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Key Points:

- Surface erosion is a major loss pathway of PyC from burned mountain soils
- PyC is transported primarily with the low-density organic fraction of sediments
- PyC can accumulate for millennia in alluvial deposits of burned watersheds

Supporting Information:

- Supporting Information S1

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Redistribution of pyrogenic carbon from hillslopes to stream corridors following a large montane wildfire

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Abstract Pyrogenic carbon (PyC) constitutes a significant fraction of organic carbon in most soils. However, PyC soil stocks are generally smaller than what is expected from estimates of PyC produced from fire and decomposition losses, implying that other processes cause PyC loss from soils. Surface erosion has been previously suggested as one such process. To address this, following a large wildfire in the Rocky Mountains (CO, USA), we tracked PyC from the litter layer and soil, through eroded, suspended, and dissolved solids to alluvial deposits along riversides. We separated deposited sediment into high- and low-density fractions to identify preferential forms of PyC transport and quantified PyC in all samples and density fractions using benzene polycarboxylic acid markers. A few months after the fire, PyC had yet to move vertically into the mineral soil and remained in the organic layer or had been transported off site by rainfall driven overland flow. During major storm events PyC was associated with suspended sediments in river water and later identified in low-density riverbank deposits. Flows from an unusually long-duration and high magnitude rainstorm either removed or buried the riverbank sediments approximately 1 year after their deposition. We conclude that PyC redistributes after wildfire in patterns that are consistent with erosion and deposition of low-density sediments. A more complete understanding of PyC dynamics requires attention to the interaction of post fire precipitation patterns and geomorphological features that control surface erosion and deposition throughout the watershed.

1. Introduction

During wildfires up to 25% of the burned biomass carbon (C) can be converted by inefficient combustion to pyrogenic C (PyC) [Santin et al., 2015]. Globally, fires are estimated to generate between 114 and 379 Tg PyC per year, corresponding to approximately 0.2–0.6% of the annual terrestrial net primary production [Santin et al., 2016]. On average 348 Mha of land have burned worldwide every year between 1997 and 2011 [Giglio et al., 2013]. While the net overall trend in global burned area since 2000 has been a decrease of 1.2% year^{−1}, the frequency and intensity of wildfires are expected to change in the future, with some areas projected to increase while others will decrease, primarily as a result of changes in vegetation and weather due to climate change [Flannigan et al., 2009; Liu and Wimberly, 2016].

The combined long-term, high quality estimates of annual burned area at global and fine resolution scales [Giglio et al., 2013] have allowed for the estimation of PyC production and deposition on the soil surface after fire [e.g., Santin et al., 2016]. In a recent estimate of the global PyC cycle, soils were recognized as a major PyC pool, ranging between 54 and 109 Pg C [Bird et al., 2015]. However, PyC soil stocks, predicted on the basis of production rate and expected mean residence time, exceed the PyC amounts measured in soils [Czimczik and Masiello, 2007]. Previous studies have proposed different mechanisms to account for this discrepancy [Czimczik and Masiello, 2007; Knicker, 2011], but they remain untested. Recent experiments demonstrated that PyC is more reactive than initially thought and is potentially susceptible to microbial degradation [Singh et al., 2013; Soong and Cotrufo, 2015]. Yet even accounting for partial degradation by microorganisms, and

including new estimates of PyC mean residence time, which range between centuries and millennia [Singh *et al.*, 2012], the difference between predicted and observed soil PyC concentrations still cannot be accounted for.

Both wind and water erosion can be dominant mechanisms for transporting PyC from the site of a wildfire to terrestrial and marine deposits outside of the burned area [Thevenon *et al.*, 2010]. In particular, water-driven surface erosion has been suggested as a major pathway for loss of soil PyC after a fire [Rumpel *et al.*, 2009]. After fires, surface erosion rates usually increase substantially due to reduced ground cover and enhanced overland flow [Shakesby and Doerr, 2006]. Eroded sediments are transported away from their source area and may be deposited on hillslopes or within stream corridors [Bodí *et al.*, 2014], forming intermediate storage pools of PyC. The supply of sediment downstream can be difficult to track, as it is punctuated in time, and depends primarily on the sequence of episodic rainfall events that trigger sediment movement after a fire [Benda *et al.*, 2003]. The timing and sequence of rainstorms in the first 2 years after a fire have a disproportionate effect on sediment transport and deposition patterns [Elliott and Parker, 2001], because erosion rates typically recover to near prefire levels within 3–4 years after burning [Benavides-Solorio and MacDonald, 2005; Shakesby and Doerr, 2006]. Thus, frequency, location, and intensity of rainfall in the first 2 years after a fire are the principal drivers of post fire sediment transport and therefore may represent a major pathway for movement and redistribution of PyC in the landscape.

