Title: Adsorption capacity of wildfire-produced charcoal from Pacific Northwest forests

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1. Introduction

Naturally ignited wildfires are a major driver of forest ecosystem disturbance that are reported in the paleoecological record as fossilized charcoal and pollen since the Devonian era (Glasspool et al., 2006; Scott, 2000). Forest fires are responsible for tree mortality, combustion of organic matter horizon (OM) on the forest floor, loss of mineral soil where high intensity convection and erosion transport particles, and stimulation of nutrient transformations (Agee, 1993; Bormann et al., 2008; DeLuca and Sala, 2006). Charcoal, a byproduct of incomplete combustion of OM and woody debris, is one of the few lasting legacies of wildfires (DeLuca and Aplet, 2008; Preston and Schmidt, 2006). This high-carbon (C) and low-nitrogen (N) residue exhibits a number of physical and chemical properties that may alter soil nutrient cycling in acidic forest soils, such as providing micro- and macro-pores (Braidá et al., 2003; Jaafar et al., 2015; Wildman and Derbyshire, 1991), stimulating net and gross nitrification (DeLuca et al., 2006; DeLuca et al., 2002; Gundale and DeLuca, 2006b) and altering soil solution chemistry via adsorption of organic compounds (Cornelissen et al., 2004; Gundale and DeLuca, 2007; Keech et

al., 2005). Dissolved OM incorporated in forest soils from throughfall represents a significant source of C, N, and phosphorus, as well as organic compounds with the potential to alter soil solution chemistry and nutrient cycling (Kalbitz and Kaiser, 2008; Qualls and Haines, 1991). Charcoal can provide a functional and active component of nutrient cycling in wildfire-affected systems (DeLuca and Sala, 2006; MacKenzie and DeLuca, 2006) where OM inputs are low and surface-horizon bacterial and fungal activity is reduced (Dooley and Treseder, 2012; Hart et al., 2005).

The ability for charcoal particles, as well as other pyrogenic C molecules such as biochar and activated carbon, to adsorb non-polar, organic molecules is a fundamental mechanism that may alter soil solution chemistry (Bormann et al., 2008; Brimmer, 2006; Cornelissen et al., 2004; Keech et al., 2005; Zackrisson et al., 1996) and nutrient cycling of forest soils (Berglund et al., 2004; DeLuca et al., 2006). Wildfire-produced charcoal contains aromatic C rings, aliphatic C structures from residual volatiles and ash, and various sized pores and cracks – the fractions of these attributes dictate physical structure and chemical composition (Gundale and DeLuca, 2006a; Preston and Schmidt, 2006; Zackrisson et al., 1996). Charcoal is a less graphitic, amorphous constituent of the BC continuum model, which describes physical and chemical attributes of pyrogenic C materials along a temperature gradient (Hedges et al., 2000).

Although many environmental conditions alter the physical and chemical characteristics of charcoal during the thermal degradation process, such as heating ramp and the presence of water, the oxidation temperature provides the greatest source of variation in residual charcoal particles (Gundale and DeLuca, 2006a; Lua et al., 2004; Manyà, 2012). Wildfire temperatures are spatially and temporally variable, which would theoretically result in a similarly large range in the surface area and adsorption capacity of charcoal deposited during fire events; however,

there are few studies of wildfire-induced physical and chemical variability on adsorption behavior or capacity (Brimmer, 2006; Gundale and DeLuca, 2006a; Zackrisson et al., 1996). Surface soil wildfire temperatures in temperate forests typically range between 400 °C and 600 °C although conditions directly under smoldering coarse woody debris can exceed 700 °C (Bormann et al., 2008; Monsanto and Agee, 2008; Neary et al., 2005). The adsorption capacity of charcoal increases asymptotically with formation temperature as graphite-like layers of aromatic double- and single-bonded covalent C molecules condense, which increases surface area and hydrophobic interactions (Cornelissen et al., 2004; Keiluweit and Kleber, 2009). An investigation of charcoal physical characteristics generated from *Eucalyptus camadulensis* reported an increased in surface area from 6 m²·g⁻¹ to 490 m²·g⁻¹ and an increase in adsorption using benzene as a sorbate from 10 mg·g⁻¹ to 150 mg·g⁻¹ in charcoal generated at 250 °C and 850 °C, respectively (Bornemann et al., 2007). Pore size distribution also increased from 17% microporosity (pores < 2nm) in the 450 °C charcoal to >90% in the 850 °C charcoal (Bornemann et al., 2007).

Charcoal formed during wildfire events is known to adsorb organic compounds present in soil solution and throughfall, but there is only limited understanding of the longevity and capacity of wildfire-produced charcoal to alter the surrounding soil environment. Over time, charcoal surfaces undergo oxidation – this reduces binding sites and the adsorption capacity of charcoal particles produced by the initial formation conditions (Cheng and Lehmann, 2009; Cheng et al., 2006; Zackrisson et al., 1996). Zackrisson and others (1996) found that the ability of wildfire-produced charcoal to adsorb phenolic compounds decreased with time since fire (TSF) over a 350-year chronosequence in Swedish boreal forests. Adsorption capacity was measured by seed germination bioassay in aqueous *Empetrum hermaphroditum* leaf extracts and

attributed to an allelopathic effect in seedling germination (Zackrisson et al., 1996). Charcoal that had reduced ability to adsorb organic compounds could be reactivated by heating the charcoal at 400°C –750 °C, suggesting that charcoal might regain the adsorptive capacity during subsequent fire events (Zackrisson et al., 1996). A subsequent study by Keech et al. (2005) established low adsorption capacity by bioassay of charcoal produced by boreal gymnosperm species (< 40%) and found no correlation between the transversal porosity and adsorption capacity.

In a separate study of charcoal adsorption capacity using catechin as a sorbate, a common allelopathic compound found in *Centaurea maculosa*, maximum adsorption increased from 1,000 $\mu\text{g} \cdot \text{g}^{-1}$ to 4,500 $\mu\text{g} \cdot \text{g}^{-1}$ when combustion temperature of *Pinus ponderosa* charcoal increased from 300 °C and 750 °C, respectively (Brimmer, 2006). Weathering of charcoal surfaces is evidenced by an increase in oxygen (O) content present in hydroxyl and carboxyl functional groups, a decrease in C content (Cheng et al., 2008), and a decrease in adsorption capacity (Zackrisson et al., 1996). Current models of wildfire-produced charcoal adsorption as a functioning component of forest ecosystems exist for boreal (Zackrisson et al., 1996) and dry *P. ponderosa*/*Pseudotsuga menziesii* ecosystems (Brimmer, 2006; DeLuca et al., 2006) and affirm the trend of decreased adsorption capacity over time.

The purpose of the work reported was to determine differences in adsorption capacity of wildfire-produced charcoal as influenced by TSF using a fire chronosequence approach in the eastern rain shadow forests of the Olympic Peninsula, in western Washington, USA. These forests represent a unique, mixed-severity fire regime class in the midst of a highly productive landscape where spatial heterogeneity of fire severity may have significant implications for below and above ground post-fire recovery (Franklin and Dyrness, 1973). Non stand-replacing

fires alter succession trajectories, forest composition, tree diameter, and are considered within the natural historical variability of these ecosystems (Perry et al., 2011; Tepley et al., 2013; Weisberg, 2004; Wendel and Zabowski, 2010; Wetzel and Fonda, 2000). The Olