash hydrological characteristics were included. Figure 8: A photograph of the Terrace Mountain wildfire, 2009 indicating a relatively thick homogenous ash layer deposited across the landscape.

342 343	CHAPTER THREE	
344 345	Figure 1: A site photograph prior to ash sampling with an inset of an ash trench for sampling collection; Terrace Mountain wildfire, 2009.	103
346 347 348 349 350	Figure 2: Dendrogram of cluster analysis results indicating similarities between all ash samples based on 12 ash characteristics (S, K_{sat} , Φ , >2 mm, D_{10} , D_{50} , P_{b} , P_{p} , pH, organic carbon, inorganic carbon, and N content).	104
351 352 353 354 355 356	Figure 3a: Scanning electron microscope pictographs indicating relative particle size shape and size for A) 300 °C, B) 500 °C, C) 700 °C and D) 900 °C laboratory ash samples. A picture of the actual ash color appears in the upper right corner of each pictograph with Munsell classification and the percentage of sample greater than 2 mm in the lower right corner.	105
357 358 359 360	Figure 3b: Particle size distribution results for all laboratory ($n = 9$ per temperature) and wildfire ($n = 3$) ash samples. Error bars have not been included to facilitate in the interpretation of the graph.	105
361 362 363 364 365	Figure 4: Representative X-ray diffraction patterns with main mineral peaks identified for laboratory ash types (300 °C, 500 °C, 700 °C and 900 °C). XRD analysis for low combustion ash was incomplete due to the high background noise associated with the elevated organic carbon levels.	106
366 367 368 369 370	Figure 5: Water retention curves for laboratory (300 °C, 500 °C, 700 °C and 900 °C; n = 9) and wildfire (Terrace and Gunbarrel; n = 3) ash samples. Values are averages for replications and straight lines were drawn to facilitate interpretation of the graph.	107
371 372 373	Figure 6: Boxplots of hydraulic conductivity and sorptivity results for all laboratory ($n = 9$ per temperature) and wildfire ($n = 3$) ash samples.	108
373 374 375 376 377 378 379 380 381 382	Figure 7: Thermogravimetric (TG) analysis of laboratory and wildfire ash before and after hydration; denoted by dry and wet respectively. TG results were interpreted according to mass loss equations; mass loss observed below 200 °C was equated to the loss of water adsorbed to ash particles, mass loss between 200 – 500 °C was primarily due to the combustion of organic carbon, mass loss in the 700 – 900 °C range was associated with the decomposition of CaCO ₃ and other carbonates (Misra et al., 1993; Liodakis et al., 2005; Li et al., 2007; Plante et al., 2009).	109
383 384 385 386 387	Figure 8: Boxplots of total porosity, effective porosity and the ratio of intrinsic permeability of air to water for all laboratory ($n = 9$ per temperature) and wildfire ($n = 3$) ash samples.	110

388	laboratory ($n = 9$ per temperature) and wildfire ($n = 3$) ash samples.	111
390 391 392 393 394	Figure 10: Scanning electron microscope pictographs of surface porosity for laboratory ash combusted at A) 300 °C, B) 900 °C, C) 700 °C and D) magnification of the 700 °C sample highlighting intricate pore structure.	112
395 396 397 398	Figure 11: Scanning electron microscope pictographs (left) and corresponding XRD peaks (right) of Terrace (A, B) and Gunbarrel (C, D) wildfire samples before and after hydration respectively.	113
399 400 401	Figure 12: An ash crust within the Terrace Wildfire a few weeks after low intensity post-fire rainfall; inset is of author holding a piece of ash crust.	114
402 403 404 405 406 407 408 409	Figure 13: Pictures 2A-D show the initial hydration of mid-combustion ash in the laboratory; an initially dry sample was saturated from below with minimal head until a point of visible saturation (2A), with the addition of more water the ash plug collapsed into a liquid state. A similar ash plug was photographed in the field (1C). Images 3A-D are graphics representing the theorized interaction of ash particles and water based on the polarity of water and the electrostatic nature of carbonate.	115
410 411 412 413 414 415 416	Table 1: A correlation matrix of cluster analysis results, indicating similarities between Douglas-fir (DF), lodgepole pine (LP) and ponderosa pine (PP) ash samples of varying combustion temperatures (n = 3). Results are based on Pearson's correlation with significant correlations highlighted in bold, at $p < 0.01$, and bold italics at $p < 0.005$ (Webster and Oliver, 1990). Values of 1 are a perfect correlation.	116
417 418 419 420	Table 2: Mean and standard deviations values of total organic content (%), total inorganic content (%), pH and elemental components (w/wt%) for laboratory ash (n = 9 per temperature) and wildfire (n = 3) ash samples.	117
421 422	CHAPTER FOUR	
423 424 425	Figure 1: Location map of the 13 wildfire sites within North America, denoted by asterisks.	145
426 427 428 429	Figure 2: A site photograph prior to ash sampling with an inset of an ash trench for sample collection; 2009 Terrace Mountain wildfire in southern British Columbia, Canada.	146
430 431 432 433	Figure 3: Photographs of the laboratory set-up for measuring A) air permeametry and B) sorptivity with a probe.	147

434 435 436 437 438	Figure 4:	to the grain size of the silica sand standard and a silt-loam soil. Error bars for ash and sand have not been included to facilitate in the interpretation of the graph.	148
439 440 441 442 443 444 445	Figure 5:	Boxplots of unsaturated hydraulic conductivity values for all wildfire ash obtained in the field (K_f) and laboratory (K_f^*) via the use of an infiltrometer ($n = 5$ per wildfire). Significant differences across wildfire sites are indicated with italic p -values above the box plot. Differences within wildfire sites are significant at the $p < 0.001$ unless otherwise stated in bold.	149
446 447 448 449 450 451	Figure 6:	Boxplots of sorptivity values for all wildfire ash obtained via sorptivity probe (S^*) and laboratory infiltrometer (S_f^*) methods. Due to limited ash availability only ten wildfires were included for S_f^* measurements ($n = 5$ per wildfire). Significant differences across wildfire sites are indicated with italic p -values above the box plot.	150
452 453 454 455 456	Figure 7:	Boxplots of saturated hydraulic conductivity values for all wildfire ash obtained via air permeametry (K_{sat}^*) and falling head conductivity (K_{sat}) methods (n = 5 per wildfire). Significant differences across wildfire sites are indicated with italic p -values above the box plot.	151
457 458 459 460	Table 1:	Summary information for ash field characteristics from the 13 wildfire sites. Five replications were preformed for each measurement. Values in bold are significant at the $p < 0.05$ level.	152
461 462 463	Table 2:	Summary information from other research studies reporting wildfire ash hydraulic characteristics.	153
464 465 466 467 468	Table 3:	Summary information for ash characteristics from the laboratory for the 13 wildfire ash samples. Five replications were preformed for each measurement. Values in bold are significant at the $p < 0.01$ level and those in bold and italics are significant at $p < 0.001$ level.	154
469 470	CHAPTI	ER FIVE	
471 472 473 474	C	A photograph of an ash crust within the 2009 Terrace Mountain wildfire, British Columbia, Canada (Balfour and Woods, 2013). The inset photograph is a photograph of the author holding a piece of ash crust (1.0 cm thick).	187
475 476 477 478 479	C	A schematic layout depicting six sites designated within each wildfire study area. Each site contained three 2.0 x 2.0 m plots, which were randomly assigned a treatment; cover (C), natural (N) or screen (S). Within each plot data was collected from a 0.25 x 2.0 m transect area (represented in grey) for each allocated collection date. Dates represented	188

480		in this figure correspond to West Riverside site collection.	
481 482	Eigung 2	(A.E). Democratative plate of infiltration magazinements for the three	189 - 191
483	rigule 3	(A-F): Representative plots of infiltration measurements for the three different treatment types, natural (A,B), screen (C,D) and cover (E, F),	109 - 191
484		within the West Riverside (top) and Avalanche Butte (bottom) wildfires	
485		over the allotted collection period. Infiltration data was not recorded for	
486		19 September or 28 August, 2011 due to insufficient ash cover, for the	
487		West Riverside and Avalanche Butte sites respectively. The coefficient of	
488		the x^2 -term is used to calculate hydraulic conductivity (mm sec ⁻¹) according	
489		to eq. 2. The coefficient of the x-term is the sorptivity value in mm sec ^{-0.5} .	
490		T. T	
491	Figure 4	: Photographs of overland flow from adjacent hydrophobic soil onto an	192
492	C	ash layer. Photographs were taken during the rainfall event (left) and	
493		three days after (right).	
494			
495	Figure 5	: Representative photographs of ash crust inter-rilling within natural and	193
496		screen plots (left) as well as overland flow and erosion into adjacent	
497		unburned areas (right).	
498			
499	Figure 6	: Boxplots of effective porosity values for West Riverside sites (upper)	194
500		and Avalanche Butte sites (lower). Significant differences are indicated	
501		with a <i>p</i> -value above the boxplot.	
502	D: 5		105 104
503	Figure 7	: Pie charts visually displaying the mean percentages of plot coverage	195 - 196
504		for the three different treatment types (natural, cover, and screen) within	
505		the (a) West Riverside and (b) Avalanche Butte wildfires over the	
506 507		collection period.	
508	Eiguro 9	: Ash crust photographs, which formed within the West Riverside site,	197
509	riguic o	natural plots, after the initial rainfall event.	197
510		natural plots, after the initial rainfair event.	
511	Table 1	Summary information for site characteristics of plots allocated to each	198
512	14010 1.	treatment type within the West Riverside and Avalanche Butte wildfire	170
513		study areas. Within and across treatment variation in site characteristics	
514		were not significant $(p > 0.05)$.	
515		(· · · · · · · · · · · · · · · · · · ·	
516	Table 2:	A list of ash characteristics measured and established methodology.	199
517		es established a second of the	
518	Table 3:	Summary information for plot characteristics of ash exposed to varying	200
519		treatment types (natural, cover and screen) within the West Riverside	
520		and Avalanche Butte study areas over the allotted collection periods.	
521		Significant ($p < 0.05$) within treatment variations over time are indicated	
522		in bold with highly significant variations ($p < 0.01$) indicated in bold italics.	
523			
524			
525			

526	CHAPTER SIX	
527		
528	Figure 1: A synthesis of key dissertation findings regarding variations in	204
529	ash characteristics.	
530		
531	Figure 2: The findings from this dissertation in the context of a runoff generation	205
532	mechanism flow chart of ash and soil following recent wildfire activity	
533	(HOF: hortonian overland flow; SOF: saturation overland flow; SSSF:	
534	subsurface storm flow). Modified from Bodi (2012).	
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536 CHAPTER ONE

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SECTION 1.0: What is a natural disturbance; is it detrimental or beneficial to ecosystems?

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A natural disturbance can be described as a physical force, which alters the current natural system by removing organisms and drastically changing environmental conditions (Agee, 1993; Reice, 1994). Disturbance events cover a range of spatial scales and intensities, which can include both exo- and endogenous factors (Agee, 1993; Rogers 1996) and are viewed as nature's "editing process," selectively removing certain elements from a system while retaining others depending upon the timing and severity of the disturbance (Franklin et al., 2000). Postdisturbance ecosystem succession is conventionally described as a linear sequence of change from early stages dominated by species that do well in open environments, to later stages dominated by species adapted to more closed conditions (Johnson and Miyanishi, 2007). This concept projects the idea that natural systems are on a path toward some climatic condition or static equilibrium in the late stages, which must be restored following a disturbance. Overall the conventional wisdom is that natural disturbances are negative and systems need to be restored following a disturbance to mitigate detrimental ecosystem effects (Wright and Heinselmann, 1973), when in fact this state of climatic equilibrium is rarely achieved and the normal state of an ecosystem is to be in dynamic flux following the last disturbance (Reice, 1994). The reality is that disturbance events of any scale increase the diversity, health and vitality of an ecosystem and are essential aspects of any ecosystem (Johnson and Miyanishi, 2007).

From an ecosystem point of view disturbances are a beneficial aspect of landscape and biotic evolution, however, they also hold considerable human and societal impacts. Following

wildfires for example there is potential risk to life and property due to catastrophic flooding and debris flows, decreased forest productivity due to reduced soil quality, and impacts to public water supplies due to reduced reservoir capacity, high suspended sediment loads and the presence of metals and other contaminants (Robichaud, 2000; Cannon et al., 2001; Moody and Martin, 2001). The predicted further increase in frequency, severity and extent of wildfires in many regions around the world can be expected to exacerbate these problems, representing a substantial challenge in watershed management both in the western U.S. and many other regions of the world (IPCC, 2007; Liu et al., 2010). Therefore wildfires are currently viewed as a dominant forest management issue, with a primary objective of post-fire management to limit the socio-economic adverse effects, if warranted, by implementing appropriate erosion prevention techniques, while allowing the ecosystem benefits of fire to exist (Robichaud, 2000; Beyers, 2004; Groen and Woods, 2008). The aim of this section of the dissertation is to highlight some often overlooked ecological benefits of wildfire, specifically regarding carbon sequestration, forest succession and aquatic ecosystems before addressing the negative socio-economic issues associated with post-fire runoff and erosion.

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1.1 Wildfire effects on long and short-term carbon cycling

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Wildfires strongly influence carbon cycling and storage in forested ecosystems (Kasischke et al., 1995; Turner et al., 1995; Schimel and Baker, 2002; DeLuca and Aplet, 2008 Scott, 2009). In the short-term (weeks) wildfires are a carbon source releasing large amount of CO₂ into the atmosphere and increasing post-fire decomposition. However, in the long-term (centuries) wildfires are a carbon sinks creating recalcitrant forms of carbon, which are

incorporated into the soil and resistant to decomposition, and by creating areas of young forests capable of sequestering more CO₂ than older forests.

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In the short-term wildfires alter the carbon balance by acting as a carbon source in two main ways. First, they directly release large amounts of carbon into the atmosphere during the combustion of biomass in the form of living, dead and decaying organic material (Turner et al., 1995; Schimel and Baker, 2002). For example, wildfires that occurred in Indonesia from 1997 to 1998 released 0.8 - 3.7 gigatonnes of carbon into the atmosphere, which is equivalent to 13-40 % of the annual emission from anthropogenic fossil fuel combustion (Schimel and Baker, 2002). Secondly, fires increase post-fire soil respiration (CO₂) due an increase in soil thermal regime and the decomposition of any remaining biomass. Following a fire the soil temperature rises due to the removal of leaf area and plant cover decreasing the amount of solar radiation that will be absorbed or reflected by vegetation, ultimately increasing incoming solar radiation to the ground; more than 90 % of incoming solar radiation reaches the forest floor in fire affected areas (Kasischke et al., 1995). The removal of insulting ground cover during the fire, such as duff and litter, also results in a more direct heat flow from the air to the ground increasing ground temperature in post-fire landscapes (Dingman, 2002; Kasischke et al., 1995). Finally the ground surface albedo will be significantly reduced due to the charring of fuel and the deposition of black or grey ash, thus increasing the amount of solar radiation absorbed into the soil. Overall the increase in soil temperature increases soil microbial activity, which in turn speeds the decomposition of soil organic matter and increases carbon dioxide emission from the soil in postfire ecosystems (Kasischke et al., 1995; DeLuca and Aplet, 2008). This thermal increase in postfire soils has additional significance in boreal forests and tundra ecosystems where the thawing

of permafrost layers has the potential to release large pools of stored carbon (Kasischke et al., 1995; Knicker, 2007).

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These post-fire increases in CO₂ production are typically short lived and dependent upon the speed of post-fire regeneration, which in large part is due to vegetation type, fire frequency, and fire intensity. Regeneration dictates how quickly the ecosystem will recover to pre-fire carbon levels, as regeneration will alter the soil thermal regimes as well as decomposition rates (Turner et al., 1995; DeLuca and Aplet 2008). With regard to fire frequency, an increase within a recently burned area can result in an ecosystem shift and a permanent reduction of carbon for that area. For example, if a forest converts to grassland or meadow rather than regenerating large amounts of carbon will be lost from the ecosystem, however, if the forest does regenerate over time it will recover the carbon lost from the fire (Kashian et al., 2006). With regards to intensity, the higher the intensity of fire the more biomass will be consumed releasing more CO₂ into the atmosphere and decreasing the amount of post-fire trees capable of acting as carbon sinks. Overall the carbon balance will generally approach zero within a decade after the fire, at which point the growth and accumulation of organic carbon on the soil surface will outpace the decomposition of the organic matter, and the forest will be re-established as a carbon sink (Kasischke, 2000; Kashian et al., 2006).

In the long-term wildfires act as a carbon sink by *i*) converting plant material into black carbon, which is resistant to decomposition and can remain stored in the soil for millennia and *ii*) impacting the carbon balance through changing the successional stage of the forest and altering the amount of carbon sequestered by biomass. During a fire the incomplete combustion of organic matter results in the formation of charcoal and soot. Charcoal is organic matter subjected to partial combustion while soot is the condensation of volatiles created during combustion;

collectively charcoal and soot are known as black carbon (Forbes et al., 2006, DeLuca and Aplet, 2008). Black carbon (BC) is resistant to biological or chemical degradation and can reside in the ecosystems for thousands to millions of years (Masiello and Druffel, 1998). The formation of BC renders carbon inert and not easily recombined with oxygen to form CO₂, thus transforming organic carbon in biomass from the rapid bio-atmospheric carbon cycle to the slower geological carbon cycle (Forbes et al., 2006). While less than 3 % of carbon is converted to BC during forest, savanna and grassland fires, it is considered a very significant component of the global carbon balance comprising up to 40 % of organic carbon in terrestrial soil and between 12-31 % in deep oceanic sediment (Forbes et al., 2006). In temperate coniferous forests, similar to those of the northwest Rocky Mountain region, charcoal originating from previous fires can account for 15-20 % of the total carbon stored in the soil (DeLuca and Aplet, 2008). The long-term storage of carbon by BC is affected by fire intensity, soil mixing, and fire frequency as these factors alter how much BC is sequestered into the soil. Fire intensity, or the degree of fuel combustion, will influence how much BC is formed and capable of sequestration (DeLuca and Aplet, 2008). Black carbon is susceptible to loss through erosion or further combustion in subsequent fires, therefore must be mixed into a soil to increase the long-term storage (Zackrisson et al., 1996) via a variety of processes including bioturbation, tree throw and freeze thaw events (Gavin, 2003). If a subsequent fire occurs prior to appropriate mixing of BC into the soil profile the carbon will be combusted and lost to the atmosphere as CO₂; therefore the fire frequency must be low enough to allow the BC to be incorporated into the soil (DeLuca and Aplet, 2008). Eroded BC can be sequestered in lake or marine deposits; however, the process of soil mixing is imperative to the sequestration of BC in terrestrial ecosystems (Deluca and Aplet,

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2008). Overall BC produced during wildfires represents an important form of long-term carbon storage in forest ecosystems.

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The second long-term affect wildfires have on the carbon balance is the creation of areas of secondary succession. At a regional level the net annual biological flux of carbon in forests depends strongly on the age-class distribution among the stands, therefore fire will determine the forest contribution to the carbon balance for centuries to come (Turner et al., 1995). The effects of burning, either directly through fire or indirectly from post-fire landscape changes (ie. debris flows), alters the area of secondary succession. Therefore fire is viewed as one mechanism that controls the pattern of living biomass within a forest ecosystem and can regulate the amount of carbon being sequestered (Turner et al., 1995). For example, immediately after a fire the amount of biomass (stored carbon) found in live trees and vegetation is extremely low or zero (Kashian et al., 2006), during this time the ecosystem acts as a carbon source due to short-term effects previously discussed. As the forest regenerates it becomes a strong carbon sink, especially during middle succession as trees have established and boles are rapidly accumulating biomass (Turner et al., 1995). In late succession the rate of carbon sequestration slows, as photosynthesis and respiration are reduced in older trees, and tree mortality is high (Ryan and Waring, 1992). Once the ecosystem reaches this older stage, in late succession, the net accumulation of carbon into living trees has decreased, however, overall the forest is still a carbon sink, with large amounts stored in fallen trees (Turner et al., 1995).

Often times one only sees destruction in post-fire landscapes and it is hard to image environmental benefits associated with a large forest fire. However, it is important to step back and be reminded of processes at a larger scale and their long-term significance.

1.2 Wildfire effects on habitat variability

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Broad scale disturbances, such as wildfire, are naturally heterogeneous in their effects across the landscape and play an important role in creating mosaics and natural variability, thus increasing the heterogeneity of plant and animal communities (Baker, 2009). One trait of wildfires that affect post-fire ecosystems is the size of the burned patch, which is attributed to variations in fire intensity. For example crown fires generate large burned patches, which often occur at greater intensities than smaller spot fires produced within the same fire complex (Turner et al., 1997). These areas of greater fire intensity create opportunity for colonizing species, release nutrients and supply important sediment pulses to aquatic ecosystems within the watersheds. Small size patches on the other hand decrease solar radiation and snow ablation within the area providing a cooler, moist growing site compared to large patches (Turner et al., 1994) resulting in habitat variability. Patch size also dictates the rate of reforestation, which is often dependent upon seed dispersal from outside sources following a wildfire (Baker, 2009). For example, when the effective seed dispersal distance is smaller than the burned patch size non-forest communities can dominate in early succession leading to ecosystem shifts (Turner et al., 1997; Baker, 2009). Overall wildfires induce changes in spatial patterns thus altering the movement of nutrients, habitat use and foraging dynamics to populations within the affected ecosystem.

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1.3 Wildfire effects on aquatic ecosystems

Wildfires influence aquatic ecosystems by increasing discharge variability, coarse woody debris, nutrient availability and solar radiation, while reducing stream channel stability and producing higher rates of downstream sedimentation due to increases in runoff and erosion from burned watersheds (DeBano et al., 1998; Bisson et al., 2003; Cerdà and Robichaud, 2009). These alterations in the aquatic ecosystem have significant negative short-term impacts to aquatic biota, through the burial of current habitats, the direct or indirect death of aquatic species via burial or reduced oxygen levels in stagnant water, reduction in fish productivity from siltation of fish reds and the reduction of pools within the affected reach (Benda et al., 2004). While such negative consequences have short-term impacts (years) to river ecology, punctuated supplies of sediment (PSS) hold significant importance for long-term habitat construction within the fluvial system.

A PSS refers to an abrupt, large and temporary increase in erosion and sediment supply, typically associated with fires and post-fire storms in the form of mass movements or debris flows (Figure 1; Benda et al., 2004). These punctuated events result in the concentration of sediment within the channel network affecting fluvial morphology and ecology for decades or centuries to come. Overall aquatic organisms have adapted to accommodate for PSS events, which shape the biodiversity of aquatic ecosystems through creating a mosaic of habitats, altering the vertical and horizontal connectivity of the river and positively increasing the genetic diversity of fish populations (Bisson et al., 2003; Hoffman and Gabet, 2007; Kemp et al., 2011).



Figure 1: A photograph showing the deposit of an alluvial fan following a punctuated sediment supply event from the 2002 Hayman Wildfire. This PSS occurred shortly after the wildfire and obstructed flow for numerous years. This image was taken in 2010, and shows the active river (running left to right) has down cut the fan (Photo: Sierra Larson, USFS).

Following PSS events an alluvial fan is often deposited drastically altering the longitudinal profile of the receiving channel and subsequently habitat development (Figure 2; Bisson et al., 2003; Hoffman and Gabet, 2007). The alluvial fan temporally truncates the main stem of the river causing a localized flattening of the upstream gradient, which increases the overall connectivity of the stream vertically and horizontally (Benda et al., 2004). Increases in upstream hydraulic head, due to this localized flattening, enhances hyporheic flow through gravel substrate and increases the vertical connectivity of the river system. For example, dissolved organic nutrients (such as nitrogen) can be chemically transformed during hyporheic transit and emerge in the surface water downstream as dissolved available forms (nitrate) increasing primary productivity downstream (Benda et al., 2004). Increases in hyporheic flow

also reduce river temperatures by increasing the influence of cooler groundwater. Sediment storage increases upstream of the alluvial fan due to a reduction in flow velocities associated with gradient decreases. This process is referred to as "interference" as the alluvial fan is interfering with the transport of upstream sediment and causing a localized increase in sediment storage, which results in a finer upstream river substrate for hundreds to thousands of meters (Benda et al., 2003). Overall these upstream changes in fluvial geomorphology increase the horizontal connectivity of the rivers ecology by allowing the river out of its banks to interact with floodplains, thus reducing scouring by dissipating flood energy, and creating side channels, which diversify the riparian zone and provide a refuge for aquatic organisms (Benda et al., 2003; 2004). For example, floodplain widths measured during a study on the Boise River found that upstream widths (50-200 m) were significantly larger than downstream (10-20 m) (Benda et al., 2004), with the input of fine sediment and organic matter from the PSS acting as an important nutrient and food source for the riverine ecosystems (Kemp et al., 2011).

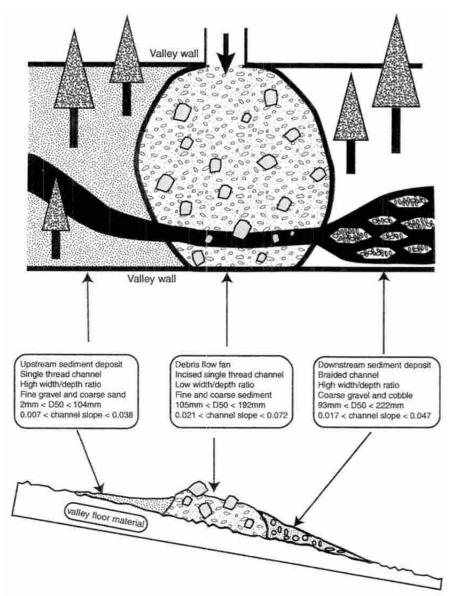


Figure 2: Planview (upper) and longitudinal view (lower) of a typical channel response to the deposition of a PSS following a wildfire (Hoffman and Gabet, 2007).

The influx of sediment from the punctuated event and increased sediment storage, due to aggrading upstream, can negatively affect pool density habitat heterogeneity above the fan. While infilling of pools occurs in the short-term, in the long-term PSS events are responsible for the creation of pools due to high inputs of coarse woody debris from post-fire trees incorporated in the event as well as the death of flooded trees upstream. Punctuated sediment events account for up to 50 % of the total coarse woody debris incorporated into river channels in the northwest

(Benda et al., 2004). The excess sediment supply to the channel from the PSS causes the downstream reaches to temporarily braid and form side-channels, which act as an important refuge or microhabitat for certain aquatic species (Benda et al., 2004; Hoffman and Gabet, 2007). Therefore in the long-term these events are considered fundamental to increasing pool density and fish habitat in riverine ecosystems.

While terrestrial and aquatic ecosystems are linked and dynamic with fire playing a critical role in maintaining the aquatic ecological diversity through punctuated events, there is a general tendency for people (managers, scientists, public, etc) to view watersheds as stable and static features with the importance of their dynamic aspect often overlooked and post-fire landscapes stabilized to reduce negative consequences to downstream resources and infrastructure. The important role of punctuated sediment supply and the formation of alluvial fans has been documented following fires in Yellowstone National Park (Meyer and Pierce, 2003) as well as other regions within the United Sates (Benda et al., 2004) and yet these post-fire sediment events are still viewed as mainly negative. The fact that disturbances, such as punctuated supplies of sediment, following wildfires enhance and shape the physical and biological diversity of the river through creating a mosaic of habitats and a dynamic network within the river should be seen as a positive aspect of wildfires.

The benefits of disturbance may be needed more now than ever, as our watersheds have lost complexity due to removal of coarse woody debris for timber, destruction of riparian areas and changes in natural flow regimes. Therefore when evaluating post-fire watershed conditions following a severe fire it is important to keep in mind that some amount of erosion, debris flows, flooding and restructuring of channels is important to maintain a healthy stream habitat. It is also important to determine if stabilization is necessary (Robichaud et al., 2010), as stabilization

efforts can be expensive and sometimes the most cost effective and justifiable option is to do nothing (Napper, 2006; Bisson et al., 2003). The natural recovery of the system may be sufficient to avoid large erosional events, as the erosion in burned watersheds typically decreases an order of magnitude annually as vegetation re-grows and the area recovers (Robichaud et al., 2008; Cerdà and Robichaud, 2009). If areas have been categorized as having little risk to resources, then punctuated sediment supplies should be allowed to occur, as they are a positive rejuvenation for the stream ecosystem.

1.4 Wildfire effects on runoff and erosion

Wildfires can temporarily increase runoff and erosion rates in forested watersheds by up to three orders of magnitude (Prosser and Williams, 1998; Robichaud, 2000; Cannon et al., 2001; Moody and Martin, 2001; Meyer and Pierce, 2003; Wondzell and King, 2003; Shakesby and Doerr, 2006), particularly in areas burned at high severity and in the first year after the fire (Shakesby et al., 2000; Huffman et al., 2001; Benavides–Solorio and MacDonald, 2001). Increases in runoff and erosion following forest wildfires have been observed throughout the globe (Scott and Van Wyk, 1990; Shakesby et al., 1993; Cerda, 1998; Fernquist and Floraberger, 2003), with sediment yields in forested watersheds of the western U.S. comparable to long term (10⁴ yrs) basin wide sediment yields, indicating that fire related erosion plays a key role in landform evolution (Meyer et al., 2001; Robichaud, 2000; Moody and Martin, 2009) and aquatic habitats (Benda et al., 2003) as previously discussed.

The magnitude of the post-fire runoff and erosion response depends in part on the extent of the loss of ground cover (Cerdà, 1998; Benavides-Solorio and MacDonald, 2001; Johansen et

al., 2001), the strength and spatial contiguity of fire-induced water repellency in the soil (Scott and van Wyk, 1990; Doerr et al., 2000; Shakesby et al., 2000; Huffman et al. 2001; Woods et al., 2007) and the effects of heating on the soil structure (Neary et al., 2005; Mataix-Solera and Doerr 2004). Consumption of the surface litter layer and other organic ground cover increases the potential for overland flow and erosion by decreasing the surface roughness and detention storage (Wilcox et al., 1988; Bryan, 2000), exposing the soil to rainsplash compaction and erosion, and releasing sediment previously stored behind logs and other debris (Wondzell and King, 2003; Shakesby and Doerr, 2006). Consequently, erosion rates tend to increase sharply when the amount of bare soil exceeds 60 to 70 percent (Robichaud et al., 2000; Benavides-Solorio and MacDonald, 2001; Johansen et al., 2001). Soil heating increases runoff by disaggregating soil particles, leading to reduced infiltration due to the loss of soil structure and the increased potential for pore clogging (Emmerich and Cox, 1994). Soil heating to temperatures of 175 to 270°C enhance soil water repellency and can result in post-fire infiltration rates that are considerably lower than in an unburned soil and last for up to a year after the fire (Robichaud, 2000; Shakesby and Doerr, 2006). Under these post-fire conditions even moderate intensity storms can generate infiltration-excess overland flow and accelerated erosion by rilling and gullying (Imeson et al., 1992; Shakesby et al., 1993; Robichaud, 2000; Martin and Moody, 2001). Severe fires generally result in stronger and more spatially contiguous water repellency and a corresponding increase in the potential for Hortonian overland flow (Tiedemann et al., 1979; Huffman et al., 2001). Post-fire increases in runoff and erosion have considerable human and societal impacts, such as the potential risk to life and property due to catastrophic flooding and debris flows,

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decreased forest productivity due to reduced soil quality, and impacts to public water supplies

due to reduced reservoir capacity, high suspended sediment loads and the presence of metals and other contaminants (Robichaud et al., 2000). Therefore a primary goal of post-fire management and rehabilitation efforts is to assess and, where possible, reduce the risk of damaging runoff and erosion events (Robichaud et al., 2000). Given the geomorphic, ecological and societal significance of the post-fire runoff and erosion response, there is an ongoing need to develop an improved understanding of the hydrologic and geomorphic processes that drive it.

1.4.1 The role of ash on post-wildfire runoff

Another important factor controlling post-fire runoff and erosion rates is the presence of ash on the soil surface (Campbell et al., 1977; Wells et al., 1979; Mallik et al., 1984; Etiegni and Campbell, 1991; Neary et al., 2005; Balfour and Woods, 2013; Leighton-Boyce et al., 2007; Cerdà and Doerr, 2008; Gabet and Sternberg, 2008; Onda et al., 2008). There is general agreement that ash alters the immediate post-fire hydrological response, however, the literature is contradictory in terms of the role that it actually plays. The most common view is that ash temporarily increases the potential for overland flow by sealing the mineral soil surface (Campbell et al., 1977; Wells et al., 1979; Mallik et al., 1984; Etiegni and Campbell, 1991; Neary et al., 2005; Gabet and Sternberg, 2008; Onda et al., 2008) either through the clogging of soil macropores by ash particles (Mallik et al., 1984; Lavee et al., 1995; Woods and Balfour, 2010), the formation of a surface ash crust (Gabet and Sternberg, 2008; Onda et al., 2008) or through hydrophobic effects (Bodi et al., 2012a). Other studies, however, suggest that the ash layer temporarily reduces runoff, primarily by intercepting and storing rainfall (Cerdà, 1998;

Martin and Moody, 2001; Leighton-Boyce et al., 2007; Cerdà and Doerr, 2008, Woods and Balfour, 2008; Zavala et al., 2009).

The effect of ash on infiltration varies temporally due to erosion, compaction of the ash layer, or gradual pore clogging as ash is washed into macropores by successive storms (Onda et al., 2008; Woods and Balfour, 2010). Due to rapid removal of the ash by wind and water erosion its effects are often confined to the first few storms (Larsen et al., 2009). However, the impact of ash on runoff during these early events can be considerable, and there are cases where ash continues to affect the runoff response for several months after a fire (Cerdà, 1998). Current research regarding the effect of ash on infiltration and runoff is focused on quantifying the hydrological properties of ash to facilitate the parameterization of hydrologic models (Moody et al., 2009; Ebel et al., 2012).