PyC that does not leave the watershed during sediment transport events may be effectively stored in an intermediate sediment pool, before being delivered to the marine environment where the largest and longest term storage pool for PyC exists [Bird *et al.*, 2015]. Intermediate PyC pools can have residence times between years and millennia [Marin-Spiotta *et al.*, 2014]. Continuous leaching from these sediment deposits during infiltration and recharge events may also result in continuous export of PyC from the watershed in the dissolved phase. This long-term leaching of PyC from intermediate deposits has been illustrated in the Amazon River basin where low levels of PyC in the dissolved phase were present decades after burning [Dittmar *et al.*, 2012]. This continuous background export may be a universal feature of the PyC cycle [Jaffe *et al.*, 2013]. Controls on the distribution and size of intermediate PyC deposits as well as our understanding of sediment transport as a mechanism for PyC redistribution remain poorly understood.

The overall goal of our study was to (1) quantify PyC concentrations within the Cache la Poudre (CLP) watershed following the 2012 High Park Fire (HPF) across different environmental matrices (soil organic layer, mineral soil, suspended and dissolved solids in river waters, riverbank sediments, and alluvial deposits) and (2) identify major PyC transport pathways over time after fire. We hypothesized that because PyC is a low-density material, it is mobilized by overland flow and tracked in the low-density fraction of sequential sedimentary pools. We thus expected the amount and intensity of rainfall and snowmelt to be important drivers of PyC movement within the watershed.

2. Material and Methods

2.1. Study Site

This study was conducted in the CLP watershed northern Colorado Front Range, USA. The forested upper portion of the CLP watershed drains 2700 km², with elevations ranging from 1590 to 4125 m, and slopes ranging from 0 to 67%. Mean annual precipitation ranges from about 400 mm at the lower elevations to 1350 mm in the headwaters [Richter, 2009]. Runoff in the main stem of the CLP is snowmelt dominated, with most of the river flow coming from the highest elevations in the watershed (>2900 m) [Kampf and Richer, 2014]. Snowmelt runoff begins in April and May, and river flow typically peaks in early June.

From 9 June 2012 to 1 July 2012, the HPF burned 350 km² of forested and scrublands within and adjacent to the CLP watershed. About 60% of the burned area was of moderate to high severity [Stone, 2015], and the burn affected mostly steep terrain with mean slopes of 19%. Convective rainstorms during summer 2012 produced elevated runoff and erosion from the burned areas. Snowmelt runoff in the following spring produced very little hillslope erosion [Schmeer, 2014] but did transport some of the deposited sediment out of channel corridors [Brogan *et al.*, 2015]. Hillslope erosion continued during summer 2013 rainstorms, and a large (>200 mm) rain event in September 2013 affected the entire study region, producing substantial channel change and sediment loading to the CLP main stem [Kampf *et al.*, 2016].

2.2. Sample Description

Soils and sediments ($n = 102$) sampled during the course of this study are from a variety of matrices and locations within the burned area of the CLP (Figure S1 in the supporting information). These samples reflect a transdisciplinary collaborative effort, with the common goal of addressing post fire ecosystem and geomorphologic dynamics. PyC data came from the soil organic layer (including litter), mineral soil, snowmelt, rainstorm and base flow driven suspended (TSS) and dissolved (TDS) solids in river water, eroded and riverbank sediments and alluvial deposits.

To assess initial post fire PyC pools, soil organic layer (including litter, $n = 24$) and mineral soil samples ($n = 48$) were collected in fall 2012, approximately 4 months postfire, in ponderosa pine (*Pinus ponderosa*) forests in severely and moderately burned areas (Figure S1) [Boot *et al.*, 2015]. All samples were collected from within a 20 by 20 cm frame, with GPS coordinates recorded. After sampling of the organic layer, the mineral soil was excavated by a hand shovel into 0–5 cm and a 5–15 cm discrete depth samples. At each site, four additional organic layer samples and three surface (0–5 cm) mineral soil samples were collected, positioning the frame orthogonally to a distance of 2.5 m from the original position, to obtain a representative sample given the high potential for spatial variability. All samples were pooled by plot, dried, and pulverized for benzene polycarboxylic acid (BPCA) analyses, as described below.

To track movement of PyC concurrent with episodic rain events, sediments eroded from hillslopes were collected in sediment collection fences constructed in fall 2012. Fences made of rebar and landscape fabric were installed along the central axes of convergent hillslopes (Figure S1) [Schmeer, 2014]. During rainstorms, sediment transported by overland flow was trapped behind the fence. Deposited sediment was manually excavated from the fences. Samples from four of the sediment fence locations collected over six dates were examined (two sediment fences sampled on two dates and two fences sampled on a single date, $n = 6$). Three of the samples representing the earliest and latest collection dates were selected to represent eroded sediment samples and were further separated into a low-density (LD; $< 1.85 \text{ g cm}^{-3}$) and a high-density (HD; $> 1.85 \text{ g cm}^{-3}$) fraction, by density fractionation [Sollins *et al.*, 2006] in order to trace the contribution of PyC from the organic or mineral soil. For the density fractionation, 5 g of sample was combined with 25 mL of 1.85 g cm^{-3} sodium polytungstate and shaken for 20 min to disrupt aggregates. Samples were then centrifuged and the LD fraction was floated off and filtered through a 25 μm filter and rinsed. The HD fraction was rinsed three times to remove remaining sodium polytungstate and both fractions were dried at 60°C. All bulk sediment samples, plus the HD and LD fractions which on average comprised 75% and 25% of the bulk sediment mass, respectively, were run for BPCA analyses.

To further track deposition of mobilized PyC we also collected sediment cores from depositional areas (generally point bars on the inside of river bends) along the CLP river from December 2012 to May 2013. Because these sediments were collected near the banks of the river, we refer to them as “riverbank sediments.” The nine sampling locations varied in length from 9 m to 60 m. At each location a grid was set up to randomly position sampling cores. Grid cells varied from 0.5 m to 5 m depending on the length of the sampling site, and two to five grid cells were sampled from each of the four quadrants: upstream, downstream, proximate to and distal from the river. A 5.4 cm inner diameter corer fitted with plastic sleeves was used to sample to a depth of 30 cm (often corresponding to the maximum depth of deposits). The samples were stored in the plastic sleeves at 4°C, until partitioned by slicing into visibly discrete layers made up of coarse organic material ($n = 48$), light mineral sediments ($n = 52$), and dark mineral sediment ($n = 53$). All samples were air dried after separation, sieved through a 2 mm mesh screen, and subsampled to obtain one composite coarse organic, one light mineral, and one dark mineral sample. Three subsamples (analytical replicates) from each of these three composite samples were run for BPCA content. In order to avoid pseudoreplication within the statistical analyses, the three analytical replicates from the composite samples were averaged for a single value, and the light mineral and dark mineral averaged composite values were binned as “riverbank mineral” sediments ($n = 2$). Because the initial test of the composite layer values suggested most of the PyC was present in the coarse organic fraction, coarse organic layers from an additional seven grids across two riverbanks were selected for BPCA analyses (total riverbank coarse organic $n = 8$). Additionally, the composite coarse organic, light mineral and dark mineral samples were separated by density fractionation, as described above into an HD and an LD, and the LD samples were analyzed for their BPCA content ($n = 3$).

Finally, during the summer 2013 water samples were collected at nine sites along the main stem of the CLP River (Figure S1), on six dates (5 and 9 May, 8 and 25 June, and 11 and 23 July). Water was collected in duplicate sets of 1 L acid-washed, triple-rinsed bottles. We concentrated total dissolved solids (TDS, $n = 54$) from a 1 L sample on each date using solid phase extraction on a modified styrene divinyl benzene polymer-type sorbant cartridges eluted with methanol [Dittmar *et al.*, 2008]. On two dates, 25 June and 11 July, the duplicate liter was used to collect base flow total suspended solids (TSS; $n = 18$) on precombusted glass fiber filters. Dried methanol extracts from the concentrated base flow and the glass fiber filters with the base flow suspended solids were used as matrices for the quantification of BPCA in TDS and TSS, respectively. Also during 2013, snowmelt and rainstorm driven TSS samples were collected at sites on the South Fork of the CLP River directly downstream of burned tributaries (Figure S1). Each sample was approximately 300 mL in volume and was collected using a DH-48 depth-integrating sampler (FISP, 2000) or an ISCO automated water sampler. Total volume was measured to the nearest 5 mL using a graduated cylinder and sediment mass was determined by filtering samples through preprocessed, preweighed glass fiber filters with a pore size of 150 μm . From the collected sediment samples, a subset was selected for PyC determination, based on when they were collected (snowmelt or during rainstorms), and the amount of material available for processing (at least 10 mg of sediment was required for PyC analysis). BPCA content was determined for two samples from the snowmelt period (15 and 24 May 2013) and three samples collected during rainstorms (13 July and 9 and 30 August 2013). This allowed us to understand which fraction of the water column PyC was being transported, in both the smaller catchments and the main stem of the CLP.

We also compared HPF samples to previous fires by sampling buried charcoal layers in alluvial fans for BPCA analyses. The dark layers in alluvial deposits ($n = 5$) were collected from exposed bank stratigraphic layers that were scoured during the September 2013 flood (Figure S1). Layers were collected using a knife or trowel. To determine PyC age, these alluvial deposit samples were radiocarbon dated using accelerator mass spectrometry following microscope-guided isolation of charcoal from the soil samples. All sample preparation including selection of charcoal particles, combustion to CO_2 , reduction to graphite, and ^{14}C measurements were performed at Direct AMS, Seattle, WA. All results have been corrected for isotopic fractionation with $\delta^{13}\text{C}$ values measured on the prepared graphite using the AMS spectrometer.

2.3. Benzene Polycarboxylic Acids

The PyC fraction of soils, sediments, alluvial deposits, and dissolved and suspended sediments in river waters was estimated using the BPCA method [Wiedemeier *et al.*, 2013] and is reported as BPCA-C. BPCAs are markers of PyC, with PyC yield varying between matrices, from 44% for sediments, 23% and 25% for organic and mineral soils, respectively, to 14% for alluvial deposits, mostly due to differences in aromatic condensation [Cotrufo *et al.*, 2016].