From a hydrologic perspective, the ash-soil profile left after a wildfire is analogous to a layered soil profile in an unburned setting. The literature indicates that the effects of ash on post-fire runoff are highly variable due to three main variables *i*) the thickness of the ash layer (Cerdà and Doerr, 2008; Larsen et al., 2009; Woods and Balfour, 2010), *ii*) variations in ash and soil composition making up the post-fire two-layer soil system (Balfour and Woods, 2007; Gabet and Sternberg, 2008; Larsen et al., 2009; Moody et al., 2009; Kinner and Moody, 2010; Woods and Balfour, 2010; Bodi et al., 2012b) and *iii*) alterations in ash properties associated with hydration (Etiegni and Campbell, 1991, Goforth et al., 2005; Balfour and Woods, 2006; Gabet and Sternberg, 2008; Onda et al., 2008; Woods and Balfour, 2008; Stoof et al., 2010).

i) The ash layer thickness partially determines the water storage capacity, and hence the potential for overland flow generation. The water storage capacity of ash layers is proportionally linked to thickness, as thicker ash layers are more capable of reducing or preventing overland

flow by protecting the soil surface (Cerdà and Doerr, 2008; Larsen et al., 2009; Woods and Balfour, 2010). Ash thickness can also alter the number of hyrologically active macropores contributing to infiltration, with thicker ash layers increasing the number of active micropores offsetting the reduced flux along each macropore (Figure 3; Balfour, 2007; Woods and Balfour, 2010).

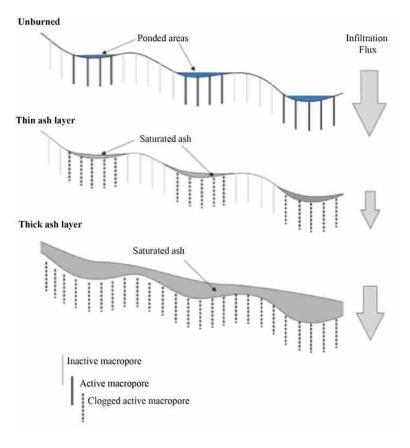


Figure 3: Conceptual sketches regarding the effect of ash thickness on macropore infiltration. In unburned areas macropore infiltration only occurs in ponded zones. With a thin ash layer the primary effect is pore clogging, and the infiltration flux is reduced. With a thicker ash layer pore clogging still occurs but the saturated ash layer increases the proportion of the plot area with macropore flow. This offsets the effects of clogging, increasing the overall infiltration flux (Balfour, 2007; Woods and Balfour, 2010)

ii) Variations in ash particle size, wettability and hydraulic conductivity contribute to the varied effect of ash on post-fire runoff. Ash particles have been observed via thin section (Balfour and Woods, 2007; Woods and Balfour, 2010), flume (Gabet and Sternberg, 2008) and

rainfall simulation analysis (Onda et al., 2008) to create a thin low conductivity layer, sealing the soil surface and reducing infiltration response, however, other research indicates no signs of pore clogging by ash (Larsen et al., 2009). The reason for this discrepancy lies in the fact that ash and soil particle size dictate whether ash is capable of blocking soil pores. For example, in research conducted by Larsen et al. (2009) ash particle size was coarser than the loamy sand soil pores causing no effect, while other research indicated ash was capable of reducing infiltration depending upon soil texture; as the fine-sand sized ash particles clogged macropores of sandy loam soils reducing infiltration by 40 % but had no effect on smaller silt loam pores (Balfour, 2007; Woods and Balfour, 2010).

In cases where soil pore plugging by ash does not occur, the ash layer may still limit the rate of infiltration into the 2-layer soil system due to variations in hydraulic conductivity. For example if ash hydraulic conductivity (K_{ash}) is less than soil hydraulic conductivity (K_{soil}) then the ash layer will dictate the infiltration rate (Moody et al., 2009; Kinner and Moody, 2010). However, if $K_{ash} > K_{soil}$ the soil will regulate the rate of infiltration into the system resulting in water ponding at the ash-soil interface (Onda et al., 2008; Woods and Balfour, 2010). This response may promote saturation overland flow or subsurface storm flow contributing to the initiation of debris flows (Figure 4a; Cannon, 2001; Gabet and Sternberg, 2008; Onda et al., 2008). In cases where $K_{ash} > K_{soil}$, the ash layer acts as a capillary barrier, storing water rather than controlling infiltration (Kinner and Moody, 2010; Woods and Balfour, 2010). The ability of the ash layer to act as a capillary barrier, however, appears to be linked to ash moisture, as it has only been observed to occur under dry ash conditions (Moody et al., 2009; Kinner and Moody, 2010). It is also theorized that this effect may be linked to chemical instability of the ash particles increasing ash sorptivity (Balfour and Woods, 2011). Variations in ash wettability have been

speculated to influence runoff production by regulating infiltration rates and the storage ability of the post-fire soil system (Gabet and Sternberg, 2008). While ash can considerably increase soil water retention (Stoof et al., 2010), ash wettability can vary from hydrophilic to hydrophobic depending upon combustion temperature and plant species (section 2.2).



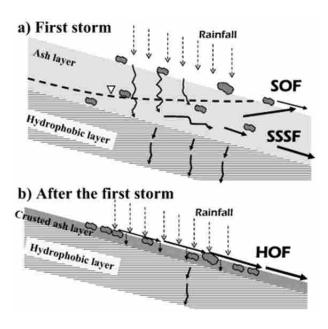


Figure 4: Schematic diagrams of runoff generation on forest-fire affected soil (HOF: Hortonian overland flow, SSSF: Subsurface storm flow, SOF: saturation overland flow; Onda et al., 2008).

iii) Due to thermal decomposition reactions ash combusted at high temperatures will contain elevated levels of carbonates and oxides. The oxides present in ash are capable of physically and chemically altering when hydrated due to their chemical instability (section 2.2). If this ash hydrates and swells prior to incorporation into the soil the resultant larger ash particles may be too coarse to be washed into soil pores decreasing the effect of ash on post-fire infiltration (Gabet and Sternberg, 2008). However, if the oxide within the ash reacts with water and swells once it is incorporated into the soil, the ash can further reduce hydraulic conductivity by creating an impermeable bridge within the soil pore (Figure 5; Goforth et al., 2005; Balfour, 2007; Woods and Balfour, 2010). While direct assessment of ash crusting is yet to be

documented, it is theorized that ash containing oxides and carbonates can crust and compact above the soil surface reducing K_{ash} and promoting Hortonian overland flow (Figure 4b; Onda et al., 2008; Woods and Balfour, 2008).

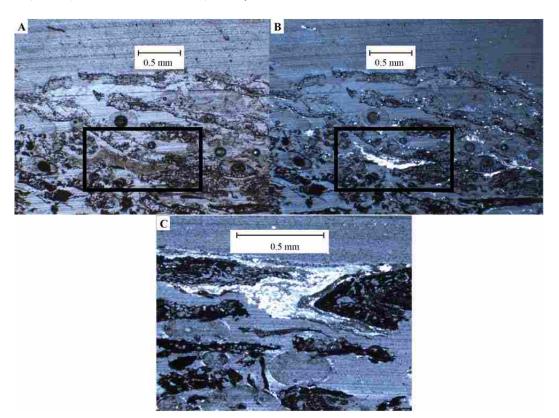


Figure 5: Polarized microscope images of burned thin sections taken within the upper 1-2 mm of the soil surface. Images A and B are of the same thin section, however, B was acquired under cross-polarized light to highlight the location of calcium carbonate ash. Image C is the magnification of another thin section emphasizing white ash filling spaces between black ash particles; the images was also acquired under cross-polarized light (Balfour, 2007)

1.4.2 The role of ash on post-wildfire erosion

There is similar uncertainty over the effect of ash on post-fire erosion rates, with the common view of ash adding to increased erosion by providing a ready supply of highly erodible material (Swanson, 1981; Meyer and Wells, 1997; Cannon et al., 2001; Wondzell and King, 2003; Shakesby and Doerr, 2006) rapidly removed via wind (Radley, 1965; Hubbert, 2006;

Boerner, 2006) rainsplash, sheetwash or rill erosion during the first post-fire rainstorms (Moody and Martin, 2001). Wind erosion impacts visibility, air quality and nutrient loss (Raison et al, 1985; Wagenbrenner et al., 2010) while entrainment of ash in overland flow results in ash-laden streams and impacts to water quality (Ryan et al., 2011). Furthermore ash is regarded as being more readily mobilized than burned mineral soil (Moody and Dungan Smith, 2005) and a necessary precursor for debris flow initiation through progressive bulking (Parrett, 1987; Cannon et al., 2001; Burns, 2007; Gabet and Bookter, 2008; Gabet and Sternberg, 2008). However, in the late 1990's an alternate view of the geomorphic effect of ash developed, indicating ash layers were capable of reducing surface erosion by reducing the rate and transport capacity of overland flow, and protecting burned soil from sealing via raindrop impact. Initially this view was based entirely on observational data (Cerdà, 1998) with observations obtained during experiments not specifically aimed at ash effects (Benavides-Solorio and MacDonald 2001; Leighton Boyce et al., 2007). For example a study addressing water repellency following the Bobcat Fire in Colorado, noted a plot containing high ash cover produced 27 % less sediment than the mean sediment yield from six other plots with less ash cover (Benavides Solorio and MacDonald, 2001). Since that time the hypothesis of ash reducing surface erosion has been validated by various researchers using rainfall simulations (Cerdà and Doerr, 2008; Woods and Balfour, 2008; Larsen et al., 2009; Zavala et al., 2009) and is viewed as a valuable soil protectant against erosional agents in parts of Spain and Portugal (Cerdà and Doerr, 2008; Pereira et al., 2010; Zavala et al., 2009) as well as an indicator of fire severity (Ubeda et al., 2009). The contradiction regarding the effects of ash on post-fire erosion most likely reflects

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obtained. For example, the potential for ash to reduce erosion is at a maximum immediately after

differences in the conditions under which the observations were made and measurements

the fire when the ash layer is thickest (Cerdà, 1998), whereas most erosion studies begin weeks months after a fire, when the ash layer may already have been partially eroded or redistributed by wind. The wetting history of the ash layer may also be a factor as low intensity rainfall may lead to a hydration-carbonation reaction, which could stabilize the ash layer in place reducing erosion (Balfour and Woods, 2008). Similarly, some ash layers are capable of developing fungal crusts, prior to the first major rainfall, which may stabilize the layer and reduce erodibility (Dunn et al., 1982; personal communications Peter Jordan, 2013). Another explanation may lie with limitations of the methodology; rainfall simulations are almost always conducted on relatively gentle slopes, where the transport capacity of overland flow is relatively low, so the measured erosion rates will not be representative of those on steeper slopes. Finally, ash thickness and characteristics of the underlying soil may alter erosion as erosion may only occur if the ash, and the underlying disaggregated wettable soil, become saturated (Woods and Balfour, 2010). Thus, higher rates of erosion are likely to occur with high intensity storms on steeper slopes with a thin ash layer. This rapid erosion of ash during the first post-fire storms may explain the reported potential of ash as a necessary precursor for debris flow initiation by progressive bulking (Parrett, 1987; Cannon et al., 2001). While a similar storm on a gentler slope or in an area with thicker ash cover will produce considerably less runoff and sediment, which supports reports of ash reducing surface erosion rates by two orders of magnitude through reducing the frequency and magnitude of overland flow and protecting the soil surface from rainsplash compaction and erosion (Benavides-Solorio and McDonald, 2001; Leighton-Boyce et al., 2007; Cerdà and Doerr, 2008). Overall there is a need for research similar to that conducted by Gabet and Sternberg (2008) to quantify the erodibility and the rheological properties of ash, as a means of refining

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post-fire erosion models such as the Erosion Risk Management Tool (ERMiT) (Robichaud et al., 2007).

1.4.3 The role of ash on post-fire management

The uncertainty over the effects of ash on runoff and erosion has important implications for post-fire management. If ash contributes to the general tendency for runoff and erosion rates to increase after a fire, then it may be beneficial to remove the ash layer as soon as possible, and the presence of ash can be used as an indicator of an increased risk of accelerated runoff and erosion in post-fire hazard assessments (Robichaud et al., 2007). Conversely, if ash temporarily reduces runoff and erosion, then there may be a benefit associated with stabilizing the ash layer *in-situ* protecting the underlying soil from wind erosion. However, post-fire hazard assessments would need to take account of the fact that the highest risk of damaging runoff and erosion events would not occur until after the ash layer is removed (Prosser and Williams, 1998; Wondzell and King, 2003). Therefore, there is a need to clarify the hydrogeomorphic role of wildfire ash in order to correctly assess and manage post-fire hazards.

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What is ash? Jones et al. (1997) proposed terminology for fire-altered matter as well as highlighted the need to make a distinction between ash, charcoal, partially charred material, soot and gases; with ash considered a mineral-rich powdery residue remaining on-site after a fire (Figure 6). The term ash, however, is still defined in various ways throughout numerous disciplines (ecology, sedimentology and bio-fuel industries, etc.), therefore must be taken in context and cannot be readily applied across disciplines. In this dissertation, the term ash is strictly related to the forest-fire research community and defined as the material deposited following the burning of vegetation; which is not entirely mineral in nature but consists of thermally altered plant material subjected to intense temperatures in the presence of oxygen (Raison, 1979; Quill et al., 2010). Furthermore ash, in this dissertation, is viewed as consisting of two main components; the relatively inorganic white mineral fraction and black organic carbon char particles resulting from relatively lower burning temperatures. While this definition is consistent with previous research within the field of post-wildfire science (Raison, 1979; Forbes et al., 2006; Kinner and Moody, 2010; Scott, 2010; Bodi et al., 2012a) it still leaves a level of vagueness regarding the properties of ash, therefore indicating that sub-categories of the term still need to be investigated within post-wildfire science. For example, Bodi (2012) highlighted problems with this basic definition due to variations in methodology pertaining to the maximum particle size sieved and the minimum combustion temperature reached, concluding that the organic carbon content of the term ash is highly variable (0-100 %) within the literature and a consistent definition poorly defined.

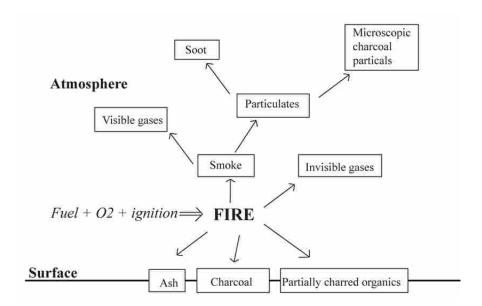


Figure 6: A replication of fire product terminology according to Jones et al. (1997).

How is ash formed? Ash is a product of the combustion process, which is a rapid physical-chemical process in which energy, stored in plants by photosynthesis, is released in the form of heat:

1033 Ignition +
$$(C_6H_{10}O_5)_n + O_2 \rightarrow CO_2 + H_2O + heat$$

with CO₂ and H₂O being reaction by-products of plant synthesize cellulose (C₆H₁₀O₅)_n combustion (Pyne et al., 1996; DeBano and Neary, 2005). This combustion process consists of four main phases; pre-ignition, ignition, combustion and extinction (DeBano et al., 1998; Pyne et al., 1996). Pre-ignition involves dehydration and pyrolysis, where the temperature of the fuel is raised to a point at which free water evaporates (>100°C) and volatiles are released to support the combustion phase. Ignition is a rapid, exothermic reaction that produces temperatures exceeding the ambient surroundings resulting in the transition of fuels from the pre-ignition to combustion phase (Drysdale, 1985). The combustion phase consists of flaming and smoldering/glowing combustion; with the fundamental difference being smoldering occurs on the surface of the fuel rather than in the gas surrounding the fuel. The result of the combustion

process can vary due to the differing stages. For example, if only pyrolysis takes place charred material will result, while during the combustion phase oxidation occurs and temperatures range between 500-1400°C yielding a mixture of charred particles and white mineral ash (Grier, 1975; Misra et al., 1993; Úbeda et al., 2009; Quill et al., 2010); smoldering combustion is more complete producing very white ash (DeBano et al., 1998; Pyne et al., 1996). In the field it is also typical for white ash layers to mantle black ash layers due to lower combustion temperatures and oxygen levels near the soil surface (Blank and Zamudio, 1998; Neary et al., 2005). Overall ash can indicate the nature of combustion and hence give information regarding the nature of the fire and an indicator of fire severity (Smith and Hudak, 2005; Lentile et al., 2009; Úbeda et al., 2009; Roy et al., 2010); usually in conjunction with other indicators such plant mortality, soil water repellency and soil heating effects (Moreno and Oechel, 1989; Keeley, 2009; Parsons et al., 2010).

2.1 The source of ash

Studies conducted in several ecosystems, Brazilian rain forest (Carvalho et al., 1998; 2011), cleared areas in Brazil (Fearnside et al., 1999, 2001), savannas in Zambia (Shea et al., 1996; Hely et al., 2003), pastures burned in the Amazon basin (Kauffman et al., 1994), scrub oak forest in Florida (Alexis et al., 2007), peat deposits in Indonesia (Page et al., 2002), and boreal regions (de Groot et al., 2009; Ohlson et al., 2009) indicate that smoldering combustion of fine surface fuels, including litter and duff layers (partially decayed organic matter) and loose detritus from trees and shrubs, are the most susceptible for complete combustion; leading to the inference that those fuels are the primary source of ash (Frandsen, 1987). Other contributions to the ash

layer come from the combustion of aerial fuels (needles, leaves, branches, vines, moss, and lichens in the canopy), which become entrained in convection plumes during the fire and deposited after the fire (Frandsen, 1987). Overall the consumption of terrestrial vegetation is highly variable across and within ecosystems and depends on such factors as weather, fire behavior and fuel conditions including fuel chemistry, loading, arrangement, particle size distribution, and packing (Raison, 1979; Ulery et al., 1993; Stocks and Kaufmann, 1997).

Terrestrial vegetation is dominated by cellulose, hemicellulose, lignin, water, and a wide variety other of compounds including heavy metals that influence the chemistry of ash produced by combustion (Jenkins et al., 1998; Demirbas, 2003). In many species of plants, siliceous structures, called phytoliths are common and can withstand high combustion temperatures typically associated with wildfires, therefore accounting for high levels of silica within ash (Albert and Cabanes, 2007; Morris et al., 2010). Plants also contain various crystals in their tissues, for example calcium oxalates and calcium carbonates (Scurfield et al., 1973; Francheschi and Nakata, 2005), which can be released or transformed during heating (Quintana et al., 2007) resulting in high variation in the inorganic component of ash (Nunez-Regueira et al.,1996, 1997; Dimitrakopoulos and Panov, 2001; Vassilev et al., 2010). Furthermore some plant species produce more inorganic ash than others as different plant parts have varying proportions of compounds; for example the foliage of four Scandinavian wood species had the highest ash content (2.4 - 7.7 %) in the leaves while bark and wood tissue had 1.9 - 6.4 % and 0.2 - 0.7 % respectively (Werkelin et al., 2005).

2.2 Ash chemical properties: alterations associated with thermal decomposition and hydration

While variations in plant species effect the composition of ash, variability in fire intensity also plays a large role altering the level of thermal decomposition organic fuels undergo to form ash (DeBano et al., 1998; Misra et al., 1993; Ulery et al., 1993; Demeyer et al., 2001; Goforth et al., 2005; Liodakis et al., 2005). Relatively low temperatures (200 - 450 °C) result in scorching and charring of organic particles due to incomplete combustion thus producing char fragments often referred to as black carbon. Black carbon is poorly soluble, rich in aromatic and carboxlic organic compounds (Almendros et al., 1992; Forbes et al., 2006; Quill et al., 2010; Scott, 2010; Dlapa et al., 2012; Bodi, 2012a), and contains a low pH and electric conductivity; very similar to unburned vegetation (Goforth et al., 2005; Ubeda et al., 2009). As temperatures pass into the 450 – 500 °C, oxidation is more intense reducing the average size of organic particles, however, carbon is still the main component (Quill et al., 2010).

High intensity fires can produce flaming combustion temperatures up to 1400 °C and smoldering temperatures up to 1200 °C (Pyne et al., 1996) resulting in a lighter colored ash with higher pH and electric conductivity levels, due to the increased presence of exchangeable ions in solution (Pereira et al., 2012). The composition of ash from high intensity fires varies with species consumed, however, is primarily comprised of calcium (Ca), magnesium (Mg), potassium (K), silica (Si), and in lower proportion phosphorous (P), sodium (Na), sulfur (S), other metals such as aluminum (Al), iron (Fe), manganese (Mn) and zinc (Zn) (Misra et al., 1993; Ulery et al., 1993; Demeyer et al., 2001; Goforth et al., 2005; Liodakis et al., 2005; Gabet and Bookter, 2011). As combustion temperature increase in the 500 – 1400 °C range, the relative proportion of these elements will vary due to differing volatilization temperatures; for example

nitrogen and sulfur levels will be low due to low volatilization temperatures (200 – 300 °C)
 compared to phosphorus (550 - 750 °C) and other elements (SiO₂ > 1500 °C; Raison et al., 1985;
 Weast, 1989; DeBano et al., 1998).

Temperatures in the 500 to 1400 °C range also result in a series of thermal decomposition reactions that affect the overall composition of ash. At the lower end of this range the dominant constituents of ash after silica are carbonate compounds, mainly calcium carbonate (CaCO₃) followed by magnesium (MgCO₃) and potassium carbonate (K₂CO₃). High calcium carbonate levels come from the thermal decomposition of whewellite (CaC₂O₄*H₂O) and weddellite (CaC₂O₄*2H₂O); both calcium oxalates that occur in the stems, roots and leaves of common plants (Misra et al., 1993; Monje and Baron, 2002; Malaninie et al., 2003; Liodakis et al., 2005) and lichens (Kloprogge et al., 2004). The first step (1a) in the thermal decomposition of oxalates is a dehydration reaction that begins around 120 °C and is complete by 280 °C. The second step (1b), which occurs around 500 °C results in the loss of CO and the transformation of oxalate to carbonate (Ulrey et al., 1993). Carbonate compounds will then dissociate (1c) to oxides at 580 to 1100 °C depending on the carbonate compound (Misra et al., 1993; 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).

1131 (1a)
$$CaC_2O_4^*2H_2O + heat \rightarrow CaC_2O_4 + 2H_2O$$

1132 (120 °C; Kloprogge et al., 2004)

1133 (1b) $CaC_2O_4 + heat \rightarrow CaCO_3 + CO$

1134 (425 - 500 °C; Kloprogge et al., 2004)

1135 (1c) $CaCO_3 + heat \rightarrow CaO + CO_2$

1136 (600 - 840 °C; Kloprogge et al., 2004; Liodakis et al., 2005)

 $K_2CO_3 + \text{heat } \rightarrow K_2O + CO_2$ (1100 – 1400 °C; Liodakis et al., 2005)

 $MgCO_3 + heat \rightarrow MgO + CO_2$ (580 – 630 °C; Liodakis et al., 2005)

While no distinct morphological changes occur during the first two steps of oxalate thermal decomposition, the transformation from carbonate to oxide is accompanied by a change in the crystal morphology from massive to sponge-like (Kloprogge et al., 2004). Furthermore, ash produced via industrial burning of biofuel and sawdust has been documented to increase in particle size when wetted and exposed to air due to agglomeration (Steenari et al., 1999) or swelling of ash particles (Etiegni and Campbell, 1991; Demeyer et al., 2001). This suggests that new carbonates can be formed by ash interacting with atmospheric moisture and carbon dioxide (CO₂). For example calcium oxide (CaO) can be hydrated to form (2a) portlandite (Ca(OH)₂), a known process in the cement industry (Odler and Colan-Subauste, 1999; Dweck et al., 2000; Kantiranis, 2003; Sakai et al., 2004), which can subsequently absorb CO₂ to form (2b) carbonate (CaCO₃) or (2c) bicarbonates (Ca(HCO₃) depending upon environmental conditions (Etiegni and Campbell, 1991; Demeyer et al., 2001).

1153 (2a)
$$CaO + H_2O \rightarrow Ca(OH)_2$$

- (2b) $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
- 1155 (2c) $CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$

Such chemical alterations associated with the hydration of ash may explain swelling (2 %) immediately after hydration (Stoof et al., 2010) and following four weeks of saturation (12.5 %; Etiegni and Campbell, 1991). However, not all ash is hydrophilic and capable of storing water as ash from chaparral (Gabet and Sternberg, 2008) and eucalypt (Khanna et al., 1996) forests have been reported to be difficult to wet. Furthermore an in depth study addressing the wettability of ash burned from Mediterranean plant species highlighted that water repellent ash is

not uncommon (Bodi et al., 2011) and that unique ash characteristics may be linked to certain plant species.

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2.3 Physical properties of ash

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Ash color is an important indicator of fire severity (Ubeda et al., 2009; Pereria et al., 2010; Pereria et al., 2011) and thus a good indirect estimator regarding the effects of fire on organic consumption (Pereria et al., 2012). Ash color is typically thought to range along the gray spectrum with black and white as end-members (Roy et al., 2010), however, the Munsell color chart (1975) is a more appropriate measurement as it accounts for color influences (reds and browns) associated with metal and organic content within ash (Figure 7; Pereria and Ubeda, 2010; Bodi et al., 2011; Pereria et al., 2011). Black to grey ash is typically associated with moderate fire severity, while dark grey to white ash is the result of high severity (DeBano and Neary, 2005; Ubeda et al., 2009; Roy et al., 2010). There are some variations in ash color across ecosystems as brown and reddish ash observed in Mediterranean environments represent low severity fires, containing un-charred organic particles (Ubeda et al., 2009), while reddish ash observed following wildfires in western North America are associated with high fire severity and the oxidation of iron-oxides (Debano and Neary, 2005). Ash color has also been linked to extractable elements and found to vary greatly across small distances within post-fire landscapes (Pereira, 2010).



Figure 7: Ash samples ranging over a variety of colors (Bodi et al., 2012a)

The particle size, particle density, bulk density, and saturated hydraulic conductivity of wildfire ash can vary substantially (Table 1). Ash particle size is often linked to variations in species composition or environmental factors, which are capable of altering plant morphology. For example, Kinner and Moody (2007) noted a sizable difference in ash particle size associated with hill slope aspect following a moderate wildfire in Colorado, with the particle size of ash from south-facing slopes ($D_{50} = 1400 \, \mu m$) considerably higher than those from north-facing slopes ($D_{50} = 750 \, \mu m$). The authors equated the increase in particle size of south-facing slopes to vegetation and trees within the area containing larger branches and needles. Other studies suggest that variations in the particle size of wildfire ash are not only associated with species composition but also combustion temperature, as ash collected from wildfire sites in Spain and Montana, U.S indicated a fining associated with a decrease in Munsell color (1975) values, suggesting finer whiter ash was correlated with more complete combustion (Woods and Balfour, 2010; Balfour and Woods, 2011; Balfour and Woods, 2013). Kinner and Moody (2007) also

suggest that variations in ash particle density are linked to particle size, as increases in ash particle density are associated with smaller ash particles. Other studies, however, suggest particle density also varies with combustion temperature, as ash produced at low temperatures (< 500 °C) results in lower densities due to the high carbon content of charred material (Mulleneers et al., 1999; Rumpel et al., 2006).

Table 1: Ash particle density (P_p) , mean particle size (D_{50}) , total porosity (Θ_{total}) , bulk density (P_B) , depth, field hydraulic conductivity (K_f) , and laboratory saturated hydraulic conductivity (K) for wildfire ash samples. Only studies containing wildfire ash hydrological characteristics obtained in the field were included.

	Wildfire	P_p (g cm ⁻³)	D ₅₀ (μm)	$\Theta_{ ext{total}} \ (\%)$	$P_{\rm B}$ (g cm ⁻³)	Depth (cm)	$K_{\rm f}$ (cm sec ⁻¹)	K (cm sec ⁻¹)
Cerda and Doerr, 2008	Sierra de la Calderona: Spain	2.53 ± 0.06	-	83	0.42 ± 0.10	3.63 ± 0.75	-	-
Gabet and Booker, 2011	I-90 Complex: MT	2.50 ± 0.60	100	-	0.39 ± 0.03	-	-	$0.00458 \\ \pm 0.000250$
Moody et al., 2009	Overland Fire: CA	2.44 ± 0.27	88	66 ± 1	0.83 ± 2.40	-	0.0120 ± 0.0000204 (3D)	-
		-	-	-	-	-	0.00450 ± 0.000405 (1D)	-
Woods and Balfour, 2008	I-90 Complex: MT	-	-	84	0.41 ± 0.01	2.25 ± 2.25	-	0.00150
Ebel et al., 2012	Fourmile Canyon Fire: CO	-	-	-	0.18 - 0.45	1.80 ± 1.60	-	0.000238

Ash bulk density and saturated hydraulic conductivity are often difficult to obtain in the field due to the thin delicate nature of some ash layers, access issues onto wildfire sites and the temporal variability of ash. Values for ash bulk density range from 0.12 to 0.45 g cm⁻³ with higher values associated with thicker ash deposits (Goforth et al., 2005; Cerdà and Doerr, 2008; Woods and Balfour, 2008; Moody et al., 2009; Gabet and Bookter, 2011; Ebel et al., 2012). These values are considerably lower than the typical value of soils with comparable grain size, however, consistent with reports of high ash water retention (Stoof et al., 2010) and ash layers

being capable of storing large amounts of water before initiating runoff (Cerdà and Doerr, 2008; Woods and Balfour, 2008; Moody et al., 2009; Woods and Balfour, 2010; Gabet and Bookter, 2011). Reported values for ash hydraulic conductivity mainly consist of laboratory measurements obtained on repacked cores, with values for the saturated hydraulic conductivity of ash ranging over an order of magnitude across fuel types of the northern Rocky Mountain region, 1.50x10⁻³ to 2.38x10⁻⁴ cm sec⁻¹ (Table 1). To date only Moody et al. (2009) have attempted to directly measure the hydraulic conductivity of ash in the field indicating laboratory results seem consistent with field measurements, however, dimensional flow must be taken into consideration. Overall these conductivities are supportive of the two-layer soil concept proposed by Kinner and Moody (2010) and the notion that ash is mainly hydrophilic in nature (Etiegni and Campbell, 1991; Leighton-Boyce et al., 2007; Woods and Balfour, 2008), however, it should be reiterated that not all ash is hydrophilic (section 2.2).

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The effects of ash within the ecosystem are not homogenous or completely understood as ash layers are highly variable in composition (section 2) and thickness, as well as temporally and spatially. Ash layers initially deposited after a fire can be contiguous across the landscape (Figure 8; Cerdà and Doerr, 2008; Woods and Balfour, 2008), however, within days to months after the fire, ash is often redistributed from the soil surface by wind, surface runoff or incorporated into the soil (Bodí et al., 2011). Removal of ash by wind can impact visibility and air quality, and is the primary cause of nutrient loss from burned areas (Raison et al., 1985; Chang Huang et al., 2006; Wagenbrenner et al., 2010; Pereira et al., 2011). Ash removed by surface runoff is relocated to surface depressions and streams (Minshall et al., 1998; Ryan et al., 2011) as well as reservoirs (Blake et al., 2006; Reneau et al., 2007) where it has the potential to affect water chemistry and aquatic organisms as well as be stored in lakes and marine deposits (Scott, 2009; Santin et al., 2012). A large proportion of ash is incorporated into soils (Czimczik and Masiello, 2007) by downward migration, enhanced by bioturbation (Topoliantz and Ponge, 2005), and freeze-thaw cycles, which can alter nutrient storage and ecosystem recovery. While the temporal evolution of ash in post-fire systems has not been directly addressed, it is generally agreed upon that ash is removed or incorporated into the underlying soil within a few years of fire activity (Blank and Zamudio, 1998; Larsen, et al., 2009; Schmidt and Noack, 2000; Novara et al., 2011; Santin et al., 2012).

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Figure 8: A photograph of the 2009 Terrace Mountain wildfire in British Columbia, Canada indicating a relatively thick homogenous ash layer deposited across the landscape.

More typically ash is viewed as a non-homogenous feature ranging in coverage from 30 - 64 % (Lavee et al., 1995; DeLuis et al., 2003; Larson et al., 2009) with a thicknesses of 1.0 - 20.0 cm (Cannon et al., 2001; Cerdà and Doerr, 2008; Gabet and Sternberg, 2008; Woods and Balfour, 2008; Larsen et al., 2009; Ebel et al., 2012; Santin et al., 2012). Thicker ash layers are commonly associated with white highly combusted ash, while thinner discontinuous layers are associated with lower severity black ash (Keeley and Zedler, 2009), however, due to combustion variations with depth ash layers in the field are commonly striated with a layer of black ash underlying thicker white ash deposits (Blank and Zamudio, 1998; Neary et al., 2005). The accumulation of these very thick white ash layers are often referred to as the "ash bed effect," altering physical, chemical and biological soil properties due to direct heating associated with the deposit of such a thick ash layer as well as the indirect residual effect of ash on the underlying soil system (Humphreys and Lambert 1965; Chambers and Attiwill, 1994; Knoepp et al., 2005).

This section aims at examining the effects of ash on varying parts of the ecosystem, specifically with regards to the physical and chemical properties of the soil, microbial activity, plant growth and water quality.

3.1 Effect of ash on soil properties

There is extensive literature on the application of industrial fly ash and ash from woodfired boilers as a soil amendment to dispose of ash by-product and improve soil quality for crop
and tree growth (Vance 1996; Nohrstedt 2001; Demeyer et al., 2001; Aronsson and Ekelund
2004; Pitman 2006; Augusto et al., 2008). However, this section focuses solely on research into
the effects on soil properties caused by ash from wildfires and prescribed fires as *i*) industrial
ashes are formed at a much higher temperature than ash from even the most severe wildfires,
therefore exhibiting potentially different properties and effects on soil and *ii*) the effects of ash
from wildfires and prescribed fires must be considered within the context of the additional
effects of soil heating, which does not occur when ash is used as an amendment.