BPCA analysis was conducted on all samples using high performance liquid chromatography (HPLC) equipped with a photodiode array detector [Wiedemeier *et al.*, 2013]. For all matrices, 50–150 mg of finely ground, oven-dried sample was oxidized in nitric acid, purified with cation exchange resin, and concentrated and analyzed via HPLC using a five-point calibration of BPCA standards, as described in Boot *et al.* [2015]. We used BPCA values on a per mass basis to compare among different matrices. This eliminates additional error that could arise from measuring C content in charred materials. Because the conversion factors to convert BPCA-C to PyC is matrix dependent (e.g., soil, and sediments), and possibly a function of the degree of PyC aromatic condensation [Cotrufo *et al.*, 2016; Wiedemeier *et al.*, 2013], here we report all values in terms of BPCA-C concentrations.

2.4. Data Analyses

Analysis of variance (ANOVA) was used to compare means among BPCA-C g kg^{-1} dry mass values (soil organic layer, mineral soils, eroded, suspended and dissolved solids, and riverbank and alluvial sediment deposits, as well as in associated low- and high-density fractions) using JMP 12.0. Data were checked for assumptions of normality and equal variance and when necessary log transformed (dark alluvial deposits, eroded sediment, and soils). Post hoc comparisons of means were performed with Tukey's HSD test.

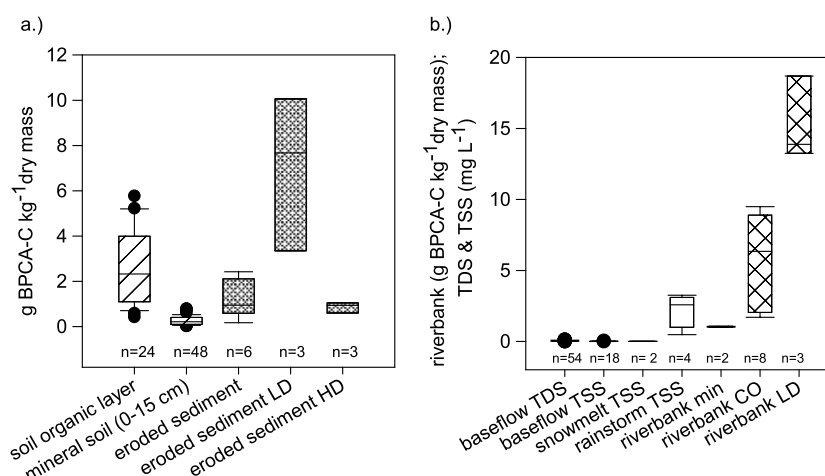


Figure 1. Pyrogenic Carbon as detected by benzene polycarboxylic acids (BPCA-C) in: (a) the soil organic layer, mineral soil, and eroded hillslope sediments, including their low-density (LD) and high-density (HD) fraction and in: (b) total dissolved solids (TDS), total suspended solids (TSS) during periods of base flow, snowmelt and rainstorms, in the mineral (min), coarse organic (CO), and LD fraction of recent alluvial deposits, collected in the Cache la Poudre watershed after the High Park Fire. Data illustrate elevated concentrations of BPCA-C, as marker of PyC, in the forest floor and LD fraction of eroded sediment and alluvial deposits, as well as in the rainstorm driven TSS.

3. Results and Discussion

3.1. PyC in Soils and Eroded Sediments

Analysis of the soil organic layer, including litter, of ponderosa pine stands burned during the HPF revealed that they held much higher and more variable BPCA-C content than respective mineral soils (Figure 1). Across all study sites mineral soils in burned stands had relatively low BPCA-C content, which did not differ significantly from that of mineral soils in unburned stands [Boot *et al.*, 2015]. The BPCA-C content of the organic layer in burned stands was similar to the BPCA-C content of the LD fraction of eroded sediments, while the HD fraction of those sediments had comparable BPCA-C content to the mineral soils (Table S1 and Figure 1). The similar concentration of BPCA-C content between the soil organic layer values and the LD eroded sediment suggests that PyC in surface runoff mostly originated from the soil organic layer. This is consistent with the idea from a previous controlled study that PyC moves preferentially in the LD fraction of eroded sediments [Rumpel *et al.*, 2009]. The transport of PyC in surface runoff observed in the CLP watershed would explain the relatively low PyC content of these soils (Figure 1) and point to surface runoff as a significant export mechanism for PyC following a fire.

In 2013, the mean erosion rate in the CLP watershed was 11 Mg/ha [Kampf *et al.*, 2016]. Using the BPCA-C concentration of LD sediments (Figure 1) this converts to a surface BPCA-C erosion rate of 20 kg/ha. This corresponds to an estimated 11% export of the organic layer BPCA-C stock that was present after the fire in fall 2012 [Boot *et al.*, 2015]. This surface erosion rate is in general agreement with a previous controlled experiment [Rumpel *et al.*, 2009], where surface runoff was estimated to be responsible for the export of 7 to 29% of the PyC initially added to the soil. In that study the amount and intensity of rainfall were suggested to be extremely important in determining the fate of PyC, with low intensity rainfall being infiltrated in the soil and more intense rain events stimulating surface runoff consistent with our understanding of post fire surface erosion [Benavides-Solorio and MacDonald, 2005; Wagenbrenner *et al.*, 2006]. Surface runoff may be higher at sites with steep slopes as in the Rumpel *et al.* [2009] study, but slope did not affect the BPCA-C content of the mineral soils of Ponderosa pine stands in this watershed [Boot *et al.*, 2015] nor was slope an important control on hillslope erosion for the range of slopes with sediment fences [Schmeer, 2014].

3.2. PyC in River Water

In this study we observed high values of PyC associated with the TSS of river water during 2013 rainstorms, whereas TSS and TDS collected during base flow consistently contained low amounts of PyC (Figures 1 and 2 and Table S1), with flux rate ranging from 0.004 mg BPCA-C/h to 322 mg BPCA-C/h TSS, for base flow and

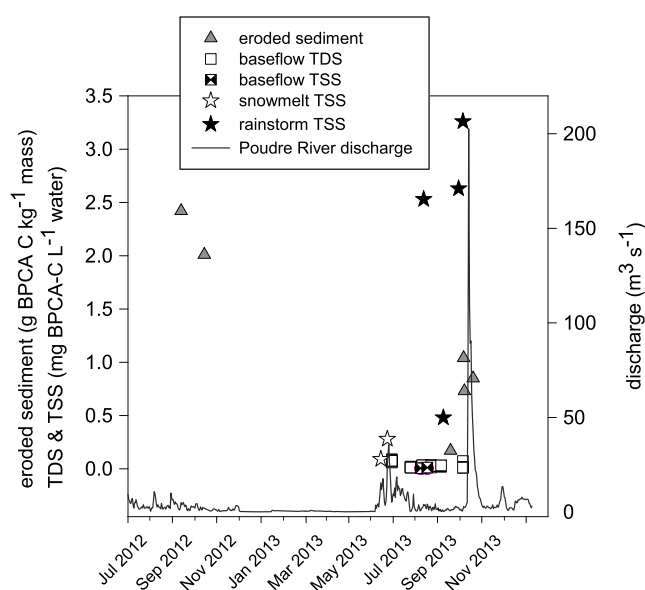


Figure 2. Pyrogenic carbon as detected by benzene polycarboxylic acids (BPCA-C) in eroded sediment and river water (base flow total dissolved solids (TDS), total suspended solids (TSS), and snowmelt and rainstorm driven TSS), sampled over time at different values of river discharge, illustrating rainstorm driven movement of BPCA-C in TSS with low contributions from baseline and snowmelt TSS.

peak events, respectively (Table S2). Other postfire measurements in the CLP watershed also showed low PyC content in the dissolved phase [Wagner *et al.*, 2015]. This suggests that postfire PyC is preferentially mobilized as compared to other soil organic carbon forms during moderate and high intensity rainstorms because of its LD structure [Downie *et al.*, 2009] and deposition on the soil surface following a fire [Boot *et al.*, 2015]. If PyC is not removed directly following a fire, it has the potential to infiltrate into the deeper soil and become an integral component of soil organic matter (SOM), bonding to minerals or forming aggregates [Herath *et al.*, 2013; Singh *et al.*, 2015; Soong and Cotrufo, 2015], thus decreasing the probability it will be mobilized in the LD phase. Once PyC is part of the SOM complex, it has the potential to provide a consistent, spatially distributed source of dissolved PyC to surface waters. This is consistent with reports that dissolved

PyC in major world rivers is about 10% of the dissolved organic carbon, suggesting a mechanistic coupling of PyC and SOM mobilization [Jaffe *et al.*, 2013] into the dissolved phase by infiltration and leaching. However, it may take a long time for PyC to increase and become a substantial part of the SOM pool in areas that experience intense and frequent fires followed by moderate or high intensity rainstorms, as these storms will induce high PyC losses by overland runoff following burning. This conceptual model of PyC movement is consistent with known values of surface water PyC in areas that have not experienced recent burns. For example, a long history of slash-and-burn clearing of the Atlantic forest in Brazil resulted in massive runoff of PyC into the drainage basin of the Paraíba do Sul River. However, low levels of PyC have continued to leach into the Paraíba do Sul River from the PyOM-SOM pool in the dissolved phase for decades after the slash and burn practices had ceased [Dittmar *et al.*, 2012].

3.3. PyC in Riverbank Deposits

For PyC to reach banks of large rivers, it must be transported from hillslopes through channel networks. Previous postfire studies have found high transport of ash and LD sediment in the first year after burning [Reneau *et al.*, 2007]. In the HPF, pulses of rain right after the fire in 2012 rapidly eroded substantial amounts of sediment from the hillslopes into the channels. Some of these sediments were deposited within tributary channels, which experienced net aggradation over the summer, and some sediment reached the main stem of the CLP River where it was either transported further downstream or formed alluvial deposits in the channel or along the riverbanks. A few months postfire, some of these alluvial deposits had up to 30 cm of lighter or darker colored mineral and coarse organic sediments, often deposited in distinct layers. The BPCA analyses of those riverbank deposits revealed that coarse organic sediments had the highest concentration of PyC, and within the sediments the LD fraction again was particularly enriched in PyC (Figure 1b and Table S1).