3.1.1 Effect of ash on soil chemistry

The effect of ash on soil chemistry has been studied since the beginning of the 20th century and included in numerous comprehensive reviews pertaining to fire effects on soil (Burns, 1952; Raison, 1979; Certini, 2005; Bodi, 2012). Research began in Sweden in 1918 where Hesselman concluded that basic salts in ash stimulated nitrification in forest soils. Decades later research in Europe and the United States investigated the role of ash in post-fire

soil nutrient cycling and soil fertility with accounts of ash significantly increasing soil pH, due to the accumulation of alkaline elements, (Finn, 1943; Allen, 1964; Nye and Greenland, 1964; Humphreys and Lambert, 1965) and varied effects associated with charcoal addition based on the fuel species and subsequent char grainsize (Tryon, 1948). Overall ash layers were found to notably increase soil available nutrients, such as K, P, Na, Mg, and Ca (Miller et al., 1955; Ahlgren and Ahlgren, 1960; Nye and Greenland, 1964; Smith, 1970), and the effects of ash on the underlying soil chemistry were dependent upon *i*) the composition and amount of ash deposited (Tyron, 1948), *ii*) the buffering capacity of the underlying soil (Sampson, 1944; Allen, 1964) and *iii*) the ecosystem type; as quantities of nutrients released from ash produced in grasslands were minor compared to forest systems (Jordon, 1965; Nye, 1959).

In the later part of the 20th century and continuing into the 21st century, research shifted towards the mechanisms controlling the effects of ash on soil chemistry and variations in the longevity of ash effects. While the ability of ash to increase soil nutrients and pH was well established, few studies had directly measured ion leaching from ash into soil following a fire until 1975 when Grier found that speciation of ash explained why some elements were readily dissolved by rainwater and leached into the soil whereas elements in carbonate form or bound to compounds had low solubilities. The main constituents of ash were then divided into three main solubility classes; easily soluble elements (K, S, Na); relatively insoluble elements (Ca, Mg, Si, Fe); and very insoluble elements (P) (Raison, 1979; Khanna et al., 1994; Nieminen et al., 2005). These differences in solubility explained the mobilization order of elements from ash into soil (Na > K > Mg > Ca > P) (Grier and Cole 1971; Grier, 1975), variations in leaching depth of cations from the ash layer (Khanna and Raison, 1986), the cation composition of post-fire soils (Khanna et al., 1994), and changes in ash solubility over time (Ludwig et al., 1998). The low

solubility of calcite in ash also explained the varied recovery of soil pH following a fire; as some studies reported the pH of soil recovered quickly (Giovannini et al., 1990; Iglesias et al., 1997), while in others indicated the low solubility of calcite from the ash maintained a moderately alkaline pH in surface soils for years after the fire (Ulrey et al., 1993; Ludwig et al., 1998; Aleksandrovskii, 2007).

3.1.2 Effect of ash on soil physical properties

When compared with the extensive research of ash effects on soil chemistry, less is known regarding the effects of ash on soil physical properties. The deposition of ash within post-fire landscapes is often associated with an observed decrease in surface albedo, thus increasing soil thermal regime within the soil (Badia and Marti, 2003). However, a prescribed burn conducted by Massman et al. (2008) indicated that ash layers were also capable of insulating the underlying soil reducing thermal increases with responses directly related to ash thickness. Ash can modify soil hydraulic properties by increasing soil water retention, however, the response is dependent upon the degree of ash combustion (Stoof et al., 2010). Ash does not significantly alter soil texture but changes in soil particle size distribution, bulk density, particle density, porosity, and aggregate stability have been linked to soil heating above 250°C (Badia and Marti, 2003).

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Ash leachate has been investigated over decades, as elements in the soluble phase are the most available in terms of plant nutrition and runoff water chemistry. Results indicate extracts are predominantly alkaline (high pH) due to compounds such as CaCO₃, MgO, CaO, Mg(OH)₂ and MgCO₃ and the chemistry of ash aqueous extracts depend upon the presence of these compounds, as they control the type and amount of elements in solution (Chojnacka and Michalak, 2009; Liodakis and Tsoukala, 2009; Úbeda et al., 2009, Pereira et al., 2012). Heavy metal ions on the other hand are commonly removed from solution by precipitation, adsorption and ion exchange (Chojnacka and Michalak, 2009; Úbeda et al., 2009; Pereira, 2010). Several studies indicate that the pH and electric conductivity of ash leachate are i) greater than that from unburned litter extract (Pereira, 2010; Pereira et al., 2011), ii) increase with combustion temperature (Henig-Sever et al., 2001; Pereira, 2010, Pereira et al., 2012) and iii) decrease as the number of leaching tests increase, overall indicating the chemistry of ash will change over time due to its partial solubility (Úbeda et al., 2009; Pereira et al., 2009; Liodakis and Tsoukala, 2009). However, under natural conditions nutrients are mainly extracted from ash in the immediate period after the fire, and due to erosional agents ash produced in one area can impact other areas thus adding a great complexity to the environmental impacts of ash chemistry (Pereira et al., 2010).

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The degree to which the underlying soil retains nutrients present in ash leachate depends upon the thickness of the remaining soil organic layer, the composition of the underlying soil and the solubility of the nutrient in question. For example, coarse textured soils typically retain low levels of nutrients from the ash (Ca, Mg, P) and in some cases lose K, while clay and peat rich

soils retain high levels of Ca and K (Burns, 1952; Elliott, 1954; Allen, 1964). Ash leachate can either increase or decrease soil aggregate stability depending on soil clay mineralogy (Holcomb and Durgin, 1979; Durgin, 1980, 1985; Durgin and Vogelsang, 1984). For example soils with predominantly 2:1 type clays, cations within the ash leachate act as a bridge between clay particles leading to flocculation and increased aggregate stability (Holcomb and Durgin, 1979) were as the opposite effect occurs in soils containing 1:1 clays, which are pH dependent and the high pH associated with ash leachate causes the surface charge of clay to become negative causing dispersion and a reduction in aggregate stability (Durgin and Vogelsang, 1984; Durgin, 1985). More recently it has been shown that the effect of ash leachate on aggregate stability is likely to depend on the ash chemistry as well as the soil clay mineralogy; as ash produced at higher temperatures contains more monovalent cations capable of causing clay dispersion (Úbeda et al., 2009).

3.2 Effect of ash on soil microbial activity and plant growth

Soil microbial activity is crucial for a functioning soil system (Brady and Weil, 2007) and often altered following fires due to direct heating and indirect modification of soil characteristics (Mataix-Solera et al., 2009). Incorporation of ash into post-fire soils increases soluble carbon and available nitrogen levels by mobilizing fixed nitrogen stored in the soil (Fowells and Stephenson, 1934; Tamm, 1950; Metz et al., 1961; Nye and Greenland, 1964) and increasing soil pH, by up to three units depending upon ash type and initial soil pH (Raison and McGarity, 1980; Badia and Martí, 2003, Knoepp et al., 2005; Molina et al., 2007). As a response to increases in soluble carbon, as well as increases in soil pH, heterotrophic bacteria within the soil increase in turn

rising the initial post-fire bacteria/fungi ratio within the soil (Raison, 1979; Mataix-Solera et al. in Cerdà and Robichaud, 2009; p149). This response is often short-lived, as once easily mineralized carbon is depleted bacteria respiration decreases, subsequently reducing the bacteria/fungi ratio and allowing ash fungal crusts to develop; potentially stabilizing the soil and reducing erodibility (Dunn et al., 1982). Overall the response of soil microbial communities to ash addition have been found to vary with soil type, as soil reparation rates decrease or increase depending upon the buffering ability of the soil, and amounts of ash added to the system.

Furthermore an active preexistent microbe population must be present within the soil for ash to alter soil respiration, indicating that sterilized soil will not be affected by ash additions (Raison and McGarity, 1980; Raison et al., 2009).

Numerous studies ranging over a variety of species within Spain, Portugal and other portions of the Mediterranean indicate that the addition of ash (> 2 cm) on to the soil surface negatively impacts seed germination (Gonzalez-Rabanal et al., 1994; Gonzalez-Rabanal and Casal, 1995; Ne'eman and Meir, 1993; Izhaki et al., 2000; Thomas and Wein, 1990). Ash leachate has little effect on germination (Herrero et al., 2007), instead decreases in seed germination are thought to be attributed to i) the high water holding capacity of ash limiting the access of seeds to water as well as exerting a high osmotic pressure, which some species are too sensitive to overcome (Ne'eman and Meir, 1993); ii) certain ions released from the ash may be toxic (Ne'eman Meir, 1993); and iii) the increase in soil pH may exceed the alkalinity threshold for certain seed species (Thomas and Wein, 1990). In contrast to the effects of ash on germination, plant growth is positively affected by ash due to the initial increases in available nutrients (Ca²⁺, Mg²⁺, K⁺, P and N) as well as the long-term increase in soil fertility associated

with the "ash-bed effect" (Raison, 1979; Chambers and Attiwill, 1994; Knoepp et al., 2005; Raison et al., 2009).

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3.3 Effect of ash on water quality

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Ash and disaggregated mineral soil can be redistributed to landscape depressions, as well as streams and lakes following wildfire activity, leading to reduced water storage capacity due to siltation of water bodies, as well as contamination from the presence of heavy metals and high nutrient loads (Moody and Martin, 2001; Johansen et al., 2003; Goforth et al., 2005; Emelko et al., 2011; Rhoades et al., 2011). The risk to water supplies depends on the likelihood that concentrations will exceed guideline minimums and durations as well as the availability of adequate treatment facilities to process contaminated water (Smith et al., 2011). While the direct effect of ash on water quality is often difficult to quantify, given that ash is often indistinguishable from mineral sediment once delivered to streams, increases in nutrient supply are often equated to ash particles and nutrients lost from burned sites as ash can form a significant component of suspended material flux within the first year after a fire (Smith et al., 2011). Cations and nitrates typically arrive to water bodies via overland flow or ash leachate (Soto and Diaz-Fierros, 1993; Haucer and Spencer, 1998; Gimeno-Garcia et al., 2000; Lasanta and Cerdà, 2005) and have been known to increase nitrogen and phosphorus levels from 5 to 60 times background levels (Spencer and Hauer, 1991) increasing algal growth and affecting (decreasing) dissolved oxygen concentrations within water bodies (Writer et al., 2012). Nutrients are also directly deposited into water bodies via aerial deposition of ash particles and dissolution of smoke into streams (Raison et al., 1985; Spencer and Haucer, 1991; Spencer et al., 2003).

Few studies have specifically addressed the effects of ash on water quality, however, in 2003 Earl and Blinn conducted a stream monitoring study in New Mexico where ash inputs resulted in an immediate increase in ammonium, nitrate, phosphate and other major cations. The dissolved oxygen content was noted to decrease with the ash input as well as increases in turbidity, pH and electrical conductivity. The changes in water chemistry were short lived and returned to baseline levels within 24 hours, with the exception of phosphate, which remained elevated for four months. Other studies indicate nutrient concentrations return to background levels within several weeks after wildfire activity (Lasanta and Cerdà, 2005) with some periodic increases in nutrient concentration associate with spring runoff and snow melt (Tiedemann et al., 1979; William and Melack, 1997; Spencer et al., 2003).

Problems associated with water supply contamination are often limited to one or two storm events directly following the wildfire, with concentrations quickly returning to baseline levels (Smith et al., 2011), however, in regions of the world where water resources are scarce and city populations are large, even these short disruptions can seriously impact drinking water needs. For example, the 2003 wildfires outside Canberra, Australia heavily impacted three of the cities reservoirs reducing water supply to 15 % (White et al., 2006; Smith et al., 2011). Furthermore, in the absence of adequate treatment facilities, water supplies may be vulnerable to prolonged disruption from large post-fire increases in suspended sediment flux (Smith et al., 2011). For example, water quality issues lasted for 5 years following the 2002 Hayman Fire, Colorado (Rhoades et al., 2011), nearly a decade after a wildfire in the Canadian Rockies (Emelko et al., 2011) and are still being treated in Colorado following the Fourmile Canyon Fire (Writer et al., 2012).

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2329 CHAPTER TWO

MAIN OBJECTIVES OF DISSERTATION

According to the National Interagency Fire Center, the 2012 wildfire season within the American West was 30 % above average and consumed over 3.6 million hectres, an area greater than the state of Maryland (NIFC, 2012). This increase in wildfire activity has been associated with shifts in climate over the last forty years, the legacy of human wildfire suppression and the increase in bark beetle activity throughout the West (Climate Central, 2012). Increases in spring and summer temperatures over the years, as well as decreases in winter snowpacks, have increased the typical burning season by two and a half months; making the wildfire season 75 days longer than 40 years ago (Westerling et al., 2006). Within the Rocky Mountain region the average number of wildfires over 400 hectares have quadrupled and the frequency of large wildfires, greater than 4,000 hectares, have increased seven times since the 1970's (Climate Central, 2012). The effect of this increased wildfire activity on resource management and ecosystem function is of increased interest to agencies and land managers within the Northern Rocky Mountain region of the United States.

My doctoral research aims to contribute to the knowledge of post-fire hydrology, specifically with regards to the role of wildfire ash within recently burned ecosystems. My dissertation is written as three manuscripts aimed to address:

- 1) Does the initial physical, chemical, and hydrological properties of vegetative ash within the Northern Rocky Mountain region vary with fuel type and combustion temperature / fire severity?
- 2352 2) If there is potential for the variability in the hydrological properties of ash, due to factors

2353 such as differences in fuel type and fire severity, to affect initial post-fire infiltration 2354 runoff response in ash-covered soils? 2355 2356 3) Are established laboratory methodologies from other fields of research could be applied 2357 to wildfire ash, thus allowing for adequate data pertaining to ash characteristics given 2358 limited ash volume, therefore allowing for more ash data to be incorporated into post-fire 2359 modeling systems. 2360 2361 4) Are the hydrological properties of ash layers change over time and if these alterations 2362 could potentially affect post-fire infiltration response in ash covered soils? 2363 2364 A series of laboratory and field based experiments were conducted to address one of the 2365 primary research questions directly or provide a proof of concept that was applied to subsequent 2366 experiments. The specific objectives of this dissertation were to: 2367 1) assess how the physical (particle size and shape, particle density, bulk density and 2368 porosity) and chemical (mineralogy and elemental composition) properties of ash might 2369 explain recorded variations in hydrologic properties (water retention, hydraulic 2370 conductivity, and sorptivity). 2371 2372 2) assess, within the laboratory setting, whether hydration of various ash types alters the 2373 physical, chemical and hydrologic properties of ash. 2374 2375 3) assess, within the laboratory setting, whether ash characteristics can be linked to various 2376 stages of thermal decomposition and whether ash produced in the laboratory can provide 2377 beneficial insight into understanding wildfire ash characteristics. 2378 2379 4) develop a non-destructive method for the rapid assessment of ash saturated hydraulic 2380 conductivity in the laboratory on disturbed ash samples. 2381

5) assess whether ash hydrologic properties can be linked to simple metrics, such as calcium carbonate content or color, in order to allow for rapid post-fire hazard assessment. 6) develop a method for directly measuring ash sorptivity in the laboratory on disturbed ash samples. 7) determine how accurately the laboratory methods (objectives 4 and 6) reflect ash field measurements taken in-situ. 8) determine if *in-situ* wildfire ash layers are capable of temporally evolving and if so the effects of ash infiltration. 9) document the formation of a post wildfire ash crust following a recent wildfire. 10) assess if ash crust formation was due to compaction by raindrop impact or mineralogical transformations associated with hydration. 11) if mineralogical transformations associated with crust formation were dependent upon direct hydration or chemical transformations associated with ambient air moisture conditions. REFERENCES: Climate Central, 2012. Report: The age of western wildfires. www.climatecentral.org National Interagency Fire Center, 2012. http://www.nifc.gov/fireInfo/fireInfo stats totalFires.html [Accessed May 12, 2013] Westerling, A. L., H.G. Hidalgo, D.R. Cayan and T.W. Swetnam, 2006. Warming and earlier Spring Increase Western U.S. Forest Wildfire Activity. Science 313: 940-943.

2413 CHAPTER THREE

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The Hydrological Properties and the Effects of Hydration on Vegetative Ash from the Northern Rockies, USA.

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ABSTRACT

Vegetative ash is known to alter post-fire runoff rates, in some cases decreasing runoff by protecting the underlying soil and in other cases aiding in the formation of a surface seal increasing runoff. Variability in this hydrological response of ash may reflect differences in the hydrologic properties of ash caused by shifts in its physical and chemical characteristics. This study investigated the physical (particle size and shape, particle density, bulk density and porosity) chemical (mineralogy and elemental composition) and hydrologic (water retention. hydraulic conductivity, and sorptivity) characteristics of laboratory and wildfire ash from the Northern Rocky Mountain region of the United States. A variety of techniques were used including scanning electron microscope, X-ray diffraction, thermogravimetric analysis, and conventional soil science techniques. Laboratory ash samples were prepared by combusting fuel from three dominant trees species of the region (Pinus contorta, Pinus ponderosa and Pseudotsuga menziesii) at various combustion temperatures (300°C, 500°C, 700°C or 900°C). The main objectives of this study were to determine (i) how the physical (particle size and shape, particle density, bulk density and porosity) and chemical (mineralogy and elemental composition) properties of ash might explain variations in hydrologic properties (water retention, hydraulic conductivity, and sorptivity); (ii) whether wetting alters the physical, chemical and hydrologic properties of ash; (iii) whether ash characteristics could be linked to various stages of thermal decomposition and whether ash produced in the laboratory could be beneficial to understanding wildfire ash characteristics and (iv) whether ash hydrologic properties can be linked to simple metrics, such as calcium carbonate content or color, which can be used in rapid post-fire hazard assessment.

Results of this study indicate that variation in the hydrological response of ash can be partially explained by differences in ash characteristics associated with combustion temperature. Depending on ash mineralogy, which was dictated by the level of thermal decomposition of organic material, ash particles can (a) contain micro-porosity contributing to total porosity values as high as 98 %; (b) shift hydraulic conductivity values orders of magnitude from 0.12 ± 0.03 to 0.002 ± 0.0003 cm sec⁻¹; and (c) chemically transform after initial hydration suggesting ash layers could alter post-fire runoff response by creating a chemical crust. Furthermore while ash color is often used as an indicator of burn severity it may not be an accurate indicator regarding the hydrologic response of ash in post-fire systems. Instead carbonate content is suggested as a more informative aid in predicting post-fire hydrologic response.

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Keywords: wildfire ash properties, ash crusting, post-fire runoff response, wildfire

1. Introduction

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An important factor controlling post-fire runoff and erosion rates is the presence of ash on the soil surface. Post-fire landscapes are often blanketed with a layer of ash formed from the combustion of vegetation, surface fuels and duff layers during a wildfire. While there is general agreement that ash alters the immediate post-fire hydrologic response, the literature is contradictory in terms of the role ash plays. The most common view is that ash temporarily increases the potential for overland flow by sealing the mineral soil surface (Neary et al., 2005; Gabet and Sternberg, 2008; Onda et al., 2008), either through the clogging of soil macropores by ash particles (Woods and Balfour, 2010) or the formation of a surface ash crust (Gabet and Sternberg, 2008; Onda et al., 2008). While post-fire related changes in soil hydrophobicity have long been established to alter post-fire hydrologic response (DeBano, 2000; Doerr et al., 2007), a new theory suggests that alterations in the hydrophobic properties of ash particles can increase post-fire overland flow (Bodi et al., 2011) as ash is not always readily wettable due variations in hydrophobic compounds associated with species type (Gabet and Sternberg; 2008). Other studies, however, suggest that the ash layer temporarily reduces runoff, by intercepting and storing rainfall (Cerda and Doerr, 2008; Woods and Balfour, 2008; Moody et al., 2009; Zavala et al., 2009; Ebel et al., 2012). The uncertainty regarding the effects of ash on runoff has important implications for post-fire management. If the ash layer contributes to the general tendency for runoff rates to increase after a fire then it may be beneficial to remove the ash layer as soon as possible, and the ash layer could be used as an indicator of accelerated runoff and erosion in post-fire hazard assessments (Robichaud et al., 2007). Conversely, if ash temporarily reduces runoff, then there may be a benefit associated with stabilizing the ash layer in-situ. Therefore,

there is a need to clarify what drives variations regarding the role of ash in immediate post-fire hydrologic response in order to correctly assess and manage post-fire hazards.

From a hydrologic perspective, the ash-soil profile present after a wildfire is analogous to a layered soil profile in an unburned setting. The literature indicates that the effects of ash on post-fire runoff are highly variable due to three main variables *i*) the thickness of the ash layer (Cerda and Doerr, 2008; Larsen et al., 2009; Kinner and Moody, 2010; Woods and Balfour, 2010), *ii*) variations in ash and soil composition making up the post-fire two-layer soil system specifically variations in ash particle size (Gabet and Sternberg, 2008; Woods and Balfour, 2010), wettability (Bodi et al., 2011) and hydraulic conductivity (Moody et al., 2009; Kinner and Moody, 2010) and *iii*) alterations in ash properties associated with hydration (Gabet and Sternberg, 2008; Onda et al., 2008; Woods and Balfour, 2008; Stoof et al., 2010; Bodi et al, 2011). Current research regarding the effect of ash on infiltration and runoff is focused on quantifying the hydrological properties of post-fire systems to facilitate the parameterization of hydrologic models (Moody et al., 2009; Ebel et al., 2012) and how variations in the hydrologic properties of the ash layer may explain alterations in post-fire runoff response.

It is well established that ash properties change with heating, as the combustion of organic matter results in volatilization of some components and the transformation of others to new substances (Ubeda et al., 2009). For example, relatively low temperatures (200 – 450 °C) result in the formation of coarse black ash containing predominantly carbon particles (DeBano et al., 1998; Plante et al., 2009), while higher combustion temperatures (600 - 1000 °C) result in fine ash composed of inorganic compounds such as carbonates, oxides, silica and small amounts of phosphorus, sulfur and nitrogen (Ulery et al., 1993; Goforth et al., 2005; Liodakis et al., 2005). While the effect of combustion temperature on the physical and chemical composition of

vegetative ash have been investigated in various fuel types (Ulrey et al., 1993; Liodakis et al., 2005; Ubeda et al., 2009; Bodi et al., 2011) and linked to changes in soil and ecosystem processes (Gabet and Bookter, 2011) there remains the need to assess distinct variations in the hydrologic properties of ash to clarify its role in altering post-fire runoff. This study aims to identify hydrologic characteristics (water retention, hydraulic conductivity, and sorptivity) of different ash types in order to address this research gap. Furthermore, while the authors are aware ash produced via industrial burning of biofuel and sawdust is not comparable to wildfire ash due to variations in heating regimes the literature does provide detailed understanding of thermal dynamic concepts, which could aid in understanding the varied hydrologic response of wildfire ash reported in the literature. For example, ash produced via industrial burning has been documented to increase in particle size when wetted and exposed to air due to agglomeration (Steenari et al., 1999) or swelling (Etiegni and Campbell, 1991) of ash particles. Similar alterations associated with the hydration of wildfire ash samples could alter ash properties as well as provide a basis for the formation of a surface ash crust in post-fire systems as noted by Onda et al. (2008) and in flume studies by Gabet and Sternberg (2008), as well as the high water retention capability observed by Stoof et al. (2010).

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The main objectives of this research were therefore to assess (*i*) how the physical (particle size and shape, particle density, bulk density and porosity) and chemical (mineralogy and elemental composition) properties of ash might explain variations in hydrologic properties (water retention, hydraulic conductivity, and sorptivity); (*ii*) whether wetting alters the physical, chemical and hydrologic properties of ash; (*iii*) whether ash characteristics could be linked to various stages of thermal decomposition and whether ash produced in the laboratory could be beneficial to understanding wildfire ash characteristics and (*iv*) whether ash hydrologic

properties can be linked to simple metrics, such as calcium carbonate content or color, which can be used in rapid post-fire hazard assessment.

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2. Materials and Methods

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Accurately gauging the temperature in which wildfire ash has been generated is not possible, therefore laboratory experiments combusting fuels at specific combustion temperatures is a useful methodology for assessing the relationship between fire temperatures and distinct ash characteristics (Liodakis et al., 2005; Ubeda et al., 2009; Bodi et al., 2011). The chemical composition of forest fire ash can be very variable and depends on various factors like the type of fuel species, the part of the plant combusted (bark, wood, leaves), the degree of litter decomposition, plant age, fuel moisture and other environmental conditions altering combustion (Liodakis et al., 2005; Bodi et al., 2011; Pereira et al., 2011). Laboratory ash samples for this study aimed to keep fuel variability to a minimum by selecting fuel exposed to similar environmental conditions, comparable plant parts and age as well as oven drying to a constant weight. Ash was produced from cast branches and needles of three dominant tree species of western Montana, lodgepole pine (*Pinus contorta*), ponderosa pine (*Pinus ponderosa*), and Douglas-fir (Pseudotsuga menziesii). Each fuel type was placed in a cool muffle furnace to be heated to a set combustion temperature (300°C, 500°C, 700°C or 900°C); temperatures are within the measured range of conifer forest wildfires of this region (Gundale and DeLuca, 2006). While the extent of flaming and smoldering combustion can vary widely in the field, fuels were held at the allocated temperature for 2 hours, which is consistent with combustion times reported for other studies (Pereria et al., 2009; Ubeda et al., 2009; Gabet and Bookter, 2011; Bodi et al.,

2011). The temperature regime within this study is considerably higher than often used in Mediterranean studies (150°C to 700°C; Pereria et al., 2009; Ubeda et al., 2009; Bodi et al., 2011), however, is consistent with limited ash production research pertaining to this region (Gabet and Bookter, 2011). Furthermore combustion temperatures within this study aimed to target temperatures associated with shifts in thermal decomposition; at 300°C incomplete combustion starts to occur resulting in the charring of fuel (Ubeda et al., 2009), around 500°C CaCO₃ begins to form with mild variations in temperature for differing fuels sources (Ulrey et al., 1993; Kloprogge et al., 2004; Quintana et al., 2007) and according to differential thermal analysis mass loss observed in the temperature range of 650–900°C is predominantly due to the decomposition of carbonates (Misra et al., 1993; Liodakis et al., 2005) therefore 700°C and 900°C temperatures aimed at assessing various degrees of carbonate disassociation. Due to the small quantity of ash (1-2g) produced via each muffle furnace burn numerous burning runs (20) were conducted for each temperature fuel type combination; ash was then pooled for analysis. Bulk wildfire ash samples (100g) were included in the study to assess if traits observed in laboratory-generated ash were observed in wildfire ash. Wildfire samples were collected from two high severity wildfires; the Gunbarrel wildfire (August 2008) occurred east of Yellowstone National Park, WY where the dominant tree species were P. ponderosa and P. contorta and the Terrace Mountain wildfire (July 2009), which occurred 14 miles northwest of Kelowna, British Columbia and burned roughly 10ha of mature *Pseudotsuga menziesii*, *P. contorta* and sparse western cedar (*Thuja plicata*) forest. High fire severity was verified based on visual indicators; duff and litter layers were completely consumed, white ash was present and contained little to no visible char fragments, and evidence of soil heating (charring or a reddish color) existed in the underlying soil (Figure 1; DeBano et al., 1998; Neary et al., 2005). Wildfire ash samples were

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collected by first creating a small trench (~1m long), to assess the ash-soil profile, then removing ash with a sharp trowel to avoid soil contamination (Figure 1). Numerous ash samples were collected and combined to produce a composite ash sample for laboratory testing.

Laboratory and wildfire samples were run in triplicate (n = 3) through a series of hydrologic, physical, and chemical tests, which are outlined in subsequent sections. The effects of initial ash hydration were also examined, in triplicate for each sample type, by saturating a sub-sample of each ash type with de-ionized water and air-drying it for 72 hours.

2.1. Hydrological analysis

Ash water repellency may govern variations in the hydrological response of ash and was classified according to the methodology outlined by Bodi et al. (2011). Ash hydraulic conductivity (K_{sat}) was determined using the falling head method (Reynolds et al., 2002), to assess variations with ash composition and the ability of an ash layer to govern infiltration in a layered soil system. Porosity was measured to aid in explaining K_{sat} results as well as the water retention ability of varying ash types. While effective porosity is known to be a more representative metric than the total porosity, most of the published values of ash porosity are based on total porosity (Cerda and Doerr, 2008; Woods and Balfour, 2008; Moody et al., 2009), therefore both effective and total porosity (ϕ) values were included in this study. Total porosity was calculated from laboratory bulk density measurements and a measured value of particle density, while effective porosity was estimated using the gravimetric water saturation method (Flint and Flint, 2002a). In order to evaluate the effect of saturation on the internal structure of ash, and hence the swelling nature of ash, the ratio of the intrinsic permeability of the sample to

air (k_a) and water (k_w) were calculated for each sample; a k_a : k_w of one is indicative of a stable substance, a ratio > 1 indicates swelling and a ratio < 1 represents dissolution. Intrinsic permeability measurements were conducted with an air permeameter to relate the relative viscosity of air and water (Chief et al., 2008). Water retention properties were obtained using the hanging column method for potentials in the 0.1 to 5 bar range (Dane and Hopmans, 2002), as variations in ashes ability to retain water may explain why some ash is documented to store rainfall and delay runoff. Sorptivity (S) was measured to identify the capacity of ash to absorb water by capillarity and address the affinity of water to move horizontally through the ash layer prior to saturation. Sorptivity measurements are typically obtained from field or laboratory based infiltration experiments (Vandervaere et al., 2000); however, the substantial volume of ash required made this approach impractical. Therefore an alternative approach was utilized based on a method for testing soil aggregate sorptivity, where a thin walled steel probe was connected to a reservoir and a horizontal glass capillary tube (Leeds Harrison et al., 1994).

2.2. Physical analysis

Measuring particle size and shape provides a basis for understanding the soil pore clogging potential of ash, as well as assessing alterations in the particle associated with hydration. A Hitachi S-4700 scanning electron microscope (SEM) was used to obtain pictographs of ash structure and particle shape before and after hydration. Particle size distribution, median particle diameter (D_{50}) and fine particle diameter (D_{10}) were determined using laser diffractometry after sieving samples to 2mm (Beuselinck et al., 1998; Malvern Instruments Ltd, Malvern, UK). Particle density (P_p) and bulk density (P_b) were determined to

calculate total porosity. The pycnometer bottle method was used to determine P_p (Flint and Flint, 2002b) while P_b was calculated from repacking ash cores in the laboratory by areal deposition. Ash color was classified according to a Munsell color chart (Munsell, 1975) to link ash characteristics to a visual proxy.

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2.3. Chemical analysis

The pH of ash pore water dictates the formation of post-hydration compounds therefore ash pH was measured by mixing 0.25g of ash with 20ml of de-ionized water (Steenari et al., 1999). The level of thermal decomposition within each ash type was assessed by the ratio of organic to inorganic carbon as well as elemental composition. A Fissons EA1100 dry combustion analyzer was used to obtain total carbon (TC), while inorganic carbon content was determined through measuring CO₂ concentrations following mixture with H₂SO₄; organic carbon content was calculated as the difference between total and inorganic carbon. To assess if ash samples were consistent with previous chemical analysis elemental composition was obtained through an Inductively Coupled Plasma Emission Spectroscopy (ICP-ES). Samples for ICP-ES were prepared by dissolving 50mg of oven-dried ash in 2 ml of trace metal grade HCl. The mixture was left undisturbed for 48 hours to insure complete dissolution, then diluted to 50ml using distilled deionized water to insure concentration of various elements lay within the linear range of detection for the ICP-ES. The solution was analyzed for B, Ca, Fe, K, Mg, Mn, Na, P, S, and Zn. In order to identify mineralogical alterations associated with initial ash hydration X-ray Diffraction (XRD) analysis was conducted on pre- and post-hydration samples using a Philips APD3720 goniometer. Thermogravimetric (TG) analysis was used to corroborate XRD data as well as determine the degree of calcination each sample incurred following

hydration. TG analysis was carried out using a Perkins Elmer STA 6000 to heat 10mg of ash in four phase steps with a hold at 500 °C (Misra et al., 1993; Liodakis et al., 2005). TG results were interpreted according to mass loss equations. Mass loss observed below 200 °C was equated to the loss of water adsorbed to ash, loss between 200-500 °C was attributed to the combustion of organic carbon and some inorganic carbon in the forms of Ca(OH)₂ and Mg(OH)₂ and loss in the 700-900 °C range was associated with the decomposition of predominantly CaCO₃ (Liodakis et al., 2005; Li et al., 2007; Plante et al., 2009).

2.4. Statistical analysis

To assess if ash characteristics were correlated to fuel type or combustion temperature, descriptive statistics (mean, minimum, maximum and standard deviation) were calculated for 12 variables (S, K_{sat} , ϕ , >2 mm, D_{10} , D_{50} , P_b , P_p , pH, organic carbon, inorganic carbon, and N content) and used to create a cluster classification; using the single-linkage agglomeration method and Pearson's correlation with significance at p < 0.01 (Webster and Oliver, 1990). Factor analysis (FA) was then applied to determine the main variables, or ash characteristics, explaining cluster results (Shuxia et al., 2003; Pereira et al., 2009). Variance maximizing (Varimax) normalized rotation was applied during FA to allow for the construction of factorial components based on the strongest variables. Significant factors were extracted based on the principal components analysis method and deemed significant based on the Kaiser criterion (eigenvalues >1). When analyzing FA results variables close to ± 1 have a strong relationship between the factor and the variable whereas values of zero have no relationship. All analysis was performed with SPSS *Version 10.0.5* statistical software for windows (SPSS Inc., 1999).