3.4. Alluvial PyC Sediment Deposits

The alluvial PyC sediment deposits from previous fires found in the CLP watershed (Figure S1) had concentrations of BPCAs ranging from 1.3 to 41.9 g BPCA-C per kg of deposit (Figure 3). For the three deposits found within Hill and Skin Gulch (Figure S1) watersheds, BPCA-C concentrations increased with the increasing ^{14}C age of the deposits (Figure 3), suggesting preferential preservation of PyC over other forms of organic matter. However, relatively lower BPCA-C concentrations were found in the alluvial deposit at Rocky Top (sampling

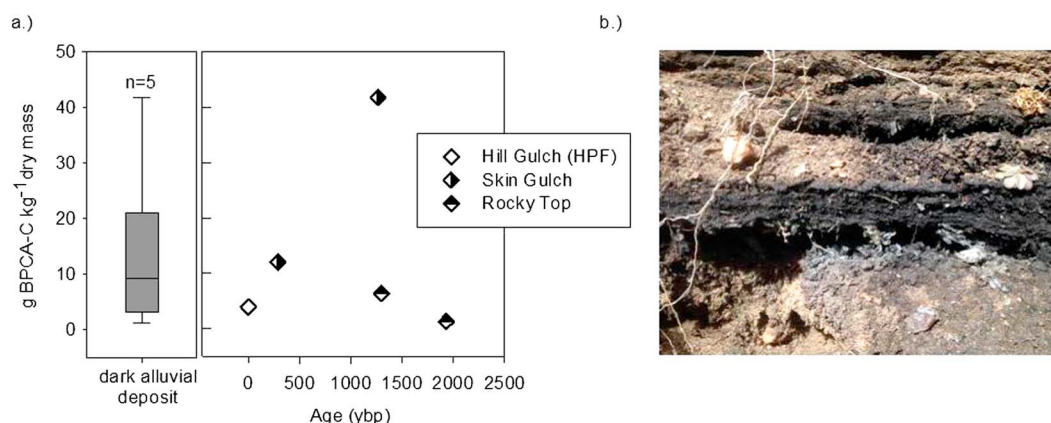


Figure 3. (a) Pyrogenic carbon as detected by benzene polycarboxylic acids (BPCA-C) in dark alluvial deposits spans a broad range of concentrations and ¹⁴C ages. (b) Photo illustrating one of the Rocky Top dark alluvial deposits.

location in Figure S1, result in Figure 3), possibly as the result of a much less intense fire. The long-term persistence (often exceeding 1000 years) of these alluvial deposits, as shown by their ¹⁴C age (Figure 3), confirms that pools of buried PyC in alluvial deposits may be an important component of the global terrestrial PyC budget [Bird *et al.*, 2015]. Because the sediment delivery ratio (i.e., the ratio of sediment delivered downstream to sediment eroded) tends to decrease with drainage area, alluvial deposits are more likely found downslope/downstream in higher order channels [Moody and Martin, 2009] and in other depositional areas such as alluvial fans [Benda *et al.*, 2003]. Sediments deposited within active channels, such as those within the CLP River in 2012, are less likely to be preserved than those on floodplains or alluvial fans, where sediment deposited after fire can be preserved for thousands of years [Elliott and Parker, 2001] and are presumably rich in PyC.

4. Conclusions

In this study, we examined PyC dynamics across landscapes within a single watershed. Specifically, we measured PyC concentrations (1) where it was generated and deposited following the HPF and (2) at multiple points during its transport within the CLP watershed. PyC moved primarily in the form of LD organic matter as a result of overland flow from higher intensity rainstorms. Its movement from the hillslopes through the tributary watersheds and in the CLP River was controlled by the magnitude and spatial extent of the rainstorms (Figure 2). These results suggest that models that represent post fire PyC dynamics should link PyC transport to precipitation patterns, overland flow, and the transport and deposition of the LD organic sediment fraction.

Furthermore, this study demonstrates that an important component of the fate of PyC on land is the potential to accumulate in alluvial deposits. Alluvial deposits in tributary watersheds contained significant amounts of PyC that were over a thousand years old (Figure 3). Features such as alluvial fans, floodplains, and terraces (abandoned floodplains) may facilitate this long-term terrestrial storage of PyC. This study illustrates how the intensity and timing of precipitation events as they interact with hillslope and channel geomorphology are principal controls in promoting the formation of long-term PyC deposits within watersheds and along fluvial (channel) networks. Once deposited, pools of PyC within the landscape may provide a consistent background source of PyC to the dissolved phase of surface waters for decades to centuries to come. Thus, the previously noted lack of coherence between PyC production rates and concentrations in soils may in part be explained by heterogeneity of PyC in the landscape created by hydrological and geomorphological controls on sediment transport and deposition.

References

- Benavides-Solorio, J., and L. H. MacDonald (2005), Measurement and prediction of post-fire erosion at the hillslope scale, Colorado Front Range, *Int. J. Wildland Fire*, 14, 1–18.
- Benda, L., D. Miller, P. Bigelow, and K. Andras (2003), Effects of post-wildfire erosion on channel environments, Boise River, Idaho, *For. Ecol. Manage.*, 178(1), 105–119.

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- Bird, M. I., J. G. Wynn, G. Saiz, C. M. Wurster, and A. McBeath (2015), The pyrogenic carbon cycle, *Annu. Rev. Earth Planet. Sci.*, 43(1).
- Bodí, M. B., D. A. Martin, V. N. Balfour, C. Santin, S. H. Doerr, P. Pereira, A. Cerdà, and J. Mataix-Solera (2014), Wildland fire ash: Production, composition and eco-hydro-geomorphic effects, *Earth Sci. Rev.*, 130, 103–127.
- Boot, C., M. Haddix, K. Paustian, and M. F. Cotrufo (2015), Distribution of black carbon in Ponderosa pine litter and soils following the High Park wildfire, *Biogeosciences*, 12, 3029–3039.
- Brogan, D. J., P. A. Nelson, and L. H. MacDonald (2015), Quantifying erosion and deposition patterns using airborne LiDAR following the 2012 High Park Fire and 2013 Colorado Flood, Abstract EP51B-0911 presented at 2015 Fall Meeting, AGU, San Francisco, Calif., 14–18 Dec.
- Cotrufo, M. F., C. Boot, S. Abiven, E. J. Foster, M. L. Haddix, M. Peisser, C. M. Wurster, M. I. Bird, and M. W. I. Schmidt (2016), Quantification of pyrogenic carbon in the environment: An integration of analytical approaches, *Org. Geochem.*, doi:10.1016/j.orggeochem.2016.07.007.
- Czimczik, C. I., and C. A. Masiello (2007), Controls on black carbon storage in soils, *Global Biogeochem. Cycles*, 21, GB3005, doi:10.1029/2006GB002798.
- Dittmar, T., C. E. de Rezende, M. Manecki, J. Niggemann, A. R. C. Ovalle, A. Stubbins, and M. C. Bernardes (2012), Continuous flux of dissolved black carbon from a vanished tropical forest biome, *Nat. Geosci.*, 5(9), 618–622.
- Dittmar, T., B. Koch, N. Hertkorn, and G. Kattner (2008), A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater, *Limnol. Oceanogr. Methods*, 6(6), 230–235.
- Downie, A., A. Crosky, and P. Munroe (2009), Physical properties of biochar, in *Biochar for Environmental Management. Science and Technology*, edited by J. Lehmann and S. Joseph, pp. 13–32, Earthscan, London.
- Elliott, J. G., and R. Parker (2001), Developing a post-fire flood chronology and recurrence probability from alluvial stratigraphy in the Buffalo Creek watershed, Colorado, USA, *Hydrol. Processes*, 15(15), 3039–3051.
- Flannigan, M. D., M. A. Krawchuk, W. J. de Groot, B. M. Wotton, and L. M. Gowman (2009), Implications of changing climate for global wildland fire, *Int. J. Wildland Fire*, 18, 483–507.
- Giglio, L., J. T. Randerson, and G. R. Werf (2013), Analysis of daily, monthly, and annual burned area using the fourth-generation global fire emissions database (GFED4), *J. Geophys. Res. Biogeosciences*, 118, 317–328, doi:10.1002/jgrg.20042.
- Herath, H., M. Camps-Arbestain, and M. Hedley (2013), Effect of biochar on soil physical properties in two contrasting soils: An Alfisol and an Andisol, *Geoderma*, 209, 188–197.
- Jaffe, R., Y. Ding, J. Niggemann, A. V. Vahatalo, A. Stubbins, R. G. M. Spencer, J. Campbell, and T. Dittmar (2013), Global charcoal mobilization from soils via dissolution and riverine transport to the oceans, *Science*, 340(6130), 345–347, doi:10.1126/science.1231476.
- Kampf, S. K., and E. E. Richer (2014), Estimating source regions for snowmelt runoff in a Rocky Mountain basin: Tests of a data-based conceptual modeling approach, *Hydrol. Processes*, 28(4), 2237–2250.
- Kampf, S. K., D. J. Brogan, S. Schmeer, L. H. MacDonalds, and P. A. Nelson (2016), How do geomorphic effects of rainfall vary with storm type and spatial scale in a post-fire landscape?, *Geomorphology*, 273, 39–51.
- Knicker, H. (2011), Pyrogenic organic matter in soil: Its origin and occurrence, its chemistry and survival in soil environments, *Quat. Int.*, 243(2), 251–263, doi:10.1016/j.quaint.2011.02.037.
- Liu, Z., and M. C. Wimberly (2016), Direct and indirect effects of climate change on projected future fire regimes in the western United States, *Sci. Total Environ.*, 542, 65–75.