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3. Results and Discussion

3.1 Ash characteristics

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Cluster analysis indicated a strong correlation between samples based on combustion temperature and a weak correlation based on fuel type, suggesting observed shifts in ash properties were linked to the rate of thermal decomposition and not variations in fuel type (Figure 2 and Table 1). Factor analysis indicated that three main factors explained clustering results, as well as 90 % of the variability within the dataset. The first factor was highly significant (eigenvalue = 5.1) and explained 40 % of the variability between ash types. This factor was highly correlated with organic carbon content (0.97), nitrogen content (0.90) and grain size greater than 2.0 mm (0.94). The second and third factors explained an additional 34 % and 16 % of data variance respectively and indicated porosity (0.97), bulk density (-0.95) and sorptivity (0.94) as key ash characteristics. Based on the factor analysis results the physical, chemical and hydrologic properties of laboratory ash were subsequently grouped into 4 combustion levels irrespective of fuel type (n = 9); 300 °C (low), 500 °C (mid), 700 °C (mid) and 900 °C (high). Furthermore 500 and 700 °C samples were collectively referred to as midcombustion ash due to their similarities. While cluster analysis revealed both wildfire samples belonged to the 700 °C level, with correlation values as high as 0.98 (Table 1), wildfire ash is not homogenous therefore the physical, chemical and hydrologic characteristics of wildfire samples were compared individually to grouped temperature results to assess wildfire ash behavior across the spectrum of ash temperatures.

Ash color ranged from black to grey with total organic carbon and nitrogen values decreasing with increasing ash lightness and combustion temperature (Table 2 and Figure 3a). The major elements (> 0.5 % by weight) of ash samples analyzed by ICP-ES were Ca. K. N. Mg and P (Table 2). Etiegni and Campbell (1991) determined that Ca, K, Mg, Si and P dominated the elemental composition of *Pinus contorta* wood ash, while Gabet and Bookter (2011) found Ca, K, Mg, P, Mn, Fe and Al dominated *Pinus ponderosa* ash. However, as emphasized by Demeyer et al. (2001), there is high variability in the elemental concentrations of ash and greater sample sizes should be utilized to determine if similarities and differences are statistically significant. Research addressing ash properties of Greek forest species further indicated that the metal content (i.e., Ca, Mg, K) of ash tended to increase and carbonate decrease with increasing ash preparation temperature (Liodakis et el., 2005). Inorganic carbon results indicated a spike in the mid-combustion range with values an order of magnitude higher than low and high combustion samples (Table 3). Compound identification from XRD analysis indicated midcombustion samples contained primarily calcium carbonate and silica, while high-combustion ash exhibited a relatively low intensity of carbonate and the presence of CaO (Figure 4). Research conducted by Liodakis et al., (2005) indicated that MgO and CaO detected in ash samples of lower combustions temperatures are not due to the decomposition of MgCO₃ and CaCO₃, but most likely due to decomposition of calcia and magnesia organic matter. While all ash samples were hydrophilic (WDPT <5 sec) there was a distinct variation in the hydrologic properties of ash based on combustion temperature. Water retention results indicated mid-combustion ash retained the greatest amount of water at field capacity (0.3 bars) and low combustion samples retained the least, 48 % and 21 % respectively (Figure 5). The majority of water lost from low combustion ash was due to gravitational forces, supporting the notion that

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ash char particles have a low water retention capability compared to other components of ash (Stoof et al., 2010). The high water retention capability of mid-combustion ash may aid in postfire ecosystem recovery by acting like a buffer (Ebel et al., 2012) and slowly releasing water to the underlying soil as well as aiding in vegetative regrowth and a providing nutrient rich seedbed. Alterations in ash water retention could also aid in explaining the varied effect of fire on plant available water, as small amount of ash incorporated into soil have been found to provide considerable increases in water retention of laboratory studies (Stoof et al., 2010). The mid-combustion K_{sat} values, 0.004 ± 0.0009 cm sec⁻¹ and 0.002 ± 0.0003 cm sec⁻¹ for 500°C and 700 °C respectively, were two orders of magnitude lower than low-combustion values, $0.12 \pm$ 0.03 cm sec^{-1} , and an order of magnitude greater than high-combustion samples, $0.03 \pm 0.006 \text{ cm}$ sec⁻¹ (Figure 6). Alterations in water retention and hydraulic conductivity were equated to changes in ash particle size associated with combustion temperature (Wesseling et al., 2009) and are consistent with ash grain size values reported in previous studies (Ulrey et al., 1993; Liodakis et al., 2005; Ubeda et al., 2009). A study conducted by Moody et al. (2009) indicated that ash had relatively large value of field hydraulic conductivity, ranging from 4.5 x 10⁻³ to 5.3 x 10⁻² cm sec⁻¹, and that infiltration into ash was controlled by sorptivity, as values were 1-5 times hydraulic conductivity terms. Sorptivity values for this study increased linearly with raising combustion temperature, 1.77 ± 0.27 mm sec^{-0.5} to 4.0 ± 0.26 mm sec^{-0.5} (Figure 6). The authors suspect that carbonate particles within the ash increased the ash textural interface increasing the absorption of water molecules (Baker and Hillel, 1990) while water was readily adsorbed to thermally produced oxide particles in order to rehydrate them, a similar effect has been documented in heated limestone (Ioannou et al., 2004). Furthermore, Kinner and Moody (2010) stated that ash conduct water better than the underlying soil under moist conditions, a

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result consistent with the experimental data of Moody et al. (2009) which showed that $K_{ash} > K_{burned \, soil}$ for varying soil textures. These shifts in ash sorptivity related to ash chemical composition could also provide an explanation for finding that ash layers are capable of increasing the rainfall rate threshold by absorbing substantial amounts of water (90 %; Moody et al., 2009).

3.2 Variations between laboratory and wildfire ash

One of the main objectives of this study was to assess if ash characteristics could be linked to varying stages of thermal decomposition and if ash produced in the laboratory could be beneficial to understanding wildfire ash characteristics. Previous research addressing laboratory and wildfire ash properties suggests laboratory ash quantitatively differs from wildfire ash due to changes in air movement and restrictions in oxygen supply (Gray and Dighton, 2006), as well as laboratory settings not adequately mimicking combustion phases of wildfires (Bodi et al., 2011). While ash produced during a wildfire cannot be adequately replicated in the laboratory due to many factors, such as the natural flammability of the fuel type (Scarff and Westboy, 2006; Ormeno et al., 2009), the parts of the fuel source consumed (Werkelin et al, 2005), fire behaviors, humidity and the degree of decomposition within the litter, understanding thermal decomposition of fuel types and alterations in ash traits associated with shifts in thermal decomposition may provide insight into how best to interpret the complexity of wildfire ash as well as the behavior and impact of ash after a wildfire.

The results from this study indicated that wildfire samples were significantly correlated (p < 0.01) to laboratory ash based on variations in the level of thermal decomposition, with

correlation coefficients as high as 0.98 and 0.95 (Table 1). The hydrologic characteristics of wildfire ash samples indicated similarities to mid- and high-combustion laboratory ash with the hydraulic conductivity of the Gunbarrel ash (0.006 cm sec⁻¹) an order of magnitude lower than Terrace ash (0.025 cm sec⁻¹) (Figure 6). Sorptivity (2.72 mm sec^{-0.5} and 3.47 mm sec^{-0.5}) and k_a:k_w (1.84 and 0.89) values also suggested these combustion temperatures, Gunbarrel and Terrace respectively (Figures 6 and 2), while water retention results were not as distinguishable to a specific combustion zone but indicated wildfire samples lay within the suite of laboratory results (Figure 5). The authors equate the variations in these results to claims that laboratory ash quantitatively differs from wildfire ash, to be due to differences in methodology as fuels for this study were allowed to heat and cool within the muffle furnace opposed to being subjected to only to a few hours of direct heating (Gray and Dighton; 2006; Ubeda et al., 2009; Bodi et al., 2011) or burnt in a open barrel (Gabet and Bookter, 2011). The goal of the burning methodology used in this study was to allow samples to heat with the surrounding air in an environment of low turbulence as well as fostering smoldering conditions as samples cooled in the oven. The rational behind this approach stemmed from the fact that highly flammable gases, known as volatile organic carbons, are emitted and accumulate as fuels are heated, especially under conditions of low turbulence and fuels high in terpenes, such as pines and Douglas fir (Maarse and Kepner, 1970; Ormeno et al., 2009), furthermore the accumulations of these gases facilitate the propagation of burning within fuel (Greenberg et al., 2006). The authors are not claiming that ash produced in the laboratory mimics wildfire ash samples but that the laboratory ash produced with this methodology was highly correlated with wildfire samples from ecosystems of similar fuel types and therefore laboratory results can be used as end members to more clearly understand traits observed in wildfire ash.

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While it can be argued that the exact temperature of the ash samples during laboratory combustion were not obtained, follow up TG analysis allowed for the level of thermal decomposition to be determined in the ash samples thus providing an indication of peak temperatures reached and the level of thermal decomposition (Liodakis et al., 2005). Thermogravimetric (TG) analysis results indicated that low combustion samples were dominated by the presence of organic carbon, evident from the 80 % mass loss between 350 - 500 °C as well as a strong exothermic reaction exhibited at 500 °C (Figure 7), mid-combustion samples were predominately calcium carbonate with the largest mass loss (15 %) occurring in the 650 -900 °C range, while high combustion samples exhibited little mass change during TG analysis indicating the initially high thermal decomposition of the sample and a composition of primarily oxides (Kloprogge et al., 2004; Liodakis et al., 2005; Plante et al., 2009; Quill et al., 2010; Pereira et al., 2012). The small discrepancies between wildfire and laboratory ash within this study can be explained by fuel variations and the non-homogenous nature of wildfire samples, as elements of varying combustion temperatures may be included in wildfire samples due thermal variability within fuels (Pyne, 1996) and post-fire aeolian mixing (Neary et al., 2005). For example, the incorporation of organic char within wildfire samples (1 - 2 %) reduced the overall particle density, by incorporating low-density char particles (Reeves et al., 2006), as well as reduced overall water-holding capacity, as char retained less gravitational water than mineral ash (Stoof et al., 2010). While the properties of laboratory ash were slightly exaggerated, due to the homogeneity of the sample, thermogravimetric analysis indicated that assigned temperatures were met and laboratory ash could be utilized to understand how wildfire ash varies in post-fire systems.

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3.3 The effects of thermal decomposition on ash porosity

Factor analysis indicated porosity to be a key characteristic in explaining variations between ash types, with a distinct relationship between ash total porosity and combustion temperature (Figure 8). The most notable measurements occurred in the mid-combustion range (500-700 °C) with values more than twice that of mineral soils of a similar silt loam texture. These exceptionally high porosity values (98 %) cannot be explained by basic soil properties but offer an explanation for the noted ability of some ash to store large amounts of water in post-fire settings (Woods and Balfour, 2010; Ebel et al., 2012). The authors suggest that this unique characteristic of mid-combustion ash can be partially explained by shifts in the chemical and physiological properties associated with ash thermal decomposition; more specifically alterations in particle shape and size, pore structure and electrostatic charge dictated by mineralogical content.

Changes in ash particle shape contributed to increasing porosity values as fine plate-like particles of carbonate decreased packing density. Bulk densities of repacked laboratory ash ranged from 0.06 to 0.19 gcm⁻³, with mid-combustion samples exhibiting the lowest densities. These values are comparable to *in situ* measurements for wildfire ash (Figure 9; Cerda and Doerr, 2008; Woods and Balfour; 2008; Moody et al., 2009; Zavala et al., 2009; Gabet and Bookter, 2011), but considerably lower than the typical range for mineral soils, 1.0-1.6 gcm⁻³, indicating a low ash packing density. The low packing density of ash can be partially explained by changes in ash particle densities, which ranged from 1.27 to 2.88 gcm⁻³ (Figure 9). This linear increase in particle density with combustion temperature reflects thermal alterations in ash composition as low combustion samples consisted primarily of low-density char particles (1.0-

2.0 gcm⁻³), mid-combustion samples were composed of carbonates (2.71 gcm⁻³) and high combustion samples were primarily oxides (Reeves et al., 2006). Ash particle size and pore structure also changed considerably with combustion temperature due to the thermal decomposition of organic fuel into carbonates and then subsequently oxides. The percentage of ash greater than 2 mm decreased with increasing combustion temperature, with mean values ranging from 32 to 1 % (Figure 3a). Below 2 millimeters, 300 °C ash contained the coarsest particle size distribution, with a D_{50} of 156 ± 30 µm. The particle size distribution became finer for the mid-combustion samples indicating an overall decrease in particle size, $81 \pm 32 \mu m$ and $45 \pm 15 \mu m$ for 500 °C and 700 °C respectively (Figure 3b), and coincided with the structural breakdown of fuel due to a transition of primarily organic fragments in the low combustion ash to crystalline flakes of carbonate in mid-combustion ash (Figure 3a). This trend, however, did not continue into high combustion levels as the D_{50} doubled relative to the 700 °C samples, 96 \pm 21 µm. SEM analysis indicated that ash particles sintered causing an overall coarsening effect and change in particle shape and size; low combustion particles were predominantly angular and heterogeneous, while mid-combustion samples were a mix of small angular particles and flakes, and high combustion particles were homogenous and rounded (Figure 3a). Further SEM analysis revealed that the surface morphology of ash particles was altered with variations in combustion temperature (Figure 10). Low combustion ash, composed of organic carbon (Table 2), exhibited no surface porosity a finding constituent with the low water retention capability of char (Stoof et al., 2010). As thermal degradation increased a high density of micro-pores emerged, a phenomenon known to occur in thermally generated carbonate used for ceramics, as the release CO₂ during thermal decomposition often creates pores under a micron in size (Cultrone et al., 2004). As combustion temperatures continued to increase the thermal breakdown of carbonates

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into oxides resulted in the sintering of micro-pores thus decreasing pore density and producing a lower density of larger pores (Figure 10). Pictographs of Terrace ash micro-porosity indicated similar surface porosity characteristics to 900 °C ash offering an explanation to the observed high total porosity (92 %) of Terrace ash (Figure 11). A similar CaO sintering effect has been documented in studies pertaining to industrial calcination temperatures (Borgwardt et al., 1989a, b; Kloprogge et al., 2004; Li et al., 2007). The high ratio of k_a : k_w further indicated the presence of micro-pores within vegetative ash (Figure 8), as the elevated values associated with mid-combustion ash could not be explained by ash swelling, due to the lack of visible signs and mineralogical shifts in XRD data, but instead could be explained by air entrapment within ash micro-pores (Al Jibury and Evans, 1965; Chief et al., 2008).

3.4 Variations in ash properties due to thermal decomposition; implications for variations in post-fire hydrological response

While the fate of ash in post-wildfire systems depends largely upon the characteristics of the first rainstorms (Cerda and Doerr, 2008; Woods and Balfour 2008), results from this study indicate that the level of ash thermal decomposition may influence the role of ash in post-fire landscapes and therefore not all ash should be treated the same. Low combustion organic carbon dominated and high combustion oxide dominated ash hold the potential to decrease post-fire infiltration rates by forming surface seals (3.4.1.), while mid-combustion carbonate dominated ash may delay post-fire runoff by increasing water retention and reported buffering effects of ash layers (3.4.2.).

3.4.1 Properties of low and high combustion ash, implications for surface sealing

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Soil surface sealing can occur in various ways with seals broadly classified as either structural or depositional depending on the mechanism of formation (Valentin and Bresson, 1992). The conditions present after wildfires are strongly conducive to surface sealing (Cerda and Doerr, 2008; Woods and Balfour, 2008; Larsen et al., 2009) as one of the primary effects of wildfire is the partial or complete destruction of the surface vegetation as well as litter and duff layers. The loss of ground cover promotes structural seal formation by exposing the underlying mineral soil to rain splash impacts leading to compaction and disaggregation of the mineral soil (Johansen et al., 2001). While there is a clear theoretical basis for structural seal formation in burned soils, only one study in the western U.S.A. has documented such an occurrence (Larsen et al., 2009). Burned soils may also develop depositional seals through the in washing of finegrained disaggregated soil and ash. While the formation of depositional seals by ash have been demonstrated at both the pore- and plot scale (Balfour, 2007; Onda et al., 2008; Woods and Balfour, 2010) and are theorized to be due to increases in ash density, as the ash layer collapses under its own weight (Cerda and Doerr, 2008), compacted by raindrops (Onda et al., 2008) or the in washing of fine-grained disaggregated soil and ash plugging soil pores (Onda et al., 2008; Woods and Balfour, 2010), the effects of ash composition have not been investigated.

Low combustion ash contains predominantly inert char particles that behave similarly to a soil of comparable grain size and are known to contribute to surface sealing and decreasing infiltration by creating a low conductive ash layer (Onda et al., 2008; Woods and Balfour, 2010). The grain size $(96 \pm 21 \ \mu m)$ and hydraulic conductivity $(0.03 \pm 0.006 \ cm \ sec^{-1})$ of high combustion ash suggests that it too could contribute to surface sealing by creating a low

conductive ash layer, however, low k_a:k_w values (0.56) indicate partial dissolution. An alternative theory could be that thermally produced oxides in high combustion ash hydrate to form a chemical carbonate crust decreasing subsequent infiltration in post-fire systems. Natural ash crusts have been observed in - situ within high severity wildfires (Figure 12), however, the mode of ash crust formation whether by internal densification (Cerda and Doerr, 2008), raindrop induced compaction (Onda et al., 2008) or mineralogical transformations due to wetting is not fully understood. The ability of ash to form a chemical crust could explain decreases in post-fire infiltration rates (Onda et al., 2008), decreases in overland flow erosion (Gabet and Sternberg, 2009), as well as decreases in wind erosion by playing a similar role to that of needle fall from stressed or dying trees (Cerda an Doerr, 2008). The production of calcium carbonate following the hydration of fly ash is a well-documented response in the cement industry (Etiegni and Campbell, 1991; Siddique and Khan, 2011) and often associated with swelling (Demeyer et al., 2001; Holmberg and Claesson, 2001; Li et al., 2007). Results from this study and others addressing vegetative ash properties in the laboratory (Ulrey et al., 1993; Ubeda et al., 2009; Gabet and Bookter, 2011) indicate no signs of ash swelling. Instead SEM pictographs highlight that ash hydration led to the growth and interlocking of crystals within the ash (Figure 11). Wildfire and high-combustion ash were the only samples to show signs of chemical alterations and crystal growth and XRD patterns showed shifts associated with crystal growth, indicating hydration led to a transformation of calcium oxide into calcium carbonate (Figure 11). Furthermore TG analysis of pre- and post-hydration samples were consistent with SEM and XRD results indicating the formation of carbonate following initial hydration; by the appearance of a mass loss (~10 - 15 %) in the 650 - 900 °C range following the hydration of high combustion and Terrace ash (Figure 7). In order to further understand the role of ash contributing

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to depositional seals within burned forests, future research aims to investigate the relationship between the internal ash layer densification, raindrop induced compaction and these mineralogical transformations in the formation of ash crusts.

3.4.2 The effect of ash thermal decomposition on ash water storage ability; the theory of electrostatic ash

In cases where ash hydrologic conductivity is greater than that of the underlying soil, the ash layer acts as a capillary barrier storing water rather than controlling infiltration (Kinner and Moody, 2010; Woods and Balfour, 2010; Ebel et al., 2012). The ability of the ash layer to act as a capillary barrier is linked to very dry ash moisture conditions (Kinner and Moody, 2010; Ebel and Moody, 2012). Mid-combustion, carbonate ash, within this study demonstrated signs of high water retention (46 ± 13 % at 0.3 bars), high porosity (97 ± 1 %), and high sorptivity (3.2 ± 0.4) indicating ash capable of storing water amounts of water and significantly delaying the generation of overland flow (Cerda and Doerr, 2008; Woods and Balfour, 2008; Larsen et al., 2009; Ebel et al., 2012). However, this same ash contained low saturated hydraulic conductivity (0.0034 ± 0.0009 cm sec⁻¹) raising the question of how a substance with a grain size distribution similar to that of a silt loam soil have an extremely high porosity, high water retention and low saturated hydraulic conductivity? The authors theorize that this unique response is partly due to alterations in micro-porosity and the possible negative surface charge of carbonate ash particles.

The change in surface micro-porosity and particle shape associated with thermal decomposition provided one explanation for high water holding capacity of ash documented in this study (section 3.3.) as well as other laboratory (Stoof et al., 2010) and field experiments

(Woods and Balfour, 2010; Ebel et al., 2012). However, another theory could lie in the development of an electrostatic charge on the surface of ash particles, caused by mineralogical shifts associated with thermal decomposition, producing repulsion between particles. Carbonate particles have been known to hold an electrostatic surface charge due to defects in their crystal lattice and ionic bonds produced during thermal decomposition not associated with wildfires (Siffert and Fimbel, 1984; Moulin and Roques, 2003). Further investigation is required, however, the authors theorize that the electrostatic repulsion of thermally produced carbonate ash within forest wildfires may further decrease packing density and contribute to the initially high porosity values of dry ash reported in this study and high effective porosity values (83 %) obtained at other field sites (Cerda and Doerr, 2008; Woods and Balfour, 2008).

A series of photographs compiled during the initial wetting of ash samples for saturated hydraulic conductivity measurements indicated a unique response of mid-combustion and Gunbarrel wildfire ash to initial hydration (Figure 13). As one would expect the ash absorbed large amounts of water due to its high sorptivity, surface porosity and water holding capacity, however, contrary to the common belief that ash swells upon wetting (Stoff et al., 2010) the ash plug displayed signs of contracting in response to water absorption. Furthermore the ash exhibited the ability to remain stable at visible saturation; a similar response observed following hydration in the field (Figure 13; 2C, 1C). Following further addition of water the ash plug displayed a threshold were structural failure resulted in liquefaction of the ash plug, (Figure 13; 2D). The authors theorize that this response may be due the negative electrostatic surface charge of carbonates within the ash, as an electrical double diffuse layer (DDL) has been documented to occur in industrially produced fly ash when negatively charged ash particles were mixed with water (Iyer and Stanmore, 2000). We suggest that once water is introduced into the charged

carbonate ash system the polarity of water attracts charged ash particles and acts as a binding agent pulling dry ash together, thus explaining the initial contraction of ash observed during initial hydration of mid-combustion ash (Figure 13; 2B and 3B), as well as the high sorptivity linked to dry ash (Ebel and Moody, 2012). As the water content increases, within the ash layer, the ionic strength of the DDL surrounding each ash particle decreases thus reducing the binding effect between ash particles until water layer between the ash particles becomes so thick the bond fails and the ash layer becomes fluid (Figure 13). The authors are currently investigating ways to measure the level of surface charge or DDL of different ash types, with one potential method being to measure ash zeta potential (Moulin and Roques, 2003). Overall the unique nature of carbonate ash could explain why some ash has been noted to act as an important hydrologic buffer (Cerda and Doerr, 2008; Woods and Balfour, 2008; Zavala et al., 2009), capable of storing 99 % of storm rainfall (Ebel et al., 2012) as well as considered an important component in the initiation of progressively bulked debris flows in mountainous terrains (Cannon et al., 2001; Gabet and Sternberg, 2008).

5. Conclusions

Variability in the effect of ash on runoff following wildfires, and hence the often conflicting findings reported in the literature, can be partially explained by variations observed in the hydrologic properties of ash, which should be viewed as consisting of three main constituents; not fully combusted carbon, thermally produced carbonates and reactive oxides capable of rehydrating into carbonates.

The main findings of the current study in this context are:

- Saturated hydraulic conductivity of laboratory-produced ash varied substantially, covering three orders of magnitude, 0.12 ± 0.03 to 0.002 ± 0.0003 cm sec⁻¹.
 - High-combustion temperatures (> 900°C) produced ash primarily consisting of oxides,
 altered the hydrologic response of ash by increasing its hydraulic conductivity an order of
 magnitude and hydrating ash to re-form carbonate crystals.
 - The thermal formation of carbonates increased ash porosity (98 %), water retention (48 % at field capacity) and sorptivity (~3.0 mm sec^{-0.5}) due to the formation of micro-porosity.
 - It is suggested that ash color is not an acceptable metric to differentiate between
 variations in the hydrologic response of ash as both oxide and carbonate ash exhibit high
 chroma values. Instead carbonate content in ash is suggested as a more reliable variable if
 measured prior to post-fire rainfall.
 - The authors suggest that, based on a specific class of fuel (Northwestern US conifer fuel types), peak combustion temperature is more dominant than fuel type in influencing the hydrologic properties of ash.

The implications of these findings for post-fire hydrological response are:

Variability in the effect of ash on runoff responses following wildfires could be partially explained by variations observed in the hydrologic properties of ash. The hydrologic response of low and high combustion ash, associated with physical (grain size) and chemical (carbonate formation) properties, could prompt the formation of surface seals in post-fire systems by either creating a low conductive ash layer or an ash chemical crust,

while mid-combustion, carbonate dominated, ash may explain reported buffering effects of ash layers.

Theories and research gaps:

- The authors theorize that the high water holding capacity at field capacity (48 %) and porosity (98 %) of carbonate ash observed here is due the negative electrostatic surface charge of thermally produced carbonates within the ash and the formation of an electrical double diffuse layer (DDL) upon initial hydration. Work is ongoing to measure the level of surface charge and DDL of different ash types in order to test the validity of this theory.
- Mineralogical alterations in oxide ash following hydration indicate that chemical
 transformation of thermally produced oxides to carbonates following initial hydration
 may aid in ash crust formation through chemical processes. The relationship between the
 internal ash layer densification, raindrop induced compaction and these mineralogical
 transformations towards the formation of ash crusts on post-fire systems is currently
 being investigated.

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Figure 1: A site photograph prior to ash sampling with an inset of an ash trench for sampling collection; Terrace Mountain wildfire, 2009.

- Figure 2: Dendrogram of cluster analysis results indicating similarities between all ash samples based on 12 ash characteristics (S, K_{sat} , Φ , >2 mm, D_{10} , D_{50} , P_b , P_p , pH, organic carbon, inorganic carbon, and N content).
 - Figure 3a: Scanning electron microscope pictographs indicating relative particle size shape and size for A) 300 °C, B) 500 °C, C) 700 °C and D) 900 °C laboratory ash samples. A picture of the actual ash color appears in the upper right corner of each pictograph with Munsell classification and the percentage of sample greater than 2 mm in the lower right corner.
 - Figure 3b: Particle size distribution results for all laboratory (n = 9 per temperature) and wildfire (n = 3) ash samples. Error bars have not been included to facilitate in the interpretation of the graph.
 - Figure 4: Representative X-ray diffraction patterns with main mineral peaks identified for laboratory ash types (300 °C, 500 °C, 700 °C and 900 °C). XRD analysis for low combustion ash was incomplete due to the high background noise associated with the elevated organic carbon levels.
 - Figure 5: Water retention curves for laboratory (300 °C, 500 °C, 700 °C and 900 °C; n = 9) and wildfire (Terrace and Gunbarrel; n = 3) ash samples. Values are averages for replications and straight lines were drawn to facilitate interpretation of the graph.
 - Figure 6: Boxplots of hydraulic conductivity and sorptivity results for all laboratory (n = 9 per temperature) and wildfire (n = 3) ash samples.
 - Figure 7: Thermogravimetric (TG) analysis of laboratory and wildfire ash before and after hydration; denoted by dry and wet respectively. TG results were interpreted according to mass loss equations; mass loss observed below 200 °C was equated to the loss of water adsorbed to ash particles, mass loss between 200-500 °C was primarily due to the combustion of organic carbon, mass loss in the 700-900 °C range was associated with the decomposition of CaCO₃ and other carbonates (Misra et al., 1993; Liodakis et al., 2005; Li et al., 2007; Plante et al., 2009).
 - Figure 8: Boxplots of total porosity, effective porosity and the ratio of intrinsic permeability of air to water for all laboratory (n = 9 per temperature) and wildfire (n = 3) ash samples.
- Figure 9: Boxplots of bulk density and particle density results for all laboratory (n = 9 per temperature) and wildfire (n = 3) ash samples.
- Figure 10: Scanning electron microscope pictographs of surface porosity for laboratory ash combusted at A) 300 °C, B) 900 °C, C) 700 °C and D) magnification of the 700 °C sample highlighting intricate pore structure.

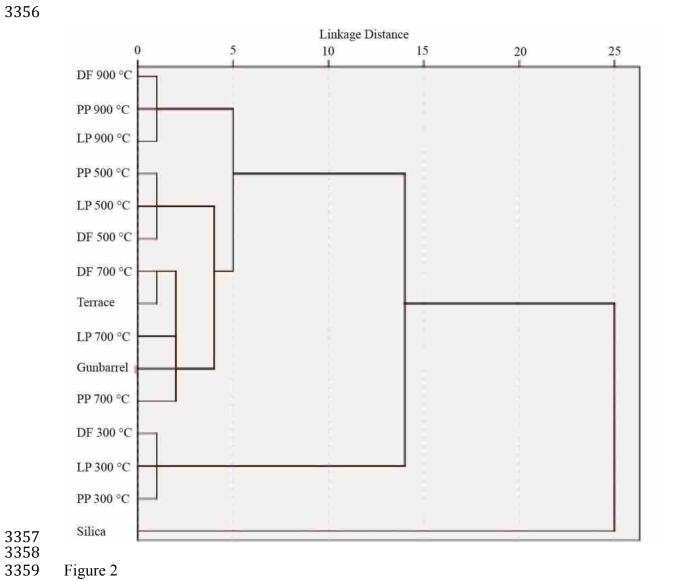
3329 Figure 11: Scanning electron microscope pictographs (left) and corresponding XRD peaks (right) 3330 of Terrace (A, B) and Gunbarrel (C, D) wildfire samples before and after hydration 3331 3332 respectively. 3333 3334 Figure 12: An ash crust within the Terrace Wildfire a few weeks after low intensity post-fire 3335 rainfall; inset is of author holding a piece of ash crust. 3336 3337 Figure 13: Pictures 2A-D show the initial hydration of mid-combustion ash in the laboratory; an 3338 initially dry sample was saturated from below with minimal head until a point of 3339 visible saturation (2A), with the addition of more water the ash plug collapsed into a 3340 liquid state. A similar ash plug was photographed in the field (1C). Images 3A-D are 3341 graphics representing the theorized interaction of ash particles and water based on the 3342 polarity of water and the electrostatic nature of carbonate. 3343 3344 Table 1: A correlation matrix of cluster analysis results, indicating similarities between Douglas-3345 fir (DF), lodgepole pine (LP) and ponderosa pine (PP) ash samples of varying combustion temperatures (n = 3). Results are based on Pearson's correlation with 3346 significant correlations highlighted in bold, at p < 0.01, and bold italics at p < 0.0053347 (Webster and Oliver, 1990). Values of 1 are a perfect correlation. 3348 3349 3350 Table 2: Mean and standard deviations values of total organic content (%), total inorganic 3351 content (%), pH and elemental components (w/wt%) for laboratory ash (n = 9 per

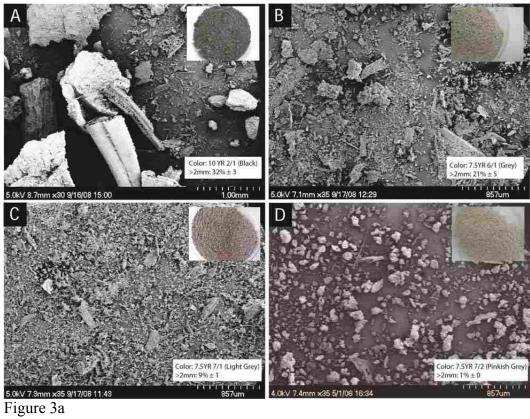
temperature) and wildfire (n = 3) ash samples.



Figure 1







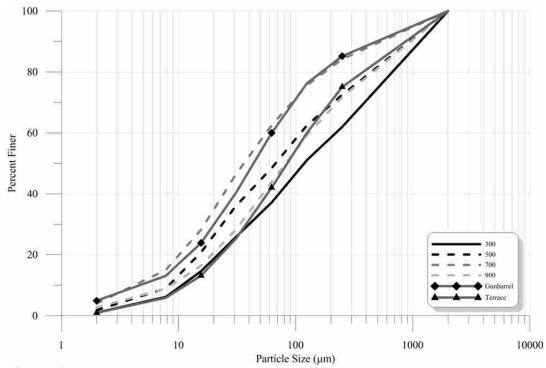
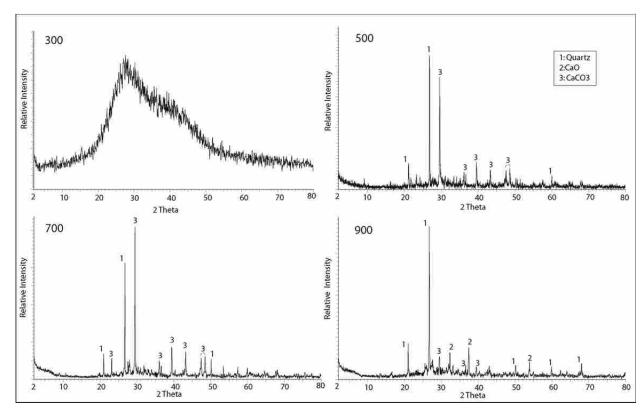
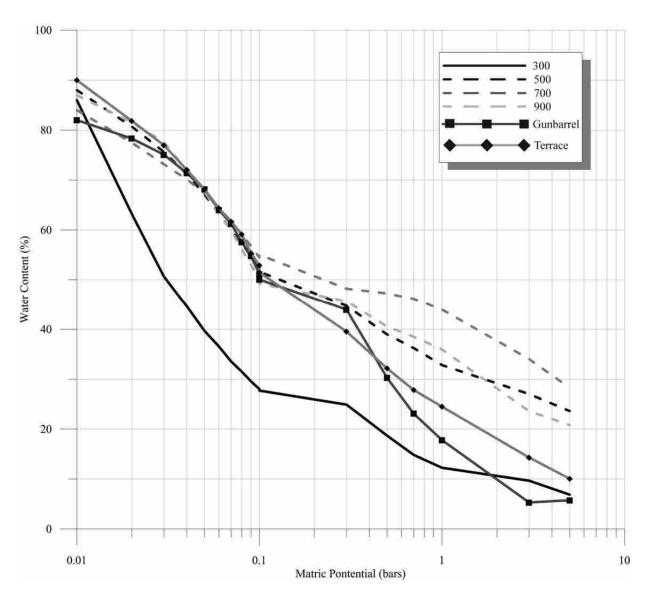


Figure 3b

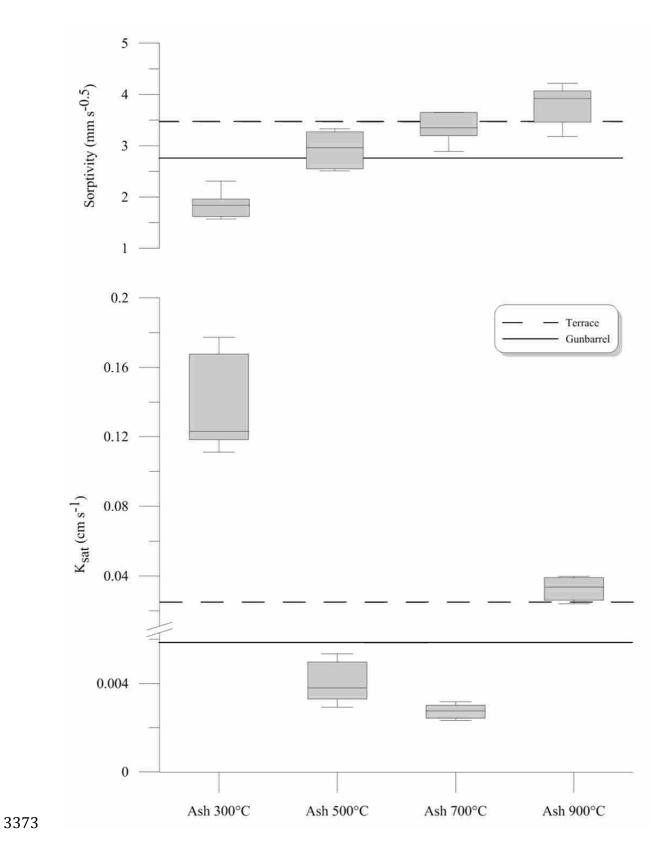




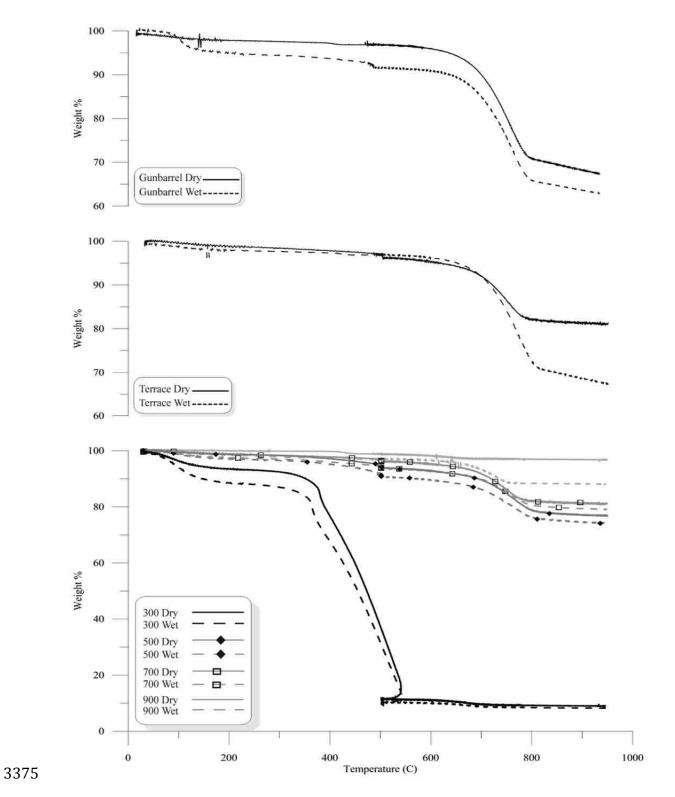
3369 Figure 4



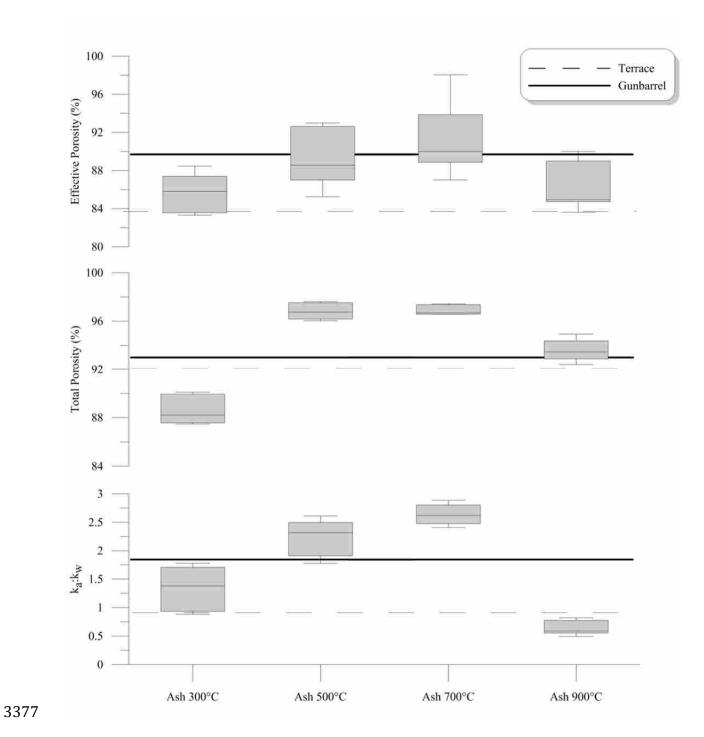
3371 Figure 5



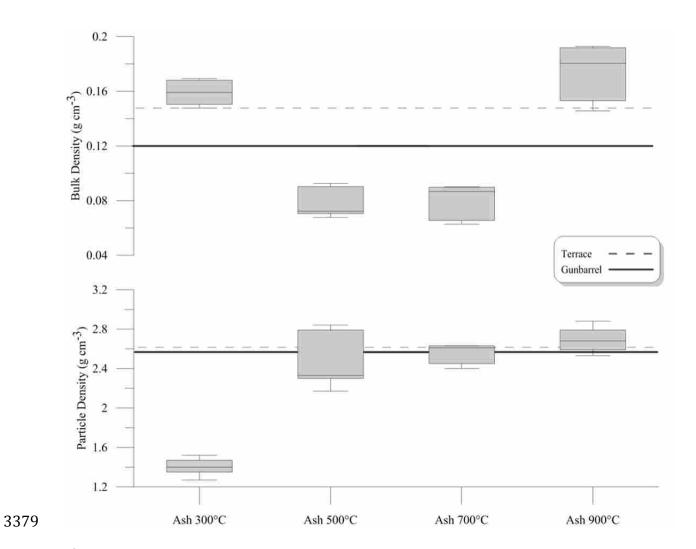
3374 Figure 6



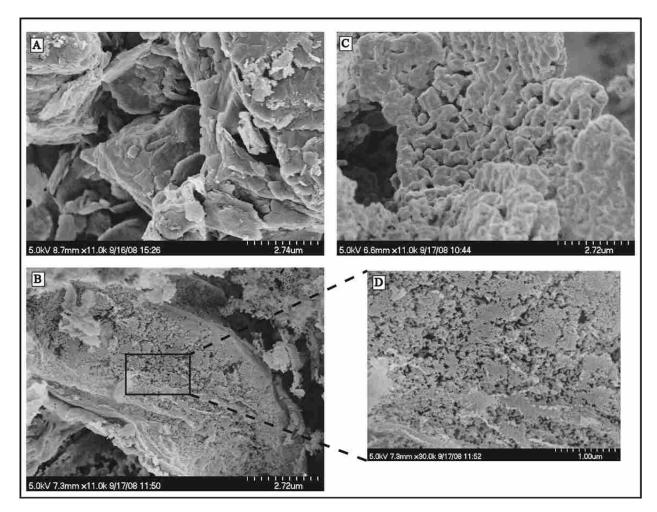
3376 Figure 7



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3380 Figure 9



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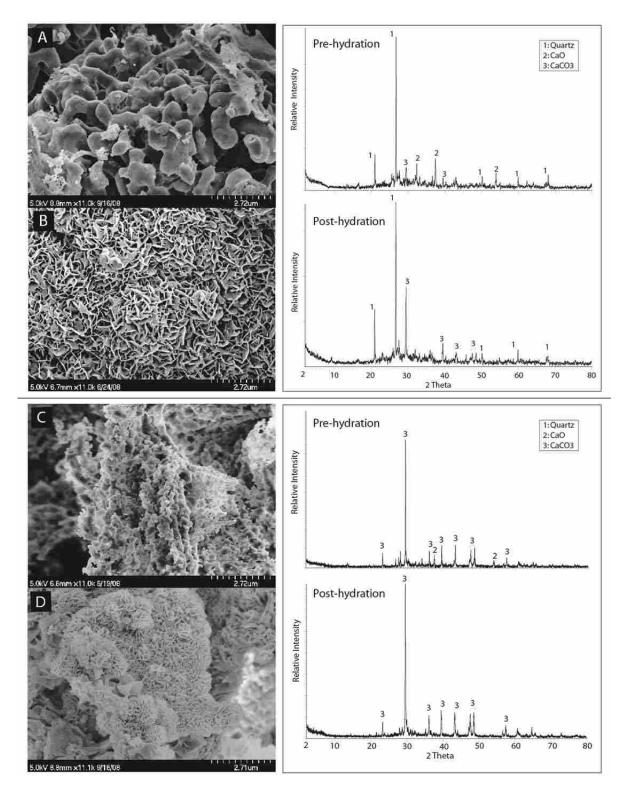


Figure 11



3388 Figure 12

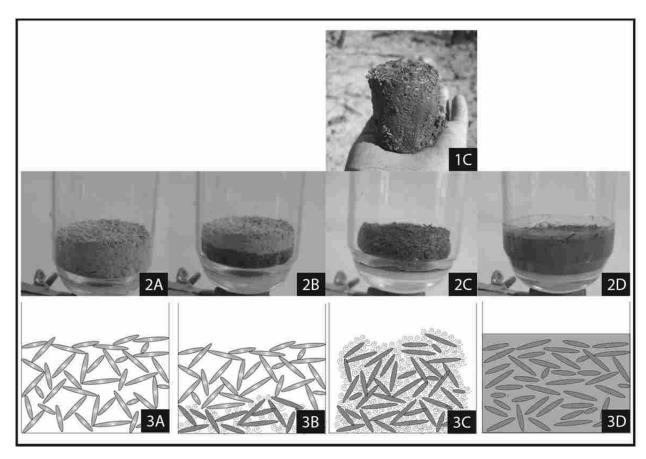


Figure 13

	DF_300	DF_500	DF_700	DF_300 DF_500 DF_700 DF_900 PP_300 PP_500 PP_700 PP_900 LP_300 LP_500 LP_700 LP_900 Terrace Gunbarrel	PP_300	PP_500	PP_700	PP_900	LP_300	LP_500	LP_700	LP_900	Terrace	Gunbarrel
DF_300	1.00													
$\overline{\mathrm{DF}}$ 500	0.40	1.00												
DF_700	0.13	06.0	1.00											
$\overline{\mathrm{DF}}$ 900	-0.02	0.54	0.74	1.00										
PP_300	I.00	0.41	0.18	0.03	1.00									
PP_500	0.58	0.97	0.86	0.56	09.0	1.00								
PP_700	0.28	0.85	0.89	0.89	0.32	0.87	1.00							
$^{-}600$	-0.05	0.56	0.76	1.00	0.00	0.57	0.89	1.00						
LP_300	1.00	0.45	0.19	0.02	0.99	0.63	0.33	-0.01	1.00					
LP_500	0.51	0.97	0.90	0.62	0.54	0.99	0.90	0.63	0.56	1.00				
LP_700	0.00	0.89	0.97	0.83	0.13	0.84	0.95	0.85	0.15	0.89	1.00			
LP_900	-0.07	0.51	0.71	0.99	-0.02	0.52	0.87	0.99	-0.03	0.59	0.82	1.00		
Terrace	0.08	0.82	0.69	0.98	0.14	0.79	0.81	0.71	0.13	0.83	89.0	0.92	1.00	
Gunbarrel	-0.06	0.75	0.95	0.69	0.00	0.69	0.76	0.71	-0.02	0.74	0.89	99.0	0.87	1.00

3396 Table 1

	Low	Mid	High		
Ash Type	(300°C)	(500°C-700°C)	(900°C)	Terrace	Gunbarrel
Aluminum	0.13 ± 0.15	1.02 ± 0.40	1.57 ± 0.74	0.81 ± 0.36	0.23 ± 0.12
Calcium	2.76 ± 0.83	13.35 ± 2.01	15.94 ± 2.50	15.14 ± 1.35	27.58 ± 2.10
Iron	0.25 ± 0.18	1.03 ± 0.30	0.85 ± 0.05	0.87 ± 0.22	0.38 ± 0.08
Potassium	2.23 ± 0.92	5.56 ± 2.15	4.28 ± 2.16	0.86 ± 1.12	9.36 ± 1.32
Magnesium	0.85 ± 0.38	3.22 ± 0.40	3.64 ± 1.48	0.95 ± 0.42	2.92 ± 0.72
Manganese	0.12 ± 0.10	0.58 ± 0.13	0.5 ± 0.24	0.8 ± 0.14	0.03 ± 0.00
Sodium	0.00 ± 0.00	0.11 ± 0.08	0.22 ± 0.12	0.06 ± 0.02	0.07 ± 0.03
Phosphorus	0.99 ± 0.42	1.02 ± 0.42	2.05 ± 0.33	0.61 ± 0.13	0.38 ± 0.17
Nitrogen	2.85 ± 0.83	0.61 ± 0.61	0.01 ± 0.01	0.01 ± 0.00	0.15 ± 0.20
Zinc	0.03 ± 0.02	0.12 ± 0.05	0.06 ± 0.08	0.05 ± 0.02	0.05 ± 0.02
Organic C	45.38 ± 0.09	2.48 ± 2.93	0.06 ± 0.70	2.41 ± 0.56	1.55 ± 0.15
Inorganic C	1.76 ± 1.12	13.41 ± 4.30	3.08 ± 0.72	3.84 ± 0.73	5.66 ± 0.23
hd	8.67 ± 0.64	9.64 ± 0.06	10.25 ± 0.06	8.76 ± 0.05	10.25 ± 0.03

Table 2

CHAPTER FOUR

Determining ash saturated hydraulic conductivity and sorptivity with laboratory and field methods.

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Abstract

Post-fire landscapes are often blanketed with a layer of ash that is capable of altering post-fire infiltration response. Documentation of ash layer characteristics, specifically ash sorptivity and hydraulic conductivity are instrumental to understanding and modeling post-fire environments and infiltration response. The aim of this study was to evaluate laboratory methodologies for determining ash hydraulic conductivity and sorptivity based on established methodologies from soil measurements. A series of field and laboratory tests were conducted on ash from 13 high severity wildfires within western North America to evaluate; *i*) a non-destructive method for the rapid assessment of saturated hydraulic conductivity in the laboratory, *ii*) a method for directly measuring ash sorptivity in the laboratory and *iii*) compare these laboratory methods, conducted on disturbed samples, to field measurements taken *in-situ*.

The air permeametery method and the use of a sorptivity probe are viable methodologies for obtaining ash saturated hydraulic conductivity and sorptivity values respectively in the laboratory. Air permeametery was non-destructive, allowing ash samples to be further processed, while the sorptivity probe provided a direct measurement of sorptivity as values were collected under zero-head conditions. Results were consistent between laboratory- and field-based methodologies, indicating that disturbed laboratory readings are a viable substitute for *in-situ* field measurements when pertaining to ash sorptivity and hydraulic conductivity. Both methodologies provide fundamental information regarding ash characteristics, which can be incorporated into modeling systems to aid in predicting post-fire infiltration response.

Keywords: wildfire ash, methodology, sorptivity, hydraulic conductivity

1. Introduction

Following wildfires the hydrological response of the landscape is often altered leading to increased runoff and erosion response (Shakesby, 2011). Ash layers, deposited from the combustion of vegetation and duff layers during a wildfire, are known to contribute to changing post-fire infiltration response (Woods and Balfour, 2008; Stoof et al., 2010; Woods and Balfour, 2010; Bodí et al., 2012; Ebel et al., 2012) by producing a two-layered soil system (Kinner and Moody, 2008; Onda et al., 2008; Kinner and Moody, 2010). Moody et al. (2009) suggests an infiltration-excess overland flow regimes in these burned two-layered systems are controlled by the hydraulic properties and changes in soil moisture conditions. Moody et al. (2009) further explain these burned two-layered systems by separating infiltration into short- and a long-term components, with the former dependent upon sorptivity, reflecting the capillary potential of initial infiltration, and the later dependent upon saturated hydraulic conductivity in which gravimetric potential is the main driver (Smith, 2002). Therefore the documentation of ash layer characteristics, specifically sorptivity and saturated hydraulic conductivity are instrumental to understanding variations in post-fire infiltration response.

A post-fire study conducted primarily on soil samples taken from three wildfires within the western U.S. highlighted the importance of wildfires altering soil physics, as well as the necessity of incorporating such changes into physically based models to accurately predict runoff response in burned watersheds (Moody et al., 2009). The importance of including ash layer hydrologic properties in post-wildfire runoff generation models was further highlighted at the catchment scale by Ebel et al. (2012) following the Fourmile Canyon wildfire in the Colorado foothills. While both studies address the importance of including post-wildfire ash

layer characteristics to fully understand the post-fire hydrological responses, limited data is often collected regarding ash. One reason for the lack of documentation of ash characteristics may be due to the delicate nature of ash and the often rapid alterations it undergoes. For example, ash can increase in particle size when wetted and exposed to air due to agglomeration (Steenari et al., 1999) or swelling (Etiegni and Campbell, 1991) as shown for ash produced via industrial burning of biofuel and sawdust. Similar alterations have been observed with the hydration of wildfire ash in laboratory settings (Stoof et al., 2010), while other studies have indicated that the chemical stability and behavior of wildfire ash may vary with exposure to water (Gabet and Sternberg, 2008; Onda et al., 2008; Balfour and Woods, 2013). The instability of ash makes the collection of characteristics time sensitive in the field, as collection should occur rapidly prior to hydration for accurate measurements. Emphasis on laboratory processing of ash characteristics would allow field time to be more effectively spent acquiring samples and focusing on necessary *in-situ* measurements.

Another reason for the lack of detailed documentation regarding ash characteristics maybe due to site availability and access issues, as access onto active wildfires is often not feasible until after control or containment of the wildfire, which occasionaly coincides with considerable rainfall and therefore alteration of ash characteristics. Finally there is the issue of adequate ash sampling for laboratory measurements and contamination of the ash layer sampled with underlying soil. According to conventional soil methodology for conducting one-dimensional infiltration measurements in the laboratory, the diameter of the sample column should be approximately equal to that of the mini-disc base (4.4 cm), whereas for three-dimensional measurements the column diameter must be large enough that the wetted part of the ash does not touch the walls of the column (Dane and Hopmans, 2002). In both cases the

column should be long enough so that the wetting front does not reach the bottom during the test, which for most ash samples requires a 20 cm high column. The relatively low bulk density of ash, 0.12 - 0.45 gcm⁻³ (Cerdà and Doerr, 2008; Woods and Balfour, 2008; Moody et al., 2009; Gabet and Bookter, 2011; Ebel et al., 2012) suggests that large quantities (35-135 g) would be needed for each laboratory infiltration measurement making replication difficult or in some cases impractical. Furthermore the chemical instability of ash precludes samples from being reused as the original characteristics may have been altered by hydration (Balfour and Woods, 2013). Therefore it is desirable to seek out non-destructive alternatives to traditional soil infiltration methodologies in order to conserves ash samples, by using smaller volumes and avoiding chemical alterations.

The intention of this study was to assess if established laboratory methodologies from other fields of research, could be applied to wildfire ash as alternatives to determining saturated hydraulic conductivity and sorptivity. Specifically a series of field and laboratory tests were conducted to address three main goals; *i*) develop a non-destructive method for the rapid assessment of saturated hydraulic conductivity in the laboratory, *ii*) develop a method for directly measuring ash sorptivity in the laboratory and *iii*) determine how accurately the laboratory methods, conducted on disturbed samples, reflect field measurements taken *in-situ*. These methodologies presented allow for collecting adequate data, pertaining to ash hydraulic characteristics, which can be incorporated into modeling systems.

2. Methods

2.1 Field sites and ash collection

Prior to post-fire rainfall, vegetative ash was sampled from 13 high severity wildfires, which occurred over a seven-year period (2005-2011) within western North America (Figure 1). Ash samples were collected by first creating a small trench (~1m long), to assess the ash-soil profile, then removing ash with a sharp trowel to avoid soil contamination (Figure 2). Numerous ash samples, at least five transects for each site, were collected and combined to produce a composite ash sample for laboratory testing. High fire severity was verified in the field based on visual indicators (duff and litter layers were completely consumed; white ash was present and contained little to no visible char fragments), and evidence of soil heating (charring or a reddish color) existed in the underlying soil (Figure 2; DeBano et al., 1998; Neary et al., 2005; Parsons et al., 2010).

2.2 Field and laboratory measurements

The hydraulic conductivity of an ash layer can be determined by using a mini-disc infiltrometer to measure the one- or three-dimensional infiltration rate (Robichaud et al., 2008; Moody et al., 2009). In order to determine how accurately laboratory methods conducted on disturbed samples reflected field measurements taken *in-situ*, ash sorptivity (S_f , mm sec^{-0.5}) and unsaturated hydraulic conductivity (K_f , cm sec⁻¹) were measured in the field and laboratory. Field sorptivity and unsaturated hydraulic conductivity were measured within each wildfire site using a mini-disc tension infiltrometer (n = 5, 4.4 cm diameter, -2.0 cm tension, Decagon Devices, Pullman, WA). This method was chosen as the mini-disc infiltrometer is portable, easy to use in the field and already established for collecting qualitative measurements in post-fire settings (Robichaud et al., 2008; Moody et al., 2009). Ash layers can be highly absorptive, with

reports of the entire capacity of the mini-disc (90 mL) infiltrating in to the ash in less than one minute (Moody et al., 2009). Therefore, prior to infiltration measurements a core ring (4.4 cm diameter) was inserted into the ash layer to limit flow to one-dimension. Field values for K_f (cm sec^{-1}) were computed using a second order polynomial function to fit cumulative infiltration versus square root of time (Dane and Hopmans, 2002; Decagon Devices, 2006; Moody et al., 2009; Ebel et al., 2012). The method requires measuring cumulative infiltration (I, cm sec^{-2}) versus time (t, sec) and fitting the results with the function

$$I = C_1 t + C_2 t^{1/2} \tag{1}$$

where C₁ (cm sec⁻¹) and C₂ (cm sec⁻¹) are parameters related to hydraulic conductivity and sorptivity respectively. The hydraulic conductivity was then computed from

$$K_f = \frac{c_1}{A} \tag{2}$$

where A is a value relating to the Van Genuchten parameters of a given textural class and the set infiltrometer suction. Van Genuchten parameters for ash were estimated based on the soil textural class of ash (Decagon Devices, 2006). Ash particle size distribution was determined in the laboratory by sieving samples to 2.0 mm prior to analysis with a laser diffractometer (Beuselinck et al., 1998; Mastersizer 2000 particle size analyzer: Malvern Instruments Ltd, Malvern, UK). Values for field ash sorptivity (S_f, mm sec^{-0.5}) were computed as the slope of the linear regression of cumulative infiltration (*I*, cm sec⁻¹) versus the square-root of time (t, sec) based on the following equation (Vandervaere et al., 2000; Clothier and Scotter, 2002, Moody et al., 2009).

$$I = S_{\rm f} t^{1/2} \tag{3}$$

The wettability of ash can vary from water repellent to rapidly wettable, thus altering the hydrological response (Bodí et al., 2011). Therefore the water drop penetration time test

(DeBano et al., 1998) was used to measure ash wettability in the field using the persistence classification of Bisdom et al. (1993). The precision of field-based ash bulk density measurements, and thus porosity, depend upon i) the accuracy of the depth and volume measurements obtained in the field and ii) soil contamination. Ash layers are typically very unconsolidated and can be easily compacted; leading to inaccuracy in depth and volume measurements therefore a 1mm diameter pin was inserted at ten locations to compute a mean ash thickness. To avoid soil contamination the full thickness of the ash layer was not sampled during bulk density collection, instead a soil core was used to sample the ash layer to a depth approximately 0.5 cm above the ash-soil interface. Ash collected from field bulk density measurements was dried at 105 °C to a constant weight and reweighed to determine initial ash moisture content (Θ_i) . Field total porosity was calculated based upon field bulk density and particle density values. The particle density of ash reported in the literature varies from 1.20 – 2.93 gcm⁻³ depending upon the organic and mineral constituents (Reeves et al., 2006; Cerdà and Doerr, 2008; Gabet and Bookter, 2011) therefore ash particle density was measured in the laboratory with a pycnometer (Dane and Hopmans, 2002). All field-based measurements were replicated five times at each wildfire site (n = 5, per wildfire).

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The level of ash combustion was ascertained to gauge fire severity by measuring organic and inorganic carbon levels. A dry combustion CNS analyzer (Model EA1100, Fissions Instruments, Milan, Italy) was used to obtain total carbon for each ash type. Inorganic carbon content was determined by measuring CO_2 concentrations following mixture with H_2SO_4 ; organic carbon content was calculated as the difference between total and inorganic carbon (Schumacher, 2002). Ash color was recorded using the Munsell (1975) soil color chart. Ash unsaturated hydraulic conductivity (K_f^* , cm sec $^{-1}$) was measured in the laboratory with a tension

infiltrometer (Decagon Devices, 2006) on re-packed pans of ash ($10 \times 10 \times 5$ cm) according to equations 1 and 2. Pans were re-packed in stages of three centimeters; with the bulk density verified at each stage to ensure no discrete density layers were present. Laboratory unsaturated hydraulic conductivity measurements were restricted to ten samples, with the exclusion of Whiskeytown, Gunbarrel and Jesusita, due to limited ash supply of these sites. Laboratory ash sorptivity (S_f^*) values were computed from laboratory tension infiltration measurements according to equations 1 and 3.

2.2.1 Air permeametery: a non-destructive method for measuring ash K_{sat}

Air permeametery works on the assumption that the intrinsic permeability for a homogeneous and inert material subject to low fluid pressures is independent of the fluid moving through the material (Chief et al., 2006). Therefore the saturated hydraulic conductivity (K_{sat}^* , cm sec⁻¹) of ash was calculated from the intrinsic permeability of air (k_a , cm²) using:

$$K_{\text{sat}}^* = \frac{k_a \rho_w g}{\eta_w} \tag{4}$$

where ρ_w is the density of water (gcm⁻³), g is acceleration due to gravity (cm sec⁻²) and η_w is the dynamic viscosity of water (gcm⁻¹ sec⁻¹). The intrinsic permeability to air (k_a) was determined from:

$$k_a = \frac{Q\eta_a L}{A\Delta P} \tag{5}$$

where Q is the flow of air across the sample (cm³ sec⁻¹), η_a is the dynamic viscosity of air (gcm⁻¹ sec⁻¹), L is the sample thickness (cm), A is the sample cross sectional area (cm²) and ΔP is the pressure differential (gcm⁻¹ sec⁻²). The ratio Q/ ΔP was obtained from the slope of a regression line based on at least five measurements at a range of different pressures. A linear Q/ ΔP

relationship confirmed the assumption of laminar flow across the sample (Chief et al., 2008). A flow cell for air permeametery was manufactured from commercially available polyvinyl chloride (PVC) piping and attached to digital flow and pressure meters (Figure 3A). Five replications were conducted (n = 5) on each ash type to assess for method consistency.

In order to verify the air permeametery technique, fine silica sand ($D_{50} = 0.2 \text{ mm}$) was included as a standard. Saturated hydraulic conductivity values for the silica sand indicated that the air permeametery method was consistent with published values, $0.032 \pm 0.0002 \text{ cm sec}^{-1}$, validating the methodology (Brady and Weil, 2007). The results from the air permeametery method were also compared to saturated hydraulic conductivity values obtained through the falling head method (K_{sat} ; Reynolds et al., 2002), in which ash samples in a cylinder were saturated slowly for 12 hours from below to ensure complete saturation. Five replications were conducted on each ash type to assess for method consistency (n = 5).

The authors realize that the air permeameter approach may not always be reliable for ash due to reports of shrinking and swelling associated with ash wetting (Etiegni and Campbell, 1991; Stoof et al., 2010; Balfour and Woods, 2013). However, estimates of k_a obtained using air permeametery provided a basis for comparing the relative permeabilities of different types of ash. Furthermore in order to assess variations between the use of water and air the intrinsic permeability of water (k_w , cm²) was calculated from hydraulic conductivity (K_{sat} , cm sec¹) measurements as saturated hydraulic conductivity is directly related to the intrinsic permeability of water by

$$k_w = K_{sat} \frac{\eta_w}{\rho_w g} \tag{6}$$

where g is acceleration due to gravity (cm sec⁻²), η_w is the dynamic viscosity (g cm⁻¹ sec⁻¹) of water and ρ_w is the density of water at 20 °C (g cm⁻³). The ratio of k_a : k_w provided evidence for

swelling or other structural changes caused by wetting that may affect hydraulic conductivity (Chief et al., 2008).

2.2.2 Sorptivity probe: a method for directly measuring ash sorptivity

Ash sorptivity was measured directly via a methodology adapted from aggregate stability tests (Leeds-Harrison et al., 1994). A 2.0 mm diameter probe was connected to a horizontal glass capillary tube to directly measure three-dimensional sorptivity by exerting zero-head water entry pressure. A piece of plastic sponge was inserted in the bottom end of the probe to improve hydraulic contact with the sample. The entire apparatus was filled with water and the height of the probe adjusted to exert zero hydraulic head. A clear repacked ash core was raised up on a scissor jack stand until barely touching the bottom of the probe (Figure 3B). The rate of infiltration was determined by recording the time the water meniscus within the capillary tube travelled 50 mm increments. Sorptivity (S*, mm sec-0.5) was then calculated:

$$S^* = \sqrt{\frac{Qf}{4bR}} \tag{7}$$

where Q is the flow rate (mm³sec⁻¹), f is the fillable or effective porosity (%), R is the radius (mm) of the sorptivity probe and b is a unit less parameter relating to the shape of the soil-water diffusivity function. Since methodologies to determine ash-water diffusivity are still yet to be investigated the authors used a typical value for soil, 0.55 (Leeds-Harrison et al., 1994).

This methodology was validated by also measuring the sorptivity of fine sand (D_{50} = 0.2 mm) as well as comparing the values obtained with those calculated from one-dimensional infiltration data in the field (S_f) and three-dimensional tension infiltrometer readings measured in

the laboratory (S_f^*) . Five replications were conducted on each ash type to assess for method consistency (n = 5).

2.2.3 Data Analysis

One-way ANOVAs were conducted on the following variables to assess for variations in ash characteristics across the 13 wildfire ash sites; grain size distribution, field sorptivity (S_f) , thickness, total porosity, bulk density, initial ash water content (Θ_i) , as well as inorganic and organic carbon content. Within each wildfire site, variations in field and laboratory unsaturated hydraulic conductivity results (K_f, K_f^*) and saturated hydraulic conductivity methods $(K_{sat}$ and $K_{sat}^*)$ were assessed via separate T-tests, while variations in sorptivity methods $(S, S_f^*, \text{ and } S_f)$ were assessed with a one-way ANOVA. One-way ANOVAs were also conducted to assess for variations in ash saturated hydraulic conductivity $(K_{sat}$ and $K_{sat}^*)$, sorptivity $(S, S_f^*, \text{ and } S_f)$ and unsaturated hydraulic conductivity $(K_{sat}$ and $K_{sat}^*)$ values across the 13 wildfire sites.

Prior to tests each dataset was assessed for normality and the equality of variances was verified with the Levene's test (StatSoft, 2012). Statistical analysis was conducted using the *SPSS Version 10.0.5* statistical software (SPSS Inc. 1999). Results were deemed significant for *p*-values < 0.05, only significant *p*-values were reported.

3. Results

3.1 Field sites characteristics and measurements

All wildfire sites were blanketed with gray (7.5YR 5/1) to white (7.5YR 8/1) ash, with little to no visible signs of char fragments as well as contained low levels organic and inorganic carbon (Table 1). Ash thickness among the sites ranged from 2.81 ± 0.63 to 8.68 ± 1.53 cm with bulk densities of 0.17 ± 0.01 to 0.35 ± 0.05 gcm⁻³ (Table 1). All bulk density results were consistent with values previously reported for *in-situ* wildfire ash (Table 2), but considerably lower than the typical range of values for mineral soils, 1.0-1.6 gcm⁻³ (Brady and Weil, 2007). There were no indications of ash water repellency occurring at any of the wildfire sites, as water drop penetration time was instantaneous (t < 0.5 sec) for all measurements. Initial ash total porosity values were extremely high (87 ± 1 to 94 ± 0 %; Table 1). Variations in particle size distribution across ash types were not significantly different. All ash samples displayed similar distribution to a silt loam soil collected from a region within Montana classified as belonging to the Crow and Courville Soil Series (USDA Soil Survey, 1995) therefore silt loam Van Genuchten parameters were utilized for infiltration calculations (Figure 4).

Field ash hydraulic conductivity (K_f) results suggested a distinct split with four wildfire sites (Whiskeytown, Eagle, Terrace Mountain and Station) containing values an order of magnitude higher than the remaining nine sites with p-values ranging from 0.01 to < 0.001 (Figure 5). Field sorptivity (S_f) values ranged from 1.60 ± 0.04 to 2.32 ± 0.03 mm sec^{-0.5}; with values significantly lower than laboratory probe (S^*) and laboratory infiltrometer (S_f^*) results (all p < 0.001; Table 3 and Figure 6). Field sorptivity readings also displayed a similar variation across wildfire sites with Whiskeytown, Eagle, Terrace Mountain and Station containing significantly greater S_f values than the remaining nine sites, with p-values ranging from 0.03 to 0.04 (Table 1).