- Marin-Spiotta, E., N. T. Chaopricha, A. F. Plante, A. F. Diefendorf, C. W. Mueller, A. S. Grandy, and J. A. Mason (2014), Long-term stabilization of deep soil carbon by fire and burial during early Holocene climate change, *Nat. Geosci.*, 7, 428–432.
- Moody, J. A., and D. A. Martin (2009), Forest fire effects on geomorphic processes, in *Fire Effects on Soils and Restoration Strategies*, edited by A. Cerdà and P. R. Robichaud, pp. 41–79, CRC Press, Boca Raton, Fla.
- Reneau, S. L., D. Katzman, G. A. Kuyumjian, A. Lavine, and D. V. Malmom (2007), Sediment delivery after a wildfire, *Geology*, 35(2), 151–154.
- Rumpel, C., A. Ba, F. Darboux, V. Chaplot, and O. Planchon (2009), Erosion budget and process selectivity of black carbon at meter scale, *Geoderma*, 154(1), 131–137.
- Richer, E. E. (2009), Snowmelt runoff analysis and modeling for the Upper Cache la Poudre River Basin, Colorado, Colorado State Univ., Fort Collins.
- Santin, C., S. H. Doerr, E. Kane, C. Masiello, M. Ohlson, J. M. de la Rosa, C. M. Preston, and T. Dittmar (2016), Towards a global assessment of pyrogenic carbon from vegetation fires, *Global Change Biol.*, 22, 76–91.
- Santin, C., S. H. Doerr, C. M. Preston, and G. Gonzalez-Rodriguez (2015), Pyrogenic organic matter production from wildfires: A missing sink in the global carbon cycle, *Global Change Biol.*, 21, 1621–1633, doi:10.1111/gcb.12800.
- Schmeer, S. R. (2014), *Post-fire Erosion Response and Recovery, High Park Fire*, Colorado, Colorado State Univ., Fort Collins.
- Shakesby, R., and S. Doerr (2006), Wildfire as a hydrological and geomorphological agent, *Earth Sci. Rev.*, 74(3), 269–307.
- Singh, B. P., Y. Fang, M. Boersma, D. Collins, L. Van Zwieten, and L. M. Macdonald (2015), In situ persistence and migration of biochar carbon and its impact on native carbon emission in contrasting soils under managed temperate pastures, *PLoS One*, 10(10e0141560).
- Singh, N., S. Abiven, B. Maestrini, J. A. Bird, M. S. Torn, and M. W. I. Schmidt (2013), Transformation and stabilization of pyrogenic organic matter in a temperate forest field experiment, *Global Change Biol.*, doi:10.1111/gcb.12459.
- Singh, N., S. Abiven, M. S. Torn, and M. W. I. Schmidt (2012), Fire-derived organic carbon in soil turns over on a centennial scale, *Biogeosciences*, 9(8), 2847–2857, doi:10.5194/bg-9-2847-2012.
- Sollins, P., C. Swanston, M. Kleber, T. Filley, M. Kramer, S. Crow, B. A. Caldwell, K. Lajtha, and R. Bowden (2006), Organic C and N stabilization in a forest soil: Evidence from sequential density fractionation, *Soil Biol. Biochem.*, 38(11), 3313–3324, doi:10.1016/j.soilbio.2006.04.014.
- Soong, J., and M. F. Cotrufo (2015), Annual burning of a tallgrass prairie inhibits C and N cycling in soil, increasing recalcitrant pyrogenic organic matter storage while reducing N availability, *Global Change Biol.*, 21, 2321–2333, doi:10.1111/gcb.12832.
- Stone, B. H. (2015), *Mapping Burn Severity, Pine Beetle Infestation, and their Interaction at the High Park Fire*, M.S. thesis, Graduate Degree Program in Ecology, Colorado State Univ. Libraries, Fort Collins.
- Thevenon, F., D. Williamson, E. Bard, F. S. Anselmetti, L. Beaufort, and H. Cachier (2010), Combining charcoal and elemental black carbon analysis in sedimentary archives: Implications for past fire regimes, the pyrogenic carbon cycle, and the human–climate interactions, *Global Planet. Change*, 72(4), 381–389.
- Wagenbrenner, J. W., L. H. MacDonald, and D. Rough (2006), Effectiveness of three post-fire rehabilitation treatments in the Colorado Front Range, *Hydrol. Processes*, 20, 2989–3006.
- Wagner, S., K. M. Cawley, F. L. Rosario-Ortiz, and R. Jaffe (2015), In-stream sources and links between particulate and dissolved black carbon following a wildfire, *Biogeochemical*, doi:10.1007/s10533-015-0088-1.
- Wiedemeier, D. B., M. D. Hilf, R. H. Smittenberg, S. G. Haberle, and M. W. I. Schmidt (2013), Improved assessment of pyrogenic carbon quantity and quality in environmental samples by high-performance liquid chromatography, *J. Chromatogr. A*, 1304, 246–250, doi:10.1016/j.chroma.2013.06.012.