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Variations in ash characteristics across the 13 wildfire sites were not significantly different with the exception of inorganic carbon content and initial ash moisture content. All ash samples exhibited very dry initial moisture contents. 1.70 x 10⁻² to 5.20 x 10⁻⁴ cm⁻³, however, four wildfires sites (Whiskeytown, Eagle, Terrace Mountain, and Station) displayed significantly drier results than the remaining sites (p < 0.001; Table 3). The same four sites also contained significantly lower levels of inorganic carbon; p-values = 0.001, 0.001, 0.01, and 0.01 respectively (Table 3). Bulk densities of repacked laboratory ash ranged from 0.24 ± 0.12 to 0.38 ± 0.02 gcm⁻³ across wildfires with effective porosity results consistently lower, by 3 to 9 %, than field total porosity values (Table 3). The ratio of intrinsic permeability of air (k_a) to water (k_w) was close to 1.0 for the silica sand indicating that wetting had no effect on the internal structure of silica sand ($k_a:k_w=1$). While the $k_a:k_w$ ratio for ash samples ranged from 0.71 \pm 0.15 to 1.43 \pm 0.39 suggesting signs of mild dissolution and swelling (Table 3). Ash samples exhibiting milddissolution (k_a:k_w < 1) were associated with higher saturated hydraulic conductivity results and presented characteristics indicative of unstable ash; represented by a high Munsell value as well as relatively low organic and inorganic carbon levels compared to other ash types (Table 1; Balfour and Woods, 2013). All ash sorptivity values were within the typical range observed for mineral soils, 0.1 to

All ash sorptivity values were within the typical range observed for mineral soils, 0.1 to $4.0 \text{ mm sec}^{-0.5}$ (Leeds Harrison et al., 1994), and within the range of previously reported ash sorptivity values (Table 2). Laboratory infiltrometer (S_f^*) results ranged from 2.64 ± 0.25 and $3.90 \pm 0.23 \text{ mm sec}^{-0.5}$ (Figure 6). Sorptivity values obtained using the sorptivity probe (S_f^*) were consistent with laboratory infiltrometer (S_f^*) measurements indicating consistency between

mythologies, however, values acquired through the field infiltrometer (S_f) were significantly less (p < 0.001, Table 1). The three-dimensional (S_f^* , S^*) results were approximately 1.5 times greater than those calculated from one-dimensional field infiltrations (S_f) with the significant difference (p < 0.001) reflecting the large capillary effect of ash during initial hydration and the limited lateral flow of one-dimensional readings. Across site variations in S^* and S_f^* indicated four wildfire sites with significantly higher readings; Whiskeytown, Eagle, Terrace Mountain and Station (Figure 6).

Air permeametery (K_{sat}^*) measurements ranged from 2.80 x 10^{-2} to 5.00 x 10^{-3} cm sec⁻¹ and were consistent with falling head (K_{sat}) results, 2.83 x 10^{-2} to 4.58 x 10^{-3} cm sec⁻¹, indicating similarities between methodologies (Figure 7). Across site variations in K_{sat}^* and K_{sat} both indicated two significantly distinct groups in the ranges of 10^{-2} and 10^{-3} , with higher values associated with the four wildfires previously mentioned with respects to sorptivity (Figure 7). Variations in K_f^* and K_f values across the 13 wildfire sites also indicated similar trends to saturated hydraulic conductivity results with Eagle, Terrace Mountain and Station sites displaying significantly higher results (p < 0.001, Figure 5). Within site variability indicated that K_f^* values were significantly greater (p < 0.001) than K_f results by approximately 1.6 times; with average values of 0.041 ± 0.025 and 0.028 ± 0.017 cm sec⁻¹ respectively (Figure 5).

4. Discussion

4.1 Assessment of methodology: air permeameter

Alterations associated with wetting, as indicated by k_a : k_w less than or greater than 1,suggest the potential for water to alter hydraulic conductivity readings of ash, therefore making

air permeametery an unacceptable methodology for ash analysis (Chief et al., 2006). Initial falling head results, however, were not significantly different from air permeametery readings implying the effects of hydration did not significantly alter the initial saturated hydraulic conductivity of ash samples (Figure 7). This contradiction of results can be explained by physical and chemical alterations that have been documented to occur with the initial wetting of some ash produced at high-combustion temperatures (700 – 900 °C); leading to crystal growth of calcium carbonate and chemical transformations of oxides into carbonates through hydration and carbonation reactions (Etiegni and Campbell, 1991; Liodakis et al., 2005; Balfour and Woods, 2013). The initial saturated hydraulic conductivity of ash in this study was not altered by water, as results from both methodologies were comparable (Figure 7), however, mild-dissolution was observed in four samples (Whiskeytown, Eagle, Terrace Mountain and Station) indicating the possibility of crystal growth and alterations to subsequent infiltration responses due crystals bridging pore spaces and limiting the downward movement of water (Woods and Balfour, 2010; Balfour and Woods, 2013).

Air permeametery appears to be an acceptable methodology for assessing the initial saturated hydraulic conductivity of ash in the laboratory. Due to the reactivity of some ash samples, air permeametery offers the practical advantage compared to conventional soil techniques of sample conservation in the laboratory setting by allowing reactive ash samples to be subjected to further laboratory analyses without risk of chemical alterations. For example, while air permeametery results were consistent with the conventional falling head method four ash samples indicated chemical instability when exposed to water therefore hindering further accurate sample analysis once the ash has been hydrated. The use of air permeametery also offers the potential to aid in assessing ash reactivity in the laboratory by measuring the intrinsic

permeability of air to water. The reactivity of ash may explain decreases in post-fire infiltration rates (Onda et al., 2008) and decreases in overland flow erosion (Gabet and Sternberg, 2009) by chemical transformations within the ash layer contributing to the formation of an ash crust. Natural ash crusts have been observed *in situ* following high severity wildfires (Balfour and Woods, 2006; Onda et al., 2008; Woods and Balfour, 2008; Balfour and Woods, 2013), however, the mode of ash crust formation whether by internal densification (Cerdà and Doerr, 2008), raindrop induced compaction (Onda et al., 2008) or mineralogical transformations due to wetting (Balfour and Woods, 2013) are not fully understood. Chief et al. (2006) developed a portable soil corer air permeameter (SCAP) capable of assessing the intrinsic permeability of soil *in-situ*. Theoretically SCAP principals could be utilized in the field in conjunction with traditional Minidisc infiltrometer measurements to assess ash k_a:k_w and gauge the susceptibility of ash to react to initial rainfall and providing insight into the crusting ability of ash.

4.2 Assessment of methodology: sorptivity probe

The sorptivity probe method allowed for quick direct measurement of ash sorptivity, as each test was conducted under zero-head conditions for a relatively short time period (< 3 mins), during which the assumption of hemispherical wetting remained valid confirming that capillary forces dominated infiltration (Leeds-Harrison, 1994). Limited values of laboratory sorptivity (S_f^*), which allowed for unrestricted lateral flow, were consistent with results reported in this study from the sorptivity probe method (S^*), indicating that the probe provided reliable and accurate results (Figure 6). The use of a sorptivity probe is advantageous as low volumes of sample are required to conduct each measurement compared to infiltrometer readings;

approximately 76 cm³ of ash was utilized for each probe test while 500 cm³ were needed for each infiltrometer run in the laboratory.

Sorptivity readings should not vary with measurement technique; however, laboratory probe (S^*) and infiltrometer (S_f^*) readings conducted in the laboratory were significantly greater than field infiltrometer (S_f) results (Figure 6 and Table 1). The authors suggest this difference to be associated with variations associated with one- and three-dimensional flow. Moody et al. (2009) highlighted a similar trend with three-dimensional measurements of field hydraulic conductivity 2.5 to 30 times greater than one-dimensional measurements, with values of one-dimensional ash sorptivity significantly less (p = 0.03) than the three-dimensional results. The sorptivity probe appears to be a reliable method for obtaining unrestricted ash sorptivity values in the laboratory. The use of this methodology will allow for a better understanding of the behavior and transport of water in ash layers, by documenting variation in ash sorptivity, while allowing for ash sample conservation.

Ash sorptivity results from this study were consistent with other reported values (Moody et al., 2009; Kinner and Moody, 2010), indicating sorptivity response was increased when lateral flow was unrestricted (Kinner and Moody, 2010). While the high sorptivity response of burned soils in Kinner and Moody (2010) was related with extremely dry soil moisture content and particle size the results from this study suggests that ash sorptivity values were linked to variations in ash composition. The authors theorize that ash exhibited extremely dry ($\Theta_i < 0.02$ cm³ cm⁻³) initial moisture content due to the presence of carbonates and oxides within the ash. Thermally produced carbonate and oxide particles have the ability to increase sorptivity. The high textural interface of carbonate has been noted to elevate sorptivity levels in soils by increasing absorption of water molecules (Baker and Hillel, 1990), while oxides readily adsorb

water to rehydrate thermally degraded compounds such as heated limestone (Ioannou et al., 2004). All ash samples within this study visually suggested high levels of thermal decomposition, as Munsell color values were high indicating low levels of organic carbon within the ash. Furthermore relatively low levels of inorganic carbon content (Table 3) were present in wildfire ash samples, low organic and inorganic carbon levels in ash samples have been associated with an increase in ash oxides (Balfour and Woods, 2013), thus suggesting that the low initial moisture content and high ash sorptivity readings of this study may be linked to increases in thermal decomposition and the production of thermally produced carbonates and oxides.

4.3 Accuracy of disturbed laboratory measurements compared to *in-situ* field measurements

One of the objectives of this study was to compare laboratory results to field based measurements to assess the feasibility of obtaining detailed ash characteristics primarily from the laboratory setting. While laboratory measurements offer the advantage of permitting replicate measurements over a wide range of predetermined conditions they are often disadvantageous as they are performed on disturbed samples and potentially exposed to numerous wetting and drying events. Overall laboratory measurements within this study were consistent with those obtained in the field, however, differences were noticeable in bulk density and porosity values. While the bulk densities of repacked ash cores were higher than those reported in the field the difference was not significant. Although the repacking of soil cores will never accurately replicate field conditions due to the loss of soil structure from microbial activity, roots and rocks (Brady and Weil, 2007), the bulk density of ash is not affected by these soil processes and

therefore suited to be fairly accurately replicated in the laboratory setting as long as it has not been previously hydrated. Therefore the results from this study suggest that fresh field ash bulk density can be accurately reproduced in the laboratory as long as one is careful not to break the fine structure of ash particles by limiting compaction and sample disruption or skewing results with soil contamination during collection. Variations in total field porosity and laboratory effective porosity were minor and explained by mild dissolution, as well as changes in microporosity associated with variations in ash chemistry; as ash containing larger initial levels of carbonate have been shown to contain micro-pores capable of increasing total porosity but not necessarily effective porosity (Balfour and Woods, 2013).

Discrepancies between field and laboratory based hydraulic measurements were suggested to be associated to dimensional differences driving infiltration as well as changes in ash composition (Moody et al., 2009). Unrestricted, unsaturated laboratory infiltration measurements (K_f^*) displayed hydraulic conductivity values 1.5 times greater than restricted measurements conducted in the field (K_f , Figure 5). When infiltration was restricted to one-dimension sorptivity response was reduced, thus decreasing unsaturated hydraulic conductivity and indicating laterally flow dominated ash infiltration prior to saturation. Comparison of laboratory (S^* and S_f^*) and field (S_f) based sorptivity results also indicate lateral flow was reduced when flow dimensions were restricted. This theory of dimensional differences is consistent with reports that some ash layers act as a buffer and create a two layered system following wildfires (Kinner and Moody, 2008; Onda et al, 2008; Woods and Balfour, 2010), as water entering the ash layer moves laterally and acts as a hydrophilic layer buffering water from the underlying soil (Moody et al., 2009). The comparison of restricted saturated hydraulic conductivity (K_{sat}) to restricted unsaturated hydraulic conductivity (K_f) indicated a significant (p < 0.001) increase

with the unsaturated response being 2.6 times greater; further indicating that the hydrophilic nature and high sorptivity of ash was the main driver in initial ash infiltration.

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Data collected during this study, as well as that compiled from previous research documenting high-severity wildfire ash characteristics, indicated hydraulic conductivity varied over two orders of magnitude within western North America (10⁻² to 10⁻⁴ cm sec⁻¹; Table 2). This large range of ash hydraulic conductivity makes post-fire ash layers very susceptible to changes in post-fire rainfall rates (Kinner and Moody, 2010) and post-fire runoff generation highly sensitive to ash thickness and hydraulic properties (Ebel et al., 2012), as ash layers have the ability to limit the downward movement of water during initial hydration due to potential changes in ash surface charge and high water retention characteristics (Kinner and Moody, 2010; Stoof et al., 2010; Balfour and Woods, 2013). While ash water repellency has not been documented in any known studies pertaining to ecosystems of western North America, it has been reported from Mediterranean sites (Bodí et al., 2011). The effects of ash hydrophobicity could alter ash sorptivity and hydraulic conductivity readings due to changes in ash moisture content similar post-fire soil response (Moody et al., 2009). Overall, in order to assess the postfire response of ash-covered soils, infiltration should be initially modeled as a two-layer system as suggested by Moody et al. (2009), as initial infiltration into an ash layer will spread laterally due to the high sorptive nature of ash and only after the wetting front forms a thin connected layer, can one-dimensional infiltration modeling be applied. The authors are not suggesting that laboratory analysis fully replace post-fire field measurements, but instead it be used to effectively determine shifts in ash characteristics in order to support initial field measurements and further the understanding of ash hydrological response.

5. Conclusion

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This study finds that laboratory based measurements, conducted on disturbed ash samples, accurately reflected field based measurements with variations suggested to be associated with dimensional differences in infiltration, due to lateral flow, not methodology. The use of air permeametery and a sorptivity probe are viable methodologies for obtaining initial ash saturated hydraulic conductivity and sorptivity values respectively in the laboratory. The use of the air permeametery method would allow one to conserve ash samples for further analysis and avoid chemical alterations when working with reactive ash. The sorptivity probe method provided a direct measurement of unrestricted sorptivity and highlighted the strong hydrophilic nature of ash. Air permeametry and sorptivity probes require relatively low volumes of ash, allowing essential information regarding ash characteristics to be obtained in the laboratory and easily incorporated into modeling systems aimed at predicting post-fire infiltration response. The comparison of field and laboratory results indicated ash sorptivity as a driving factor in the initial hydrological response of ash. Results were comparable to previously conducted research as well as consistent between laboratory- and field-based methodologies, indicating that disturbed laboratory readings are a viable substitute for *in-situ* field measurements of initial ash sorptivity and hydraulic conductivity.

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Figure 1: Location map of the 13 wildfire sites within North America, denoted by asterisks.

Figure 2: A site photograph prior to ash sampling with an inset of an ash trench for sample collection; 2009 Terrace Mountain wildfire in southern British Columbia, Canada.

Figure 3: Photographs of the laboratory set-up for measuring A) air permeametry and B) sorptivity with a probe.

Figure 4: Particle size distribution of ash from the 13 wildfires (n = 5) compared to the grain size of the silica sand standard and a silt-loam soil. Error bars for ash and sand have not been included to facilitate in the interpretation of the graph.

 Figure 5: Boxplots of unsaturated hydraulic conductivity values for all wildfire ash obtained in the field (K_f) and laboratory (K_f^*) via the use of an infiltrometer (n = 5 per wildfire). Significant differences across wildfire sites are indicated with italic p-values above the box plot. Differences within wildfire sites are significant at the p < 0.001 unless otherwise stated in bold.

Figure 6: Boxplots of sorptivity values for all wildfire ash obtained via sorptivity probe (S^*) and laboratory infiltrometer (S_f^*) methods. Due to limited ash availability only ten wildfires were included for S_f^* measurements (n = 5 per wildfire). Significant differences across wildfire sites are indicated with italic *p*-values above the box plot.

Figure 7: Boxplots of saturated hydraulic conductivity values for all wildfire ash obtained via air permeametry (K_{sat}^*) and falling head conductivity (K_{sat}) methods (n = 5 per wildfire). Significant differences across wildfire sites are indicated with italic *p*-values above the box plot.

4080 Table 1: Summary information for ash field characteristics from the 13 wildfire sites. Five replications were preformed for each measurement. Values in bold are significant at the p < 0.05 level.

Table 2: Summary information from other research studies reporting wildfire ash hydraulic characteristics.

 $\begin{array}{c} 4085 \\ 4086 \end{array}$

Table 3: Summary information for ash characteristics from the laboratory for the 13 wildfire ash samples. Five replications were preformed for each measurement. Values in bold are significant at the p < 0.01 level and those in bold and italics are significant at p < 0.001 level.



4095 Figure 1 

Figure 2

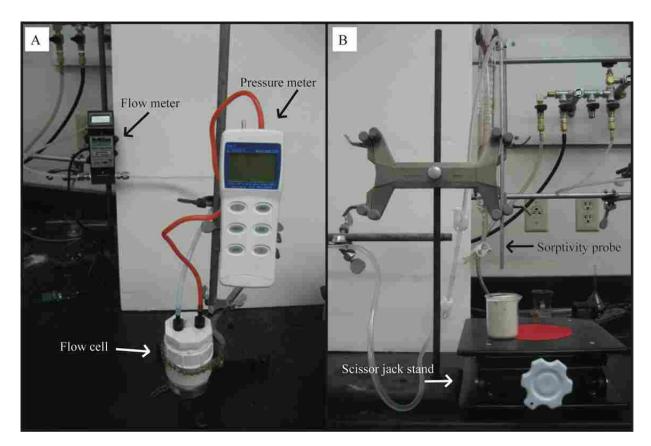
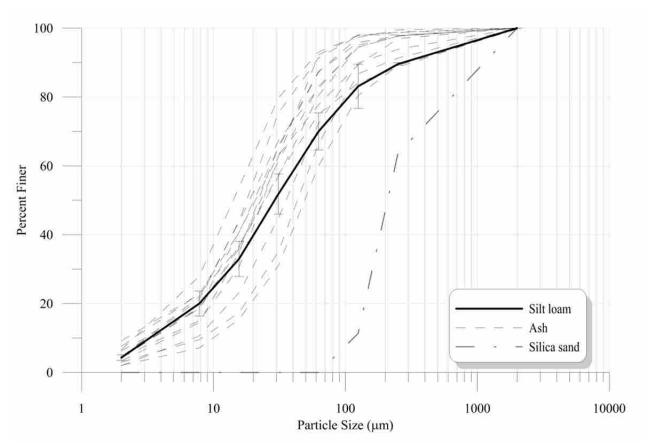


Figure 3



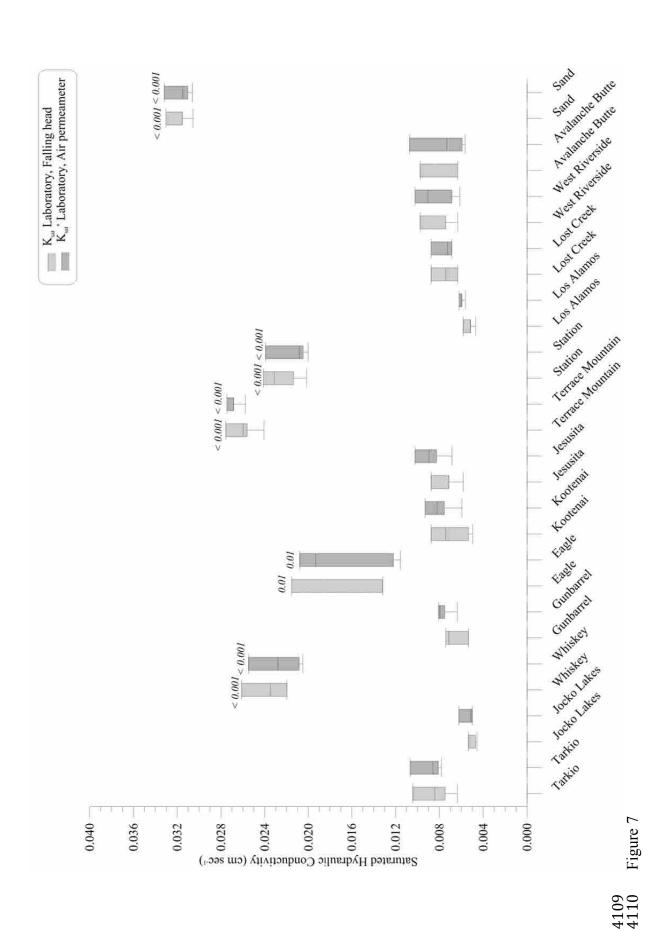
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Figure 5

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Figure 6



			Ash Thickness		Total Porosity	Bulk Density	Sorntivity
Wildfire	Location, Year	Forest Type	(cm)	Ash Color*	(%)		$(S_{\rm f}, { m mm sec}^{-0.5})$
Tarkio (I-90 complex)	Montana, 2005	Pinus contorta, Pinus ponderosa, Pseudotsuga menziesii	4.00 ± 0.82	7.5 YR 7/1	88 ± 3	80	1.85 ± 0.03
Jocko Lakes	Montana, 2007	Pinus contorta, Pinus ponderosa, Pseudotsuga menziesii	4.06 ± 0.36	7.5 YR 6/1	90 ± 1	0.27 ± 0.02	1.97 ± 0.02
Whiskeytown	California, 2008	Quercus agrifolia, Pinus sabiniana, Pinus ponderosa, Pseudotsuga menziesii	2.81 ± 0.63	7.5 YR 8/1	91 ± 1	0.24 ± 0.02	2.32 ± 0.03
Gunbarrel	Wyoming, 2008	Pinus contorta, Pinus ponderosa	3.46 ± 1.18	7.5 YR 7/1	93 ± 1	0.19 ± 0.04	1.87 ± 0.05
Eagle	Arizona, 2008	Arctostaphylos Manazia, Quercus agrifolia, Pseudotsuga menziesii	3.20 ± 0.79	7.5 YR 8/1	87 ± 1	0.32 ± 0.04	$\boldsymbol{2.11 \pm 0.05}$
Kootenai	Montana, 2009	Pinus contorta, Pinus ponderosa, Pseudotsuga menziesii	5.11 ± 0.60	7.5 YR 5/1	87 ± 2	0.35 ± 0.05	1.86 ± 0.04
Jesusita	California, 2009	Quercus turbinella	4.20 ± 0.30	7.5 YR 8/1	90 ± 1	0.27 ± 0.03	1.76 ± 0.06
Terrace Mountain	British Columbia, Canada 2009	Pinus contorta, Pseudotsuga menziesii, Thuja plicata	8.68 ± 1.53	7.5 YR 8/1	94 ± 0	0.17 ± 0.01	2.27 ± 0.03
Station	California, 2009	Quercus turbinella, Yucca filamentosa	3.77 ± 1.12	7.5 YR 8/1	91 ± 2	0.24 ± 0.05	2.24 ± 0.03
Los Alamos	New Mexico, 2011	Pinus ponderosa, Quercus arizonica, Arctostaphylos Manazia	6.90 ± 0.39	7.5 YR 7/1	89 ± 1	0.29 ± 0.03	1.79 ± 0.03
Lost Creek	Montana, 2011	Pinus contorta, Pseudotsuga menziesii, Thuja plicata	5.60 ± 0.38	7.5 YR 6/1	89 ± 1	0.29 ± 0.04	1.75 ± 0.03
West Riverside	Montana, 2011	Pinus contorta, Pinus ponderosa, Pseudotsuga menziesii	4.39 ± 0.90	7.5 YR 6/1	89 ± 2	0.32 ± 0.07	1.60 ± 0.04
Avalanche Butte	Montana, 2011	Pinus contorta, Pinus ponderosa, Pseudotsuga menziesii	4.56 ± 0.62	7.5 YR 7/1	91 ± 2	0.25 ± 0.06	1.62 ± 0.04

* Munsell soil chart, 1975.

Table 1

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	Wildfire	Particle Density (g cm ⁻³)	Effective Porosity (%)	Total Porosity (%)	Bulk Density $(g \text{ cm}^{-3})$	Sorptivity (mm sec ^{-0.5})	k_a : k_w	Ash Thickness (cm)	Unsaturated hydraulic conductivity (K _f , cm sec ⁻¹)	Saturated hydraulic conductivity (K _{sat} , cm sec ⁻¹)
Gabet and Booker, 2011	I-90 Complex: Tarkio, Montana	2.50 ± 0.60	,		0.39 ± 0.03	ı			1	0.00458 ± 0.000250
Moody et al., 2009	Overland Fire, California	2.44 ± 0.27	66 ± 1	ı	0.83 ± 2.40	1.40 (3D)	ı	ı	0.012 (3D)	$0.012 \pm 0.0000204 \text{ (3D)}$
		ı	ı	ı	1	0.53 (1D)	1		0.0045 (1D)	$0.0045 \pm 0.000405(1D)$
Balfour and Woods, 2013	Terrace Mountain, British Columbia	$\begin{array}{c} 2.62 \pm \\ 0.07 \end{array}$	83	92	0.15	3.47	0.89	8.68 ± 1.53	ı	0.025
	Gunbarrel, Wyoming	$\begin{array}{c} 2.57 \pm \\ 0.13 \end{array}$	68	93	0.12	2.72	1.84	3.46 ± 1.16	ı	9000
Woods and Balfour, 2008	I-90 Complex: Tarkio, Montana	ı	ı	84	$\begin{array}{c} 0.41 \pm \\ 0.01 \end{array}$	ı	1	2.25 ± 2.25	ı	0.0015
Ebel et al., 2012	Fourmile Canyon, Colorado	ı	ı	ı	0.18 - 0.45	ı	ı	1.80 ± 1.60	ı	0.000238
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		Inorgainc C		Organic C Initial Moisture	Effective	Bulk Density
Wildfire, Year	$\mathrm{k_a:k_w}^*$	(%)	(%)	$(\theta_{\rm i},{ m cm}{ m cm}^{-3})$	Porosity (%)	$(g cm^{-3})$
Tarkio, 2005 (I-90 complex)	1.18 ± 0.23	22.23 ± 1.23	2.03 ± 0.23	0.0019	83 ± 2	0.33 ± 0.06
Jocko Lakes, 2007	1.06 ± 0.11	12.57 ± 1.02	3.75 ± 0.32	0.0170	84 ± 1	0.30 ± 0.02
Whiskeytown, 2008	0.82 ± 0.17	$I.07 \pm 0.08$	0.97 ± 0.08	0.00052	82 ± 1	0.24 ± 0.03
Gunbarrel, 2008	1.30 ± 0.24	5.66 ± 0.23	1.55 ± 0.15	0.0012	90 ± 3	0.24 ± 0.12
Eagle, 2008	0.71 ± 0.15	$I.23\pm0.80$	0.81 ± 0.07	0.00045	78 ± 1	0.38 ± 0.02
Kootenai, 2009	1.43 ± 0.39	10.57 ± 0.31	2.03 ± 0.81	0.0023	82 ± 3	0.31 ± 0.04
Jesusita, 2009	1.18 ± 0.21	12.23 ± 0.28	0.82 ± 0.13	0.0015	86 ± 4	0.25 ± 0.04
Terrace Mountain, 2009	0.94 ± 0.26	$\boldsymbol{3.84 \pm 0.73}$	2.41 ± 0.56	0.00033	85 ± 7	0.26 ± 0.02
Station, 2009	0.73 ± 0.02	$\boldsymbol{2.08 \pm 0.15}$	1.89 ± 0.15	0.00041	86 ± 1	0.30 ± 0.02
Los Alamos, 2011	1.15 ± 0.12	15.23 ± 0.73	2.13 ± 0.82	0.00155	80 ± 4	0.29 ± 0.04
Lost Creek, 2011	1.06 ± 0.09	20.02 ± 0.18	1.25 ± 1.01	0.00162	80 ± 3	0.31 ± 0.04
West Riverside, 2011	1.05 ± 0.18	15.78 ± 0.82	2.23 ± 0.33	0.0021	82 ± 3	0.35 ± 0.07
Avalanche Butte, 2011	1.05 ± 0.18	8.23 ± 0.31	1.20 ± 0.07	0.00173	83 ± 5	0.24 ± 0.05
Sand	1.06 ± 0.06	0.00 ± 0.01	0.00 ± 0.01	0.00970	51 ± 1	1.23 ± 0.02
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 $[\]mbox{\ ^*}$ The ratio of the intrinsic permeability of air (k_a) to water (k_w)

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CHAPTER FIVE

The Temporal Evolution of Wildfire Ash and Implications for Post-fire Infiltration

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Abstract

Changes in the properties of an ash layer with time may affect the amount of post-fire runoff, particularly by the formation of ash surface crusts. The formation of depositional crusts by ash have been observed at the pore- and plot-scale, but the causes and temporal evolution of ash layers and the associated crusts have not yet been thoroughly investigated. In the long-term ash crusting effects will decrease as the ash layer is removed by wind and water erosion, however, in the short-term ash crusting could contribute to the observed changes in post-fire runoff. This research addresses these topics by studying the evolution over time of highly combusted ash layers from two high severity wildfires, which occurred in Montana, 2011. More specifically, this research was designed to assess the potential for ash crusts to form and thereby contribute to the observed decreases in infiltration after forest fires.

Results indicate that high-combustion ash can evolve due to post-fire rainfall. Sites that exhibited a visible ash crust also displayed a significant decrease in effective porosity and hydraulic conductivity. These decreases in ash layer characteristics were attributed to raindrop compaction and ash hydration resulting in the formation of carbonate crystals, which decreased effective porosity and flow within the ash layer. The initial effective porosity was high for all plots with values of 86 ± 5 %. A decrease in effective porosity (73 ± 5 %) was documented following the first post-fire rainfall event in plots that exhibited ash crusting. Further decreases in porosity over time were not recorded in crusted plots after this initial decrease. Plots not exposed to hydration did not exhibit significant changes in effective porosity throughout the course of the study. The mean initial hydraulic conductivity was 0.21 ± 0.02 mm sec⁻¹, however, following the first rainfall event conductivities of crusted plots decreased an order of magnitude, from 10^{-1} to 10^{-2} mm sec⁻¹, while plots not exposed to rainfall indicated no significant change. During this same time period, inorganic carbon content more than doubled from 11 to 26 % and bulk density significantly increased from 0.22 to 0.39 g cm⁻³ within crusted plots.

While raindrop impact increased the robustness of the ash crust, mineralogical transformations must occur to produce a hydrologically relevant ash crust. These results indicate that post-fire rainfall is an important control on the properties of the ash layer after burning and on crust formation. The observed temporal changes indicate that the timing of ash sampling can alter the predictions as to whether the ash layer is effecting post-fire infiltration and runoff. The formation of post-fire ash crusts could prove beneficial to post-fire hazard mitigation by stabilizing the ash layer, reducing aeolian mixing and erosion.

Keywords: wildfires, ash evolution, ash crust formation

1. Introduction

Following wildfire, burned landscapes are often blanketed with a layer of
vegetative ash. These ash layers can be initially contiguous across the landscape (Cerdà
and Doerr, 2008; Woods and Balfour, 2008), and be of varying thickness (1-20 cm;
Cannon et al., 2001; Cerdà and Doerr, 2008; Gabet and Sternberg, 2008; Woods and
Balfour, 2008; Larsen et al., 2009; Ebel et al., 2012; Santin et al., 2012) and chemical
composition dependent upon various factors such as combustion temperature, fuel
arrangement and density, fuel species type, the plant part combusted and the duration of
combustion (Goforth et al., 2005; Liodaskis et al., 2005; Pereira et al., 2011; Bodí et al.,
2011; Balfour and Woods, 2013). Ash layers are known to alter the hydrological response
in post-fire systems with variations often attributed to three main variables i) the
thickness of the ash layer altering ash water storage and soil pore clogging capability
(Cerdà and Doerr, 2008; Larsen et al., 2009; Stoof et al., 2010; Woods and Balfour,
2010), ii) variations in ash and soil properties composing a layered post-fire soil system,
such as particle size, moisture content and wettability (Moody et al., 2009; Kinner and
Moody, 2010; Woods and Balfour, 2010; Bodí et al., 2011, 2012, 2012a) and iii)
alterations in ash mineralogical composition associated with initial hydration (Etiegni and
Campbell, 1991, Goforth et al., 2005; Balfour and Woods, 2006; Balfour and Woods,
2013). However, little is known as to what extent ash layers change over time and if the
temporal evolution of ash layer characteristics alter the hydrological response of post-fire
ash layers.

Within days to months after fire activity ash layers are often redistributed from the soil surface by wind, surface runoff or incorporated into the soil (Blank and Zamudio, 1998; Larsen, et al., 2009; Schmidt and Noack, 2000; Novara et al., 2011; Santin et al., 2012). As a result the effect of ash on infiltration is often considered to be confined to the first few storms (Larsen et al., 2009). However, the impact of ash on infiltration during these early events can be considerable, and there are cases where ash continues to affect the runoff response for several months after a fire (Cerdà, 1998) suggesting that the effect of ash layers varies temporally. Changes in ash layer properties with time, such as porosity, thickness, water repellency and hydraulic conductivity may affect infiltration response. While the formation of an ash depositional seal on the soil surface, consisting of a thin compacted ash layer, has been shown to decrease infiltration response at both the pore and plot scale (Onda et al., 2008; Woods and Balfour, 2008; Larson et al., 2009), less is understood regarding the formation or hydrological importance of ash crusts a top thicker ash layers. Natural ash crusts have been observed *in situ* following high-severity wildfires, however, the mode of formation is not fully understood (Figure 1). The ability of ash to form a crust was first suggested by Onda et al. (2008) where decreases in postfire infiltration rates were attributed to the formation of a low hydraulic conductivity ash layer due to raindrop compaction. Gabet and Sternberg (2008) further noted that distinct ash layers reduced the ability of flowing water to infiltrate into underlying soil substrate during laboratory flume experiments suggesting the possibility of an ash crust. During the same time Cerdà and Doerr (2008) suggested a mode of crust formation to be attributed to internal densification of the ash layer as it became compacted over time under its own weight. More recently Balfour and Woods (2013) suggested a theory that thermally

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produced oxides in highly combusted ash may be capable of forming a chemical crust, stabilizing the ash layer and altering subsequent infiltration in post-fire systems. However, it is uncertain whether chemical crust formation by re-crystallization within the ash layer can be caused simply by exposure of ash to air or whether direct rainfall is required to hydrate and compact the ash. Over the long term, the potential for ash crusting will undoubtedly decrease as the ash layer is removed via wind and water erosion or incorporated into the soil, however, changes in the ash layer evolution as well as the formation of a surface ash crust may further explain variations in the hydrological response of ash within recently burned ecosystems.

Understanding temporal changes in post-fire infiltration rates and the role of ash crust formation is essential for accurately modeling post-fire hydrologic processes (Robichaud, 2000; Pierson et al., 2001). While research regarding the effect of ash on infiltration and runoff is currently focused on quantifying the hydrological properties of ash to facilitate the parameterization of hydrologic models (Moody et al., 2009; Ebel et al., 2012), less attention is being applied to understanding if and how ash layers may evolve or change over time. The lack of investigation into understanding ash evolution represents a significant research gap for the following reasons. First, there is a clear theoretical basis for ash layers to form crusts based on physical-chemical changes that have been documented to occur in vegetative ash combusted at high temperatures, either from wildfire or laboratory settings (Etiegni and Campbell, 1991; Liodakis et al., 2005; Úbeda et al., 2009; Balfour and Woods, 2013). Furthermore numerous authors have theorized that ash associated with high combustion temperatures, thus containing oxides and carbonates, could compact above the soil surface reducing ash hydraulic conductivity

and promoting Hortonian overland flow (Cerdà and Doerr, 2008; Onda et al., 2008; Woods and Balfour, 2008; Balfour and Woods, 2013). Preliminary tests conducted prior to this study indicated the formation of a chemically produced ash crust was possible following the hydration of wildfire ash containing oxides within the laboratory, suggesting a similar process may lead to the formation of chemical ash surface crusts within the field. Secondly, the lack of information regarding how ash layers change within the initial weeks after a fire limit the ability to develop refined models to predict fire-related flooding and erosion events. In order for post-fire models to be the most effective, they must accurately represent the infiltration, runoff and erosion processes taking place and therefore account for any significant changes in ash layers over time. For example, if ash crust formation alters infiltration in post-fire environments, then models need to account for this by incorporating ash-sealing effects into infiltration algorithms (Moody et al., 2009; Kinner and Moody, 2010).

Research is still needed to systematically evaluate the effect of ash layer evolution on the post-fire infiltration as well as to determine the conditions under which ash crusting occurs and its effect on subsequent infiltration response. The overall goal of this study was to address this research gap by examining changes in ash layer properties over time following high-severity wildfire activity within the Rocky Mountain region of the Western US. The specific aims were to *i*) determine if the temporal evolution of *in situ* ash layers alter ash infiltration, *ii*) document the formation of a post wildfire ash crust, *iii*) assess if ash crust formation was due to compaction by raindrop impact or mineralogical transformations associated with hydration and *iv*) if mineralogical transformations associated with crust formation were dependent upon direct hydration.

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4262 2. Methods

2.1 Study sites and treatment effects

This experiment consisted of study areas located within two separate western Montana wildfires that occurred in 2011; the West Riverside wildfire (WR) near East Missoula (46.883° N, 113.888° W) and the Avalanche Butte wildfire (AV) located near Helena (46.684° N, 111.379° W). The West Riverside wildfire started on the 22 August and consumed 1,538 hectares of mixed conifer forest; lodgepole pine, ponderosa pine and Douglas-fir (Pinus contorta, Pinus ponderosa and Pseudotsuga menziesii). The Avalanche Butte wildfire was ignited by lighting within the Helena National Forest on the 26 July and burned 16 hectares of sub-alpine fir (Abies lasiocarpa) and white bark pine (Pinus albicaulis) forest. According to the national incident information system (Inciweb, 2011) both wildfires were classified as severe. High fire severity was verified in the field based on the presence of visual indicators (the complete consumption of duff and litter layers; white ash present with little to no visible char fragments), and evidence of heating in the underlying soil (charring or a reddish color; DeBano et al., 1998; Neary et al., 2005; Parsons et al., 2010). Random soil samples were collected within each wildfire to determine underlying soil texture. Western Montana has a modified continental climate in which topography is the primary driver of local precipitation and during the summer months precipitation typically occurs as intermittent, localized, high-intensity thunderstorms. The mean annual precipitation in East Missoula (NOAA, 2013), which is approximately 2 km from the

West Riverside area and 150 m lower in elevation, is 350 mm of which 27 mm fall in the

month of September and 21 mm fall in October. The mean annual precipitation in Helena (NOAA, 2013), which is approximately 30 km from the Avalanche Butte area and 300 m lower in elevation, is 290 mm of which 32 mm fall in the month of August and 27 mm fall in September. Rainstorm intensities within western Montana can range from 12 mm hr⁻¹ for 1-hour 2-year return period events to 130 mm hr⁻¹ for the 5-min 100-year return period events.

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Within each study area, six sites were established based on similar aspect, slope, ash color and depth (Figure 2). All sites were situated with a southwest aspect containing slopes ranging from 16 to 27 % within the West Riverside (WR) area and 9 to 17 % within the Avalanche Butte (AV) area (Table 1). A tipping-bucket rain gauge was installed within each study site with a data logger to monitor changes in precipitation throughout the course of the study. In order to determine the effect of raindrop impact and ash hydration on ash crust formation three 4-m² treatment plots were installed at each site. At each site, one plot was exposed to natural rainfall, one plot was sheltered from rainfall by a canopy cover, and the third plot was exposed to natural rainfall but protected from raindrop impact by a fine mesh screen. This design allowed us to distinguish the effects of natural rainfall on ash properties and ash crust formation as compared to rainfall with minimal raindrop impact and the exposure of the ash layer to moist air but without direct hydration. The evolution of ash layer characteristics (Table 2) were measured within each plot over time in response to natural rainfall to gauge if in situ wildfire ash layers displayed similar alterations to wetting as documented in laboratory settings (Stoof et al., 2010; Bodí et al., 2011, 2012; Balfour and Woods, 2013) and were capable of producing an ash crust in the field.

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2.2 Site characteristics and field measurements

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Initial ash characteristics were assessed as soon as possible after containment of the wildfires and then recorded every ten days for roughly one month. Field measurement sets were collected within a designated 0.25 x 2 m wide transect area at plots within West Riverside on the 15 and 25 September as well as the 2,9 and 19 October and on the 14 and 23 August as well as the 2, 8 and 28 September within Avalanche Butte (Figure 2). A new transect area within each plot was used for each of the aforementioned dates to assess changes in ash characteristics over time as well as changes associated with the three treatment effects (Figure 2). Ash field measurement sets (Table 2) consisted of water repellency (n = 10), color (n = 3), infiltration (n = 3), thickness (n = 10) and bulk density (n = 3). Prior to each measurement set the percentage of ash, bare soil and rocks within the transect area were recorded using a 2 cm x 10 cm cell grid. The wettability of ash can vary from water repellent to rapidly wettable, thus altering the hydrological response (Bodí et al., 2011), therefore the water drop penetration time test (DeBano et al., 1998) was used to measure ash wettability randomly six times within the transect area. Ash color was recorded using the Munsell (1975) soil color chart. Ash infiltration was measured randomly within the transect area using a mini-disk tension infiltrometer (4.4 cm diameter, 2.0 cm tension, Decagon Devices, 2006). This method was chosen as the mini-disk is portable, easy to use in the field and already established for collecting qualitative measurements in post-fire settings (Robichaud et al., 2008; Moody et al., 2009). Ash layers, however, can be highly absorptive with reports of the entire capacity

of the mini-disk (90 mL) infiltrating into the ash in less than one minute (Moody et al., 2009; Balfour and Woods, 2013). Therefore, prior to infiltration measurements a core ring (4.4 cm diameter) was inserted into the ash layer to limit lateral flow to one-dimension. After infiltration readings were conducted a trench was dug exposing the ash-soil interface as well as visually assessing for ash crusts. A 1.0 mm diameter pin was then inserted at ten locations along the trench to compute a mean ash thickness. To avoid soil contamination the full thickness of the ash layer was not sampled during bulk density collection, instead a soil core was used to sample the ash layer to a depth approximately 0.5 cm above the ash-soil interface. All field-based measurements were replicated in triplicate unless otherwise stated and a composite ash sample was collected for laboratory analysis.

Following ash measurements three random soil samples were collected at each plot for each collection date to determine consistent underlying soil texture conditions. Soil hydrophobicity, with depth, was recorded at six locations within the transect area according to DeBano et al. (1998). The hydraulic conductivity of non-water repellent soil layers were measured in triplicate using a mini-disk tension infiltrometer (Decagon Devices, 2006).

2.3 Calculations and laboratory analysis

Laboratory analysis consisted of ash mineralogy, effective porosity, particle size distribution as well as organic and inorganic carbon content (Table 2). X-ray diffraction analysis was used to identify ash mineralogy and changes in ash composition associated

with hydration over time (Etiegni and Campbell, 1991; Balfour and Woods, 2013).

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Existing values of ash porosity are typically based on total porosity, however, internal ash 4355 pores (Balfour and Woods, 2013) may alter porosity readings therefore effective porosity 4356 was determined via the gravimetric saturation method (Flint and Flint, 2002) in order to 4357 calculate pores contributing to fluid flow. Organic and inorganic carbon content were 4358 determined via the following method, a dry combustion CNS analyzer (Model EA1100, 4359 Fisons Instruments, Milan, Italy) was used to obtain total carbon, while inorganic carbon 4360 content was determined by measuring CO₂ concentrations following mixture with H₂SO₄; 4361 organic carbon content was calculated as the difference between total and inorganic 4362 carbon (Schumacher, 2002). Soil and ash particle size distribution were determined using 4363 laser diffractometry after sieving samples to less than 2.0 mm (Beuselinck et al., 1998; 4364 Balfour and Woods, 2013; Malvern Instruments Ltd, Malvern, UK). The percentage of

Values for ash and soil hydraulic conductivity (K mm sec⁻¹) were computed using a second order polynomial function (eq. 1) to fit cumulative infiltration (I, mm) to the square root of time (t, sec; Dane and Hopmans, 2002; Decagon Devices, 2006; Moody et al., 2009; Ebel et al., 2012; Balfour and Woods, 2013).

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$$I = C_1 t + C_2 t^{1/2}$$
 (eq. 1)

the sample greater than 2.0 mm were recorded as coarse fragments.

Variables C_1 (mm sec⁻¹) and C_2 (mm sec^{-0.5}) are parameters related to hydraulic 4371 4372 conductivity and sorptivity, respectively. The hydraulic conductivity was computed from

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$$K = \frac{c_1}{A}$$
 (eq. 2)

where A is a value relating to the Van Genuchten parameters of a given textural class and the set infiltrometer suction. Van Genuchten parameters for ash were estimated based on

the soil textural class of ash (Balfour and Woods, 2013). Values for ash sorptivity (S, mm sec^{-0.5}) were computed as the slope of the linear regression cumulative infiltration (*I*, mm) versus the square-root of time (t, sec) based on the following equation (Vandervaere et al., 2000; Clothier and Scotter, 2002; Moody et al., 2009).

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$$I = S t^{1/2}$$
 (eq. 3)

2.4 Statistical analysis

Between wildfire variability was not compared as the study only aimed at addressing within wildfire variability of ash characteristics over time. One-way ANOVAs were conducted on initial site and plot characteristics (aspect, slope, ash depth, soil hydraulic conductivity and water repellency) to assess for variations across sites and plots within each wildfire. Repeated one-way ANOVAs were conducted on the following variables to assess for variations in ash characteristics over time within plots of similar treatment; depth, bulk density, effective porosity, water repellency, sorptivity, hydraulic conductivity, ground cover as well as organic and inorganic carbon content. One-way ANOVAs were also used to test for differences between treatment types (natural, screen, cover) for each measurement date. Prior to ANOVAs, the variables were tested for normality using the Kolmogorov–Smirnov test. Statistical analysis was conducted using the SPSS Version 10.0.5 statistical software (SPSS Inc. 1999). Only significant p-values (< 0.05) are reported in the results.

3. Results

3.1 Site characteristics and rainfall data

Prior to initial data collection ash layers within all plots were dry to the touch with no evidence of rainfall or compaction. Within and across treatment variations in site and plot characteristics were not significant. All plots were 100 % covered with grey (10YR 6/1) to light grey (10YR 7/1) ash with an overall mean thicknesses of 54 ± 7 mm and 37 ± 11 mm for WR and AV plots respectively. All ash layers were hydrophilic (WDPT < 0.5 sec) and the initial characteristics (depth, bulk density, carbon content and color) were consistent within and across treatment types (Table 3). Initial ash hydraulic conductivity and sorptivity values were consistent across plots within each wildfire site, with rates of 0.107 ± 0.0034 mm sec⁻¹ and 1.47 ± 0.33 mm sec^{-0.5} for WR plots and 0.032 ± 0.0062 mm sec⁻¹ and 1.15 ± 0.46 mm sec^{-0.5} for AV plots (Figure 3).

The underlying soil texture of all plots, irrespective of site location, was a gravelly silt loam containing a mean of 7 ± 3 % clay, 68 ± 4 % silt and 25 ± 4 % sand in the fine earth fraction and a mean of 50 ± 15 % of coarse fragments for WR plots and a mean of 6 ± 2 % clay, 64 ± 5 % silt and 31 ± 4 % sand in the fine earth fraction and a mean of 38 ± 10 % of coarse fragments for AV plots (Table 1). Underlying soils were highly water repellent with the overall mean WDPT > 300 seconds within each wildfire. Underlying soil in West Riverside sites contained a mean hydraulic conductivity of 0.00373 ± 0.00021 mm sec⁻¹, while values of 0.00392 ± 0.0015 mm sec⁻¹ were measured in Avalanche Butte sites (Table 1). Soil water repellency and hydraulic conductivity were not significantly variable across plots within each site or between sites within each wildfire (Table 1).

Within each of the study areas, West Riverside and Avalanche Butte, precipitation did not significantly vary across sites and two storm events were recorded during data collection. The first storm within West Riverside occurred on the 22 September 2011 as a brief low-intensity (10 mm hr⁻¹) event lasting 30 min. A natural plot, which was situated approximately a meter downslope from a patch of bare, water repellent soil was exposed to overland flow following this event. Visual assessment indicated that the ash layer absorbed the flow and an ash crust was formed upon reassessment three days later (Figure 4). The second rainfall event was much larger and occurred on the 17 October 2011 producing 20 mm of rain over a 30 min period. This storm resulted in substantial overland flow into adjacent unburned areas, the formation of inter-rills in the ash crust as well as erosion and substantial removal of large portions of the ash layer (Figure 5). The first storm event to occur within Avalanche Butte was of low intensity (8 mm hr⁻¹) and duration (15 min) on the 20 August 2011, with no signs of overland flow or erosion. The second rainfall event occurred on the 15 September 2011 and produced 25 mm of rain over a 60 min period resulting in erosion and the removal of large portions of the ash layer.

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3.2 Temporal and treatment variations

West Riverside wildfire

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Ash crust formation was visually documented in screen and natural plots within the West Riverside fire on the 25 September 2011, following the initial 10 mmhr⁻¹ rainfall event that occurred on the 22 September 2011. During this same time period,

inorganic carbon content more than doubled (p < 0.01) and bulk density significantly increased from 0.22 to 0.39 g cm⁻³ (p < 0.05) for natural and screen plots (Table 3). Associated with these alterations was a darkening of the dry ash color, which was not observed in cover plots, as well as a mineralogical shift indicating a loss of relative oxides present within the ash and an increase in carbonate on 25 September. Mineral identification from X-ray diffraction (XRD) analysis indicated oxides only present in samples collected on the 15 September 2011. It should be noted that oxides within XRD signatures were low and not present in all these samples, however, the increase in the relative intensities of carbonate, on the 25 September, indicate a mineralogical shift associated with visible ash crust formation. The initial (15 September) effective porosity was high for all plots with values of 86 ± 3 , 86 ± 2 and 87 ± 3 % for natural, cover and screen respectively. On the 25 September a significant decrease in porosity was documented within natural and screen plots (p < 0.01; Figure 6). Further decreases in porosity over time were not recorded in natural and screen plots after this initial decrease. Covered plots did not exhibit significant changes in effective porosity throughout the course of the study.

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Ash ground cover began to decrease starting the 25 September 2011 where as screen and natural plots exhibited complete ash cover until the 9 October 2011 (Figure 7a). Bare soil significantly increased for all plots following the second rainfall event (17 October) resulting in approximately 50 % bare soil coverage (Figure 7a). Regardless of treatment, variations in organic carbon content over time and across treatment type were not significantly different. Ash depth within screen and natural plots significantly (p < 0.05) decreased for data collection on the 25th of September 2011 and again on the 19th of

October following the second rainfall event, while depth within cover plots decreased continuously for all collection dates (Table 3). Based on ash grain size distribution data, Van Genuchten parameters for silt loam were used to calculate ash hydraulic conductivity according to equation 2. The mean initial hydraulic conductivity was 0.23 ± 0.14 , 0.17 ± 0.06 and 0.21 ± 0.07 mm sec⁻¹ for natural, cover and screen respectively (Figure 3). Following the first rainfall event hydraulic conductivity within natural and screen plots decreased an order of magnitude, from 10^{-1} to 10^{-2} mm sec⁻¹ (p < 0.01), while cover plots indicated no significant change. All initial sorptivity values were within the range of 1.04 to 1.74 mm sec^{-0.5} and regardless of treatment there was no significant change in ash sorptivity over time (Figure 3).

Avalanche Butte wildfire

Ash crust formation was not documented within any plots situated in the Avalanche Butte wildfire (AV) and no significant treatment effect was noted within AV sites (Table 3). Initial inorganic carbon content (30 %) was triple that of West Riverside ash and did not significantly change over time (Table 3). The main X-ray diffraction peaks of the ash were associated with silica and carbonate and no significant change occurred throughout the course of the study. Ash organic carbon content ranged from 5 to 18 % with a mean of 11 ± 3 %, 10 ± 4 % and 12 ± 3 % for natural, screen and cover plots respectively (Table 3). There was no significant change in ash organic content over time within any plot. Regardless of plot treatment or temporal variation, mean ash bulk density values were consistently within the range of 0.34 ± 0.05 gcm⁻³ for all plots (Table 3). Ash

depth linearly decreased over the course of the whole study, however, changes between subsequent dates were not significant. Ash ground cover began to decrease in all plots starting 23 August, 2011, with bare soil significantly increasing over time to a final value of greater than 50 % for all plots on 28 September (p = 0.032; Figure 7b). The mean initial ash hydraulic conductivity within all AV plots was 0.0323 ± 0.0058 mm sec⁻¹ (Figure 3). While ash hydraulic conductivity decreased over the course of the whole study, changes between subsequent dates were not significant and within an order of magnitude. Initial ash sorptivity values ranged from 0.43 to 2.01 mm sec^{-0.5} with no significant change over time irrespective of treatment (Figure 3). Initial effective porosity was in the range of 69 to 88 % and no significant change was documented over the course of the study, irrespective of treatment.

4. Discussion

4.1 Variations in temporal changes in ash layer characteristics

The two wildfires sites within this study displayed contrasting results regarding changes in ash layer characteristics over time. The formation of an ash crust and subsequent changes in ash layer characteristics (decreases in porosity, bulk density and hydraulic conductivity) were documented to occur within the West Riverside (WR) ash layer, while ash within the Avalanche Butte (AV) wildfire did not show signs of ash crust formation or variations in ash layer characteristics over time. The most likely explanation for the contrasting effects of the ash layers is due to variations in the chemical composition of the initial ash produced within each wildfire. While both wildfires were

classified as high severity and contained light gray (10YR 7/1) to gray (10YR 6/1) ash according to Munsell (1975). WR sites contained ash with initially lower levels of carbonate and the presence of oxide, while AV sites contained initially three times higher organic and inorganic carbon values than that of WR sites (Table 3). Furthermore there was no evidence of oxides within ash collected from AV sites or visual signs of ash crust formation within this wildfire. This difference in the initial composition of the ash suggests that chemical transformation and the production of hydrated carbonate are an important component to the formation of an ash crust within the Western region of North America.

To the authors knowledge only one study has aimed at documenting changes in ash layer characteristics or evolution immediately after the wildfire activity (Periera et al., 2013a). The lack of research may be due to the fact that post-fire ash is often viewed as ephemeral; highly movable and often removed within days to months after a fire. It is known that ash can be redistributed from the soil surface of a burned area by aeolian or water erosion, with aeolian erosion as a primary cause of nutrient loss from burned areas and significant impact to air quality (Wagenbrenner et al., 2011; Pereira et al., 2013a). Data collected form the WR sites within this study indicated variations in ash thickness and bare soil percentage were associated with treatment type. While values were not deemed statistically significant, for ash layers protected from hydration by a 'canopy', thickness decreased and bare soil increased continuously over the course of the study, while ash thickness within the 'natural' and 'screen' treatment plots stabilized after the rain event on the 25 September 2011 (Table 3 and Figure 7a). A study conducted at the hill-slope scale by Pereira et al. (2013) tracked the evolution of ash thickness over a 45-

day period and attributed increases in thickness to redistribution by wind and decreases to off-site removal by wind or downward migration into the soil. While the authors of this study did not gauge wind erosion or wind speed, they suggest that the continuing changes in 'cover' treated sites were attributed to redistribution by wind, where as ash plots containing an ash crust were not as susceptible to wind redistribution and therefore more stable over time. This was indicated by a constant ash depth measured for the 2 and 9 October within 'natural' WR plots and the 2 October for 'screen' WR plots. All plots within the AV sites displayed similar trends to un-crusted plots within WR sites (Table 3 and Figure 7b), again suggesting the absence of an ash crust may enhance aeolian erosion as ash depth continuous decreased within AV plots.

Sites that exhibited a visible ash crust (WR: natural and screen) also displayed a significant decrease in effective porosity (p < 0.01; Figure 6), bulk density (p < 0.05; Table 3), and hydraulic conductivity (p < 0.01; Figure 3). These decreases in ash layer characteristics are attributed to raindrop compaction and ash hydration resulting in the formation of carbonate crystals, which decreased effective porosity and flow within the ash layer (Balfour and Woods, 2013). The conversion of oxides to carbonates has also been shown to decrease the packing density of ash by changing the overall particle density of the ash (Balfour and Woods, 2013). The formation of carbonate associated with crusting was confirmed by a doubling of inorganic carbon content within 'natural' and 'screen' WR sites following the 25 September rain event as well as a loss of oxide presence within X-ray diffraction signatures (Table 3). Woods and Balfour (2010) suggested that compaction of ash by raindrop impact during initial post-fire rainfall may reduce the hydraulic conductivity of the ash layer, however, we found no difference

between the hydrological response of plots with and without a screen treatment immediately after rainfall therefore concluding that this was not the case.

The results from this study, however, do suggest that raindrop impact contributes to ash crust formation, which can subsequently reduce ash hydraulic conductivity (Figure 3). Visual assessment of the ash crusts within the 'natural sites' indicated cratering within the ash as a result of raindrop impact (Figure 8). Temporal increases in bare soil and decreases in ash thickness also suggest that raindrop impact contributed to the formation of ash crusts. The differences between 'screen' and 'natural' treatments were not significant, however, based on changes in ground cover ash crusts formed under 'screen' treatments did not appear as stable as those formed under 'natural' conditions. Results indicate that crusts formed under the 'screen' treatments began to erode prior to the large rainfall event that occurred on the 17 October, as ash thickness within these plots began to significantly (p < 0.05) decrease on the 10 October and the percentages of bare soil and rocks increased during this period (Table 3 and Figure 7a).

4.2 Mechanisms and significance of ash crust formation

Natural ash crusts have been observed *in situ* following high severity wildfires (Balfour and Woods, 2006; Onda et al., 2008; Woods and Balfour, 2008; Balfour and Woods, 2013; Bodi et al., *in review*), however, the mode of ash crust formation whether by internal densification (Cerdà and Doerr, 2008), raindrop induced compaction (Onda et al., 2008) or mineralogical transformations due to wetting (Balfour and Woods, 2013) have yet to be directly assessed. The initial light rainfall event that occurred within the

West Riverside (WR) wildfire in the current study hydrated the ash layer, which formed a crust via chemical transformations and raindrop impact. The data also indicate that raindrop impact alone was not sufficient to produce an ash crust, as only sites containing initially low inorganic and organic carbon levels (Table 3) as well as the presence of oxides were observed to crust when exposed to direct hydration. Furthermore crust formation was observed in 'natural' and 'screen' plots indicating that a chemical transformation, not raindrop impact, was the main mechanism of crust formation within 'screen' plots. The formation of a chemical crust is also known to occur in industrial wood ash produced at high temperatures, a process termed by Steenari and Lindqvist (1997) as "self-hardening". The resultant hardened ash reported within this current study was associated with a substantially lower hydraulic conductivity, porosity and higher bulk density than unhardened ash (Figures 3 and 6 and Table 3).

Similar responses to those recorded in this study have been noted within other ecosystems of post-fire research. In Spain, Cerdà (1998) commented that the initial ash layer was highly absorptive and the high infiltration rates were attributed to the low moisture content and high porosity of the ash layer. Four months later, however, infiltration decreased by more than 50 %, with the ash layer reported to have "crusted" on the soil surface. Following the 1995 Mt. Vision Fire in California, raindrop impact significantly compacted the ash increasing the runoff response by a factor of 4 relative to the first post-fire storm (Onda et al., 2008). A similar response was also noted within the laboratory setting by Gabet and Sternberg (2008), where the addition of a 1.0 cm ash layer increased runoff 3 to 4 times. Gabet and Sternberg attributed the increase to the ash layer decreasing infiltration to the underlying soil surface. It should, however, be noted

that the effects noted by Gabet and Sternberg (2008) are not the result of an ash crust, as suggested in this study, but of sealing of the soil surface by ash particles similar to finding by Woods and Balfour (2010) were calcium-rich ash was found to fill and clog soil pore necks upon thin section analysis. In cases where the ash pore plugging effect does not occur the ash layer may still limit the rate of infiltration into the 2-layer soil system due to variations in hydraulic conductivity. For example if ash hydraulic conductivity (K_{ash}) is less than soil hydraulic conductivity (K_{soil}) then the ash layer will dictate the infiltration rate (Moody et al., 2009; Kinner and Moody, 2010). However, if $K_{ash} > K_{soil}$, as in this study, the soil will regulate the rate of infiltration into the system resulting in water ponding at the ash-soil interface (Onda et al., 2008; Woods and Balfour, 2010). This response may promote saturation overland flow or subsurface storm flow contributing to the initiation of debris flows (Cannon, 2001; Gabet and Sternberg, 2008; Onda et al., 2008). In cases where $K_{ash} > K_{soil}$, the ash layer also acts as a capillary barrier, storing water rather than controlling infiltration (Kinner and Moody, 2010; Woods and Balfour, 2010). The ability of the ash layer to act as a capillary barrier, however, appears to be linked to ash moisture, as it has only been observed to occur under dry ash conditions (Moody et al., 2009; Kinner and Moody, 2010). While research conducted by Onda et al. (2008) highlights that the mechanisms of runoff generation at the soil surface will change over time, this study provides detailed observations that ash layer properties can change over time and thus the mechanisms of

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documentation of ash crusting in the field and indicates that ash containing oxides and

carbonates can crust and compact above the soil surface reducing K_{ash}. This reduction in

runoff generation could account for these changes. This study supplies direct

 K_{ash} may contribute to the production of Hortonian overland flow depending upon the hydraulic conductivity of the underlying soil and changes in runoff mechanisms as outlined by Onda et al. (2008).

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4.3 Implications for post-fire mitigation treatments

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Robichaud et al. (2007) indicated that the presence of ash on the soil surface can be used as an indicator of soil burn severity and linked to increases in runoff and erosion; therefore variations in ash have important implications for post-fire management. The documentation of ash crust formation presented in this study supports the notion outlined by Cerdá and Doerr (2008) that burnt landscapes are the most susceptible to runoff and erosion following wind or rain event sufficient enough to remove the protective ash layer but before the onset of vegetation recovery. While the hydraulic conductivity of the West Riverside (WR) ash layer presented in this study decreased an order of magnitude with the formation of an ash crust, the conductivity was still higher (10⁻² mm sec⁻¹) than the underlying soil (10⁻³ mm sec⁻¹) suggesting that the ash layer would not be the limiting infiltration layer within the soil system but instead continue to act as a capillary layer storing water (Kinner and Moody, 2010; Woods and Balfour, 2010). While the low hydraulic conductivity of the underlying silt loam soil was consistent with other measurements of silt loams within the region (0.0025 mm sec⁻¹; Woods and Balfour, 2010) they are extremely small values suggesting ash layers could act as the limiting infiltration layer atop more conductive soil types.

Results from this research also indicate that ash crust formation acted as a

protective seal, reducing the removal of the ash layer; as ash cover remained at 100 % for 30 days within crusted plots and began to be removed via aeolian erosion after only ten days within plots without crust formation (Figure 7a). Visual observations of erosion associated with the larger rainfall event, on the 17 October, within the WR area indicated that ash crust rilling occurred, however, the crust was still intact in places suggesting that the stabilized ash layer may have protected the underlying soil from direct sheetwash and interrill erosion (Figure 5).

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Ash is currently viewed as a valuable soil protectant against erosional agents based on studies in Spain and Portugal (Cerdá and Doerr, 2008; Pereira and Úbeda, 2010; Zavala et al., 2009) and the formation of an ash crust has the potential to decrease postfire sediment yields by protecting the underlying soil from raindrops impact and soil sealing similar to the effects of mulching. Furthermore depending upon ash depth and plant species the germination of post-fire vegetation may be aided by the long-term fertilization associated with ash layers (Raison et al., 2009; Bodi et al., in review). Overall the noted response of a stabilized ash crust within a burnt watershed by this study suggests that ash layers could potentially be considered as a natural aid in reducing wind erosion as well as aiding in vegetation recovery: although it is very transient and further study is needed to assess these effects. Whilst precipitation and its temporal and spatial variability are often the primary drivers of post-wildfire runoff and erosion (Moody et al., 2013), it is important to make note of ash evolution and crusting as well. Ash layers have the ability to increase the rainfall threshold of the hillslope, as runoff generation occurs when the conductivity or storage capacity of the ash layer, which is proportional to thickness, is exceeded (Kinner and Moody, 2010; Woods and Balfour, 2010). Therefore

in order to fully assess the need for mitigation treatments after severe wildfires the ash layer should be taken into consideration. Furthermore the authors plan to conduct a mass balance analysis of varying ash types in order to better account for what happens to ash in these post-fire systems.

5. Conclusions

This research was motivated by the need to understand how and to what extent ash layers change over time and if that temporal evolution could alter the hydrological response of post-fire ash layers. While numerous authors have commented on the presence of an ash crust within post-fire ecosystem, the results from this study are the first to document the formation of an *in situ* ash crust after recent wildfire activity. Results from this indicate the following key findings:

- 1) Ash crust formation does not occur following all severe wildfire events. Initial ash composition, the presence of oxides and a hydrating rainfall event are all necessary precursors for crust formation.
- 2) The formation of an ash crust can aid in stabilizing the ash layer, potentially reducing aeolian mixing and erosion.
- 3) While raindrop impact increased the robustness of an ash crust, raindrop impact alone is not sufficient to form an ash crust. Instead mineralogical transformations must occur to produce a hydrologically relevant ash crust.

4697 4) The formation of an ash crust can decrease ash hydraulic conductivity by an order
4698 of magnitude as well as significantly decrease ash layer porosity and increase
4699 bulk density.

4700 Acknowledgements

This manuscript is dedicated to the late Dr. Scott W. Woods, whose contribution to Ms. Balfour's research was paramount. He was a great mentor, scientist, teacher and friend, who will be missed by many, but forgotten by none.

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- Figure 1: A photograph of an ash crust within the 2009 Terrace Mountain wildfire, British
 Columbia, Canada (Balfour and Woods, 2013). The inset photograph is a photograph of the
 author holding a piece of ash crust (1.0 cm thick).
- Figure 2: A schematic layout depicting six sites designated within each wildfire study area. Each site contained three 2 x 2 m plots, which were randomly assigned a treatment; cover (C), natural (N) or screen (S). Within each plot data was collected from a 0.25 x 2 m transect area (represented in grey) for each allocated collection date. Dates represented in this figure correspond to West Riverside site collection.

- Figure 3 (A-F): Representative plots of infiltration measurements for the three different treatment types, natural (A, B), screen (C, D) and cover (E, F), within the West Riverside (top) and Avalanche Butte (bottom) wildfires over the allotted collection period. Infiltration data was not recorded on 19 October or 28 September due to insufficient ash cover, for the West Riverside and Avalanche Butte sites respectively. The coefficient of the x²-term is used to calculate hydraulic conductivity (mm sec⁻¹) according to eq. 2. The coefficient of the x-term is the sorptivity value in mm sec^{-0.5}.
- Figure 4: Photographs of overland flow from adjacent hydrophobic soil onto an ash layer. Photographs were taken during the rainfall event (left) and three days after (right).
- Figure 5: Representative photographs of ash crust inter-rilling within natural and screen plots (left) as well as overland flow and erosion into adjacent unburned areas (right).
- Figure 6: Boxplots of effective porosity values for West Riverside sites (upper) and Avalanche Butte sites (lower). Significant differences are indicated with a *p*-value above the boxplot.
- Figure 7: Pie charts visually displaying the mean percentages of plot coverage for the three different treatment types (natural, cover, and screen) within the (a) West Riverside and (b) Avalanche Butte wildfires over the collection period.
- Figure 8: Ash crust photographs, which formed within the West Riverside site, natural plots, after the initial rainfall event.
- Table 1: Summary information for site characteristics of plots allocated to each treatment type within the West Riverside and Avalanche Butte wildfire study areas. Within and across treatment variation in site characteristics were not significant (p > 0.05).
- Table 2: A list of ash characteristics measured and established methodology.
- Table 3: Summary information for plot characteristics of ash exposed to varying treatment types (natural, cover and screen) within the West Riverside and Avalanche Butte study areas over the allotted collection periods. Significant (p < 0.05) within treatment variations over time are indicated in bold with highly significant variations (p < 0.01) indicated in bold italics.



Figure 1

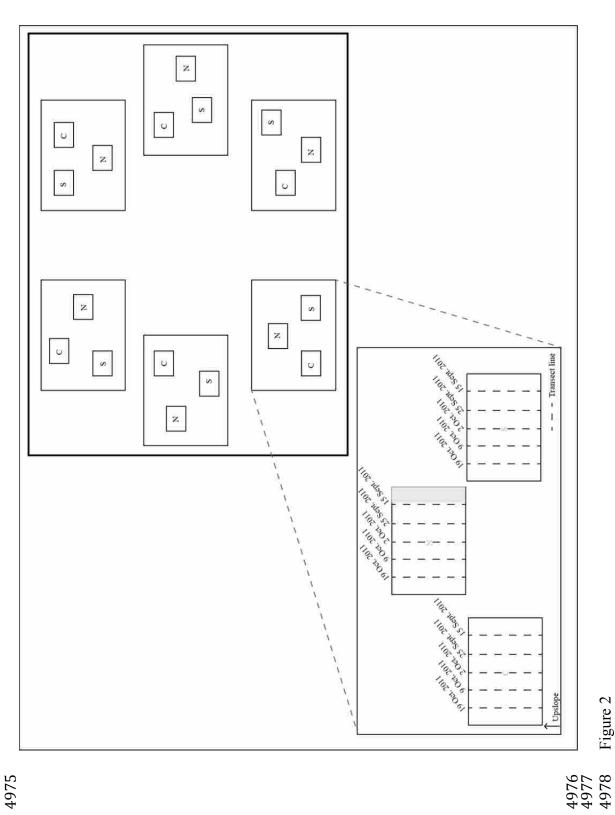


Figure 2



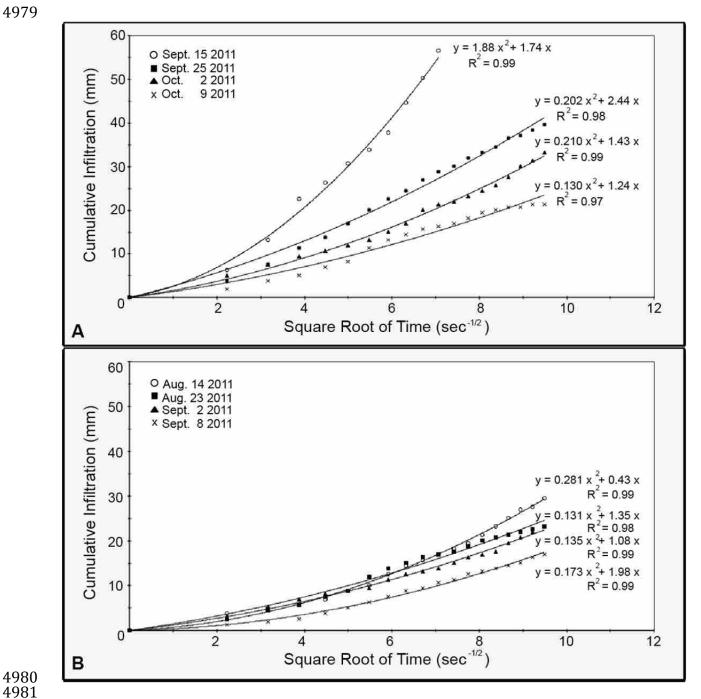


Figure 3A-B

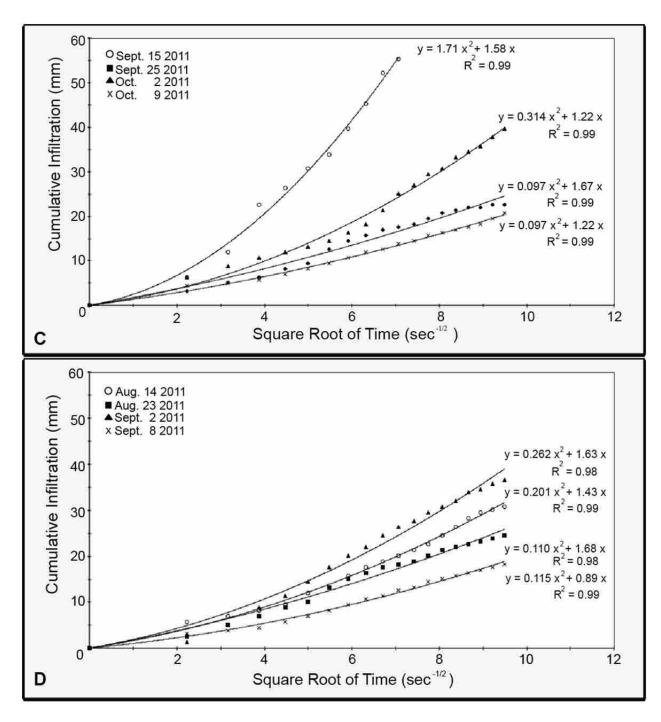


Figure 3 C-D



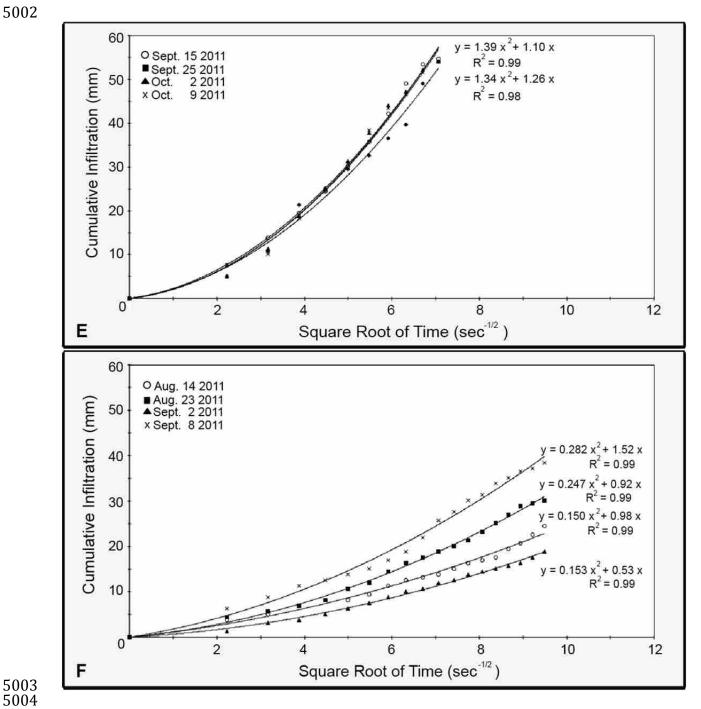


Figure 3E-F

Figure 4

Figure 5

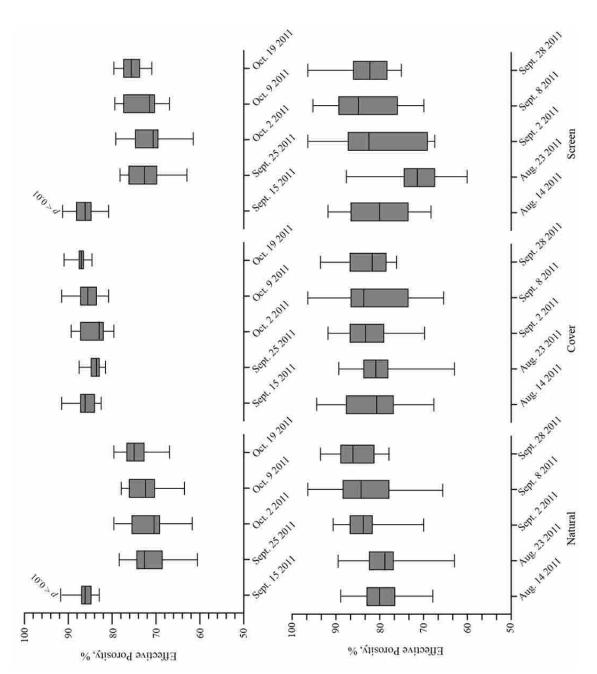


Figure 6

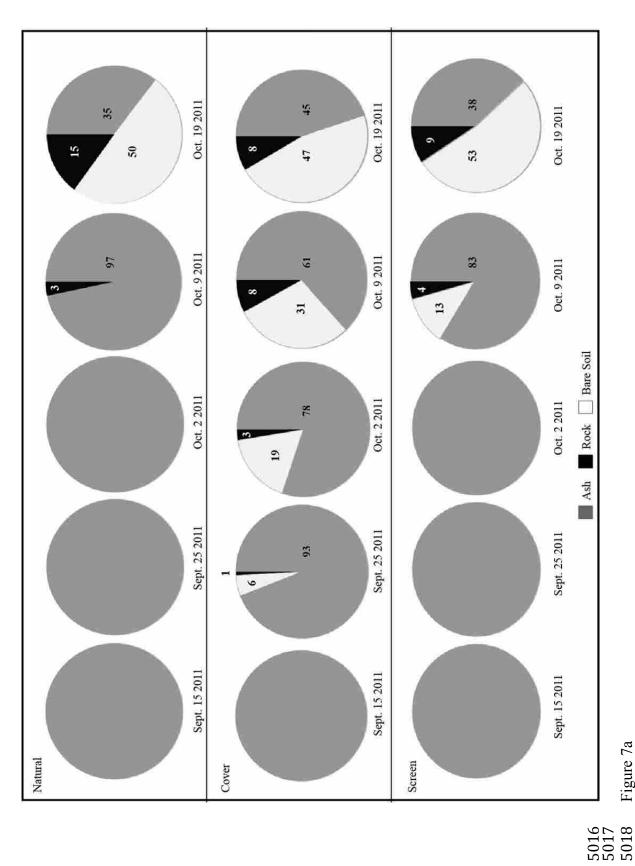


Figure 7a

Figure 7b

Figure 8

				1		Ash			Soil	
Study		Plot	•	5	<u>.</u>	; ;	* -	Water	Hydraulic	
Area		Treatment	Aspect	Slope	Depth	Clay/Silt/Sand	Color	Repellency	Conductivity	Clay/Silt/Sand
			(degrees)	(%)	(cm)	(%)		(WDPT; sec)	(mm sec ⁻¹)	(%)
	n		9	9	09	18	18	30	18	18
West										
Riverside	Mean	Natural	219	22	5.30	3/47/49	10YR 7/1	296	0.00328	9/66/20
	SD		21	3	0.83	2/5/5	ı	94	0.00192	3/3/2
	Mean	Screen	237	21	5.47	5/45/49	10YR 7/2	312	0.00240	6/68/20
	SD		19	3	0.72	2/4/4	ı	70	0.00352	3/3/3
	Mean	Cover	228	18	5.48	5/47/48	10YR 7/1	303	0.00439	7/71/20
	SD		26	7	0.59	2/3/3	ı	86	0.00215	3/4/4
	Mean	Overall	228	20	5.42	5/47/49	10YR 7/1	303	0.00373	7/68/25
	SD		22	3	0.72	2/4/4	1	87	0.00205	3/4/4
Avalanche										
Butte	Mean	Natural	225	13	3.76	7/41/53	10YR 6/1	317	0.00379	7/60/33
	SD		18	7	1.13	3/1/6	ı	72	0.00161	2/5/4
	Mean	Screen	239	111	3.50	8/31/61	10YR 6/1	343	0.00386	6/65/29
	SD		12	3	1.12	3/8/7	ı	48	0.00148	2/4/3
	Mean	Cover	245	15	3.71	7/36/57	10YR 6/1	304	0.00411	4/66/30
	SD		7	2	1.24	2/9/8	ı	125	0.00160	1/4/4
	Mean	Overall	236	13	3.65	7/36/57	10YR 6/1	321	0.00392	6/64/31
	SD		14	2	1.16	3/9/8	ı	88	0.00154	2/5/4
*N 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.0	1.1 -1	1075								

*Munsell soil chart, 1975.

5025 5026 Table 1

Ash Characteristic	Method	Location	Citation
Color	Soil Color Chart	Field	Munsell, 1975
Particle Size Distribution	Laser Diffractometer	Lab	Beuselinck et al., 1998; Balfour and Woods, 2013
Bulk Density	Soil Core	Field	Grossman and Reinsch, 2002
Inorganic, Organic Carbon	CNS Analyzer	Lab	Schumacher, 2002
Mineralogy	X-Ray Diffraction	Lab	Etiegni and Campbell, 1991; Balfour and Woods, 2013
Effective Porosity	Gravimeteric Saturation	Field	Flint and Flint, 2002
Sorptivity	Mini-disk Tension Infiltrometer	Field	Vandervaere et al., 2000; Clothier and Scotter, 2002; Moody et al., 2009
Water Repellency	Water Drop Penetration Time	Field	Bodí et al., 2011
Hydraulic Conductivity	Mini-disk Tension Infiltrometer	Field	Dane and Topp, 2002; Moody et al., 2009; Ebel et al., 2012; Balfour and Woods, 2013

Table 2

		ı			Natural				30	SCIECII				2	Cover		
Study Area	Date		Depth (cm)	Bulk Density (g cm ⁻³)	Organic C (%)	Inorganic C (%)	Color*	Depth (cm)	Bulk Density (g cm ⁻³)	Organic C (%)	Inorganic C (%)	Color*	Depth (cm)	Bulk Density (g cm ⁻³)	Organic C (%)	Inorganic C (%)	Color*
		и	09	18	9	9	18	09	18	9	9	18	09	18	9	9	18
West Riverside	15 Sept	Mean	5.30	0.22	4.70	11.87	10YR 7/1	5.47	0.22	5.35	10.44	10YR 7/2	5.48	0.23	5.59	10.96	10YR 7/1
		QS	0.83	0.04	3.83	3.88	- axor	0.72	0.03	3.68	2.78	- 0.00	0.59	0.04	2.62	3.58	- 4001
	25 Sept	Mean	3.90	0.39	8.09	26.95	5/1	3.91	0.38	7.60	23.01	101 R 6/1	3.94	0.23	6.32	10.06	7/1
		SD	0.70	0.04	2.87	6.95	- axor	0.70	0.05	3.01	10.18	- 0.00	0.80	0.03	3.38	2.80	- 4001
	2 Oct	Mean	3.83	0.40	89.9	29.62	5/1	3.76	0.38	6.83	22.03	101 K 6/1	2.85	0.24	6.71	11.25	101 K 7/1
		QS	0.64	0.05	4.60	9.05	1	99.0	0.05	3.88	10.18	1	0.92	0.04	3.42	4.32	1
	9 Oct	Mean	3.86	0.40	8.01	26.69	10YR 3/1	1.95	0.38	80.9	22.03	10YR 5/1	1.56	0.23	7.12	11.28	10YR 5/1
		QS	0.69	0.03	3.58	8.89	1	0.57	0.04	3.61	11.52	1	0.85	0.04	3.08	3.57	1
	19 Oct	Mean	0.58	0.43	6.15	32.74	10YR 3/1	0.56	0.40	7.35	24.63	10YR 5/1	0.70	0.25	6.65	9.48	10YR 5/1
		QS	0.25	90.0	3.42	7.89	1	0.23	0.05	2.71	10.66	,	0.31	0.04	2.94	3.27	1
Avalanche Butte	14 Aug	Mean	3.76	0.35	11.29	30.04	10YR 6/1	3.50	0.30	10.31	31.01	10YR 6/1	3.71	0.31	11.74	30.57	10YR 6/1
		QS	1.13	0.07	4.35	7.91	1	1.12	0.00	3.23	9.82	1	1.24	0.00	3.01	11.44	1
	23 Aug	Mean	2.28	0.36	10.19	27.56	10YR 4/1	2.26	0.35	66.6	27.12	10YR 4/1	1.99	0.29	13.06	26.51	10YR 4/1
		QS	0.84	0.05	3.81	7.28	1	0.87	90.0	3.18	8.44	1	0.65	90.0	3.29	12.81	1
	2 Sept	Mean	1.37	0.39	9.24	31.89	10YR 4/1	1.36	0.35	11.01	29.20	10YR 4/1	0.97	0.33	12.51	22.01	10YR 4/1
		QS	0.7	90.0	2.30	7.93	'	0.72	0.00	4.34	12.34	'	0.53	0.00	3.33	12.45	
	8 Sept	Mean	1.63	0.36	11.33	32.20	10YK 4/1	1.57	0.33	10.56	28.62	10 Y K 4/1	1.53	0.30	11.15	25.09	10YK 4/1
		QS	0.44	90.00	3.67	7.92	- 0X01	0.44	0.09	4.66	8.70	- 0.001	0.40	0.10	3.01	6.88	- 10VB
	28 Sept	Mean	1.24	0.38	9.50	31.68	4/1	1.21	0.36	12.11	32.96	101 N 4/1	1.08	0.31	12.01	23.52	4/1
		QS	0.5	0.07	1.81	8.16	ı	0.55	0.07	3.42	8.34	,	0.59	0.09	3.09	10.76	1

Table 3

CHAPTER SIX

KEY FINDINGS AND OVERALL CONCLUSIONS

The research conducted for this dissertation contributes to an ever-growing knowledge base of post-fire systems, with emphasis on how variations in wildfire ash characteristics influence post-fire hydrological response. Overall this research finds that ash should not be considered a generic term, as not all ash is created equal, in regards to its effects on immediate post-fire systems. Variability in the effect of ash on runoff following wildfires, and hence the often conflicting findings reported in the literature, can be partially explained by variations observed in the hydrologic properties of ash (Figure 1). Wildfire ash is an important element of post-fire landscapes and should be categorized and taken into consideration when assessing post-fire ecosystems and hazards (Figure 2). The main conclusions, from laboratory and field based experiments carried out during the research conducted for this dissertation, are as follows:

I) The initial physical, chemical, and hydrological properties of vegetative ash within the

Northern Rocky Mountain region mainly varies with combustion temperature / fire severity.

The saturated hydraulic conductivity of ash varies substantially, covering three orders of magnitude with some ash capable of decreasing an order of magnitude following initial hydration. The hydration of ash containing oxides results in the formation of carbonate and therefore it is suggested that ash color is not an acceptable metric to differentiate between variations in the hydrologic response of ash, as both oxide and carbonate ash exhibit high chroma values. Instead carbonate content in ash is suggested as a more reliable variable if measured prior to post-fire rainfall. The author is currently working in conjunction with

colleagues from the US Department of Agriculture to assess how best to measure ash carbonate and ash post-fire alterations with remote sensing in the field.

II) There is potential for the variability in the hydrological properties of ash to affect initial postfire infiltration and runoff response in ash-covered soils. Variability in the effect of ash on
runoff responses following wildfires could be partially explained by variations observed in
the hydrologic properties of ash. The hydrologic response of low and high combustion ash,
associated with physical (grain size) and chemical (carbonate formation) properties, could
prompt the formation of surface seals in post-fire systems by either creating a low conductive
ash layer or an ash crust, while mid-combustion, carbonate dominated, ash may explain
reported buffering effects of ash layers.

III) The use of air permeametery and a sorptivity probe are viable methodologies for obtaining initial ash saturated hydraulic conductivity and sorptivity values respectively in the laboratory. Furthermore laboratory based measurements; conducted on disturbed ash samples, can accurately reflected field based measurements. Air permeametry and sorptivity probes require relatively low volumes of ash, allowing essential information regarding ash characteristics to be obtained in the laboratory and easily incorporated into modeling systems aimed at predicting post-fire infiltration response.

IV) The hydrological properties of ash layers were shown to change over time. While numerous authors have previously commented on the presence of an ash crust within post-fire ecosystem, this work is the first to document the formation of an *in-situ* ash crust recently

after wildfire activity. The formation of an ash crust was documented to decreases ash hydraulic conductivity by an order of magnitude, as well as significantly decreasing ash layer bulk density and porosity. While raindrop impact increases the robustness of an ash crust, raindrop impact alone is not sufficient to form an ash crust, instead mineralogical transformations must occur to produce a hydrologically relevant ash crust. Therefore initial ash composition, the presence of oxides and a hydrating rainfall event are all necessary precursors for crust formation. Ash crust formation, however, does not occur following all severe wildfire events.

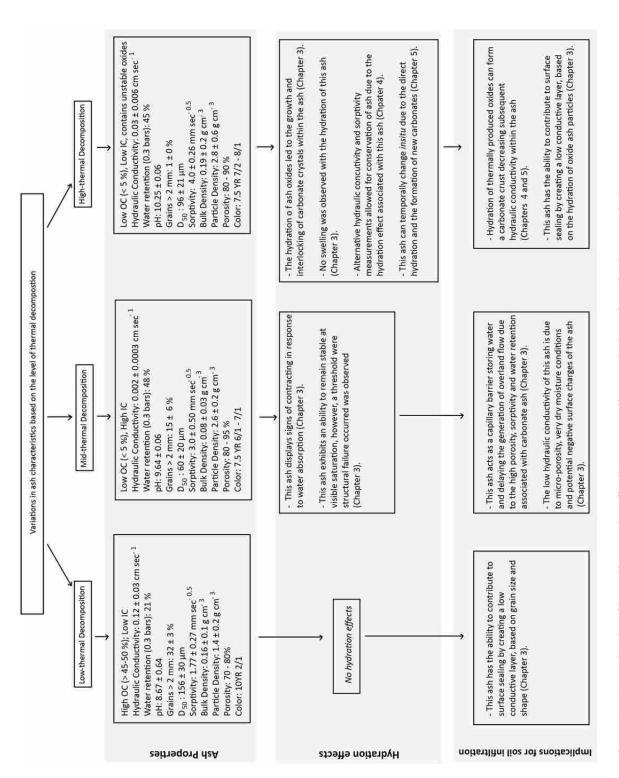


Figure 1: A synthesis of key dissertation findings regarding variations in ash characteristics.

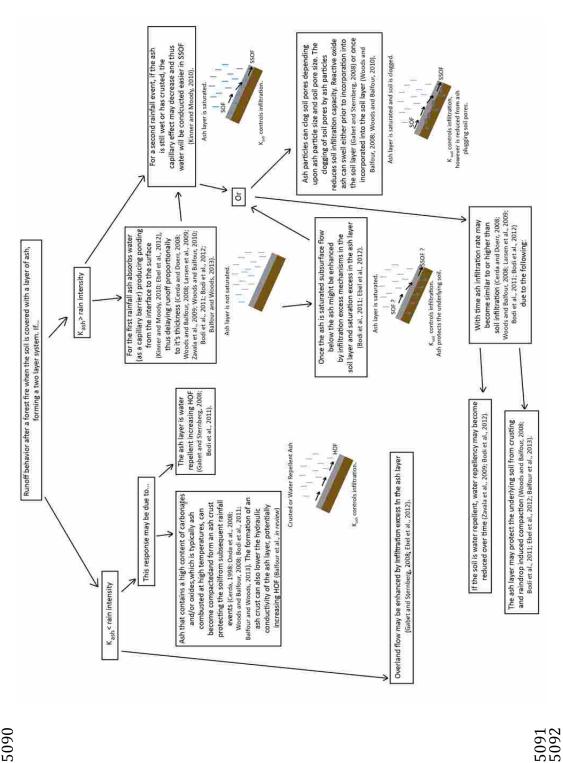


Figure 2: The findings from this dissertation in the context of a runoff generation mechanism flow chart of ash and soil following recent wildfire activity (HOF: hortonian overland flow; SOF: saturation overland flow; SSSF: subsurface storm flow). Modified from Bodi (2012)

5096	References:
5097 5098 5099 5100	Balfour, V.N., and S.W. Woods, 2013. The Hydrological Properties and the Effects of Hydration on Vegetative Ash from the Northern Rockies, USA. <i>Catena</i> 111:9-24.
5100 5101 5102 5103	Balfour, V.N., S.H. Doerr and P. Robichaud, <i>in review</i> . The temporal evolution of wildfire ash and implications for post-fire infiltration. <i>International Journal of Wildlandfire</i> .
5104 5105 5106	Balfour, V.N., <i>in review</i> . Determining wildfire ash saturated hydraulic conductivity and sorptivity with laboratory and field methods. <i>Catena</i> , Manuscript # 3065.
5107 5108 5109 5110	Bodí, M.B., J. Mataix-Solera, S.H. Doerr and A. Cerdà, 2011. The wettability of ash from burned vegetation and its relationship to Mediterranean plant species type, burn severity and total organic carbon content. <i>Geoderma</i> 160: 599-607.
5111 5111 5112 5113	Bodí, M.B., 2012. Ash and water repellency effects on soil hydrology in fire-affected Mediterranean ecosystems. Doctoral Thesis, University of Valencia, Spain.
5114 5115 5116	Bodí, M.B., S.H. Doerr, A. Cerdà, and J. Mataix-Solera, 2012. Hydrological effects of a layer of vegetation ash on underlying wettable and water repellenet soil. <i>Geoderma</i> 191: 14-23.
5117 5118 5119	Cerdà, A., 1998. Changes in overland flow and infiltration after a rangeland fire in a Mediterranean scrubland. <i>Hydrological Processes</i> 12: 1031-1042.
5120 5121 5122	Cerdà, A., and S.H. Doerr, 2008. The effect of ash and needle cover on surface runoff and erosion in the immediate post-fire period. <i>Catena</i> 4: 256-263.
5123 5124 5125	Ebel, B.A., J.A. Moody and D.A. Martin, 2012. Hydrologic conditions controlling runoff generation immediately after wildfire. <i>Water Resources Research</i> 48: 1-13.
5126 5127 5128 5129	Gabet, E.J., and P. Sternberg, 2008. The effects of vegetative ash on infiltration capacity, sediment transport and the generation of progressively bulked debris flows. <i>Geomorphology</i> 101: 666-673.
5130 5131 5132	Kinner, D.A., and J.A. Moody, 2010. Spatial variability of steady-state infiltration into a two-layer soil system on burned hillslopes. <i>Journal of Hydrology</i> , 381: 322-332.
5133 5134 5135 5136 5137	Larsen, I.J., L.H. MacDonald, E. Brown, D. Rough, M.J. Welsh, J.H. Pietraszek, Z. Libohova, J.D. Benavides-Solorio and K. Schaffrath, 2009. Causes of post-fire runoff and erosion: water repellency, cover, or soil sealing? <i>Soil Science Society of America Journal</i> 73: 1393-1407.
5138 5139 5140	Onda, Y., W.E. Dietrich and F. Booker, 2008. Evolution of overland flow after a severe forest fire, Point Reyes, California. <i>Catena</i> 72: 13-20.

5141	Woods, S.W., and V.N. Balfour, 2008. Effect of ash on runoff and erosion after a severe forest
5142	wildfire. Montana, USA. International Journal of Wildland Fire 17: 1-14.
5143	
5144	Woods, S.W., and V.N. Balfour, 2010. Variability in the effect of ash on post-fire infiltration due
5145	to differences in soil type and ash thickness. <i>Journal of Hydrology</i> 393 (3-4): 274-286.
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5147	Zavala, L.M., A. Jordán, J. Gil, N. Bellinfante and C. Pain, 2009. Intact ash and charred litter
5148	reduces susceptibility to rain splash erosion post-wildfire. Earth Surface Processes and
5149	<i>Landforms</i> 34: 1522-1532.

5150	APPENDIX A: Co-author Publications
5151 5152	Peer-reviewed Journal Articles
5153	1 cor reviewed vournar ritioles
5154 5155 5156 5157	Bodí, M., D. Martin, C. Santín, V.N. Balfour , P. Pereira, S. H. Doerr, J. Mataix and A. Cerdà, <i>in review</i> . Wildfire ash: its production, composition and hydro-eco-geomorphic effects in forested landscapes. <i>Earth Science Reviews</i> .
5157 5158 5159 5160 5161	Bodí, M., F.J. Leon Miranda, A. Cerda, V.N. Balfour , J. Mataix-Solera and S.H. Doerr, 2011. Runoff rates, water erosion and water quality from a soil covered with different types of ash. <i>International Meeting of Fire Effects on Soil properties:</i> 80-83.
5162 5163 5164 5165	Bodí, M., G. Sheridan, P. Noske, J. Cawson, V.N. Balfour , S.H. Doerr, J. Mataix-Solera and A. Cerda, 2011. Types of ash resultant from burning different vegetation and varied combustion processes. <i>Journal of the University of Valencia</i> : 53-55.
5166 5167 5168	Bodí, M., V.N. Balfour and P. Pereira, 2011. Cendres: de l'oblit al cim de la investigació científica. Resultats de tres joves investigadors. <i>Mètode</i> , 70: 89-95.
5169 5170 5171 5172	Pereira, P., M.B. Bodi, X. Ubeda, A. Cerda, J. Mataix-Solera, V.N. Balfour and S.W. Woods, 2010. Las cenizas en el ecosistema suelo, En: Cerdà, A., Jordán, A. (Eds.) Actualización en métodos y técnicas para el estudio de los suelos afectados por incendos forestales. Cátedra de Divulgació de la ciència. <i>Feugo Red</i> : 349-402.
5173 5174 5175 5176 5177	Woods, S.W. and V.N. Balfour , 2010. The effects of soil texture and ash thickness on the post-fire hydrological response from ash-covered soils. <i>Journal of Hydrology</i> , 393: 274-286.
5177 5178 5179	Woods, S.W. and V.N. Balfour , 2008. The Effect of Ash on Runoff and Erosion after a Severe Forest Wildfire, Montana, U.S.A. <i>International Journal of Wildland Fire</i> , 17: 535-548.
5180 5181 5182	International and National Conference presentations (presenting author in bold)
5183 5184 5185 5186 5187 5188	Aug. 2013: American Geophysical Union (AGU) Chapman conference: Synthesizing Empirical Results to Improve Predictions of Post-wildfire Runoff and Erosion Response. Estes Park, CO. "The Evolution of Wildfire Ash and Implications for Post-fire Infiltration." (Oral- Balfour , V.N.).
5189 5190 5191 5192	May 2013: International Conference BioHydrology: "The impact of ash from wildfires on hydrological and biological processes." (Oral- S.H. Doerr , M. Bodí, C. Santin, V.N. Balfour, S.W. Woods, A. Cerda, J. Mataix-Solera and R. Shakesby).
5192 5193 5194	Dec. 2012: Fall Meeting of the American Geophysical Union (AGU): San Francisco, California. "Wildfire ash: its production and hydro-eco-geomorphic effects in forested

5195 5196 5197		landscapes" (Oral- S.H. Doerr , M. Bodi; C. Santin; V.N. Balfour; S.W. Woods; J. Mataix-Solera; A. Cerda and R. Shakesby).
5198 5199 5200 5201	April 2011	: Annual Congress of the European Geophysical Union (EGU): Vienna, Austria. "Characterizing the hydrological properties of Laboratory and wildfire ash from North America." (Oral- Balfour , V.N. and S.W. Woods).
5202 5203 5204	March 201	1: The 3 rd International Meeting of Fire Effects on Soil Properties (FESP): Guimaraes, Portugal. " <i>Characterizing the hydrological properties of wildfire ash.</i> " (Oral- Woods , S.W. and V.N. Balfour).
5205 5206 5207 5208 5209 5210	March 201	1: The 3 rd International Meeting of Fire Effects on Soil Properties (FESP): Guimaraes, Portugal. "Runoff rates, water erosion and water quality from soil covered with different types of ash." (Oral- Bodi , M.B, F.J. Leon Miranda, A. Cerda V.N. Balfour, J. Mataaix-Solera and S.H. Doerr).
5210 5211 5212 5213 5214	Dec. 2010:	Fall Meeting of the American Geophysical Union (AGU): San Francisco, California "Characterizing the hydrological properties of wildfire ash" (Poster- Balfour , V.N. and S.W. Woods).
5214 5215 5216 5217 5218	Oct. 2010:	Annual Meeting of the Montana Chapter of the American Water Resources Association (AWRA): Helena, Montana. "Physical and Hydrological properties of vegetative ash." (Oral- Balfour, V.N. and S.W. Woods).
5219 5220 5221 5222	Dec. 2009:	University of Swansea Conference: Swansea, Wales. "Physical and chemical alterations associated with the hydration of wildfire ash" (Poster-Balfour, V.N. and S.W. Woods).
5223 5224 5225 5226	Oct. 2009:	Annual Meeting of the Geological Society of America (AGU): Portland, Oregon. "Causes of variability in the effects of vegetative ash on post-fire runoff and erosion." (Poster- Balfour , V.N. and S.W. Woods).
5227 5228 5229 5230	July 2009:	International Conference of Geomorphology (ANZIAG): Melbourne Australia. "Causes of Variability in the Effects of Vegetative Ash on Post-Fire Runoff and Erosion." (Oral- Balfour, V.N. and S.W. Woods).
5231 5232 5233 5234	Feb. 2009:	Annual International Meeting of Fire Effects on Soil Properties (FESP): Barcelona, Spain. "Effect of vegetative ash on runoff and erosion after forest wildfire." (Oral-Woods, S.W. and V.N. Balfour).
5235 5236 5237 5238	Dec. 2008:	Fall Meeting of the American Geophysical Union (AGU): San Francisco, California "Causes of Variability in the Effects of Vegetative Ash on Post-Fire Runoff and Erosion." (Poster- Balfour , V.N. and S.W. Woods).

5239 5240 5241	"Physical and chemical characteristics of wildfire ash." (Poster- Balfour , V.N. and S.W. Woods).
5242	
5243	April 2008: Annual Congress of the European Geophysical Union (EGU): Vienna, Austria.
5244	"Vegetative Ash: an important factor in the short term response to rainfall in the
5245	post-fire environment." (Oral- Balfour, V.N. and S.W. Woods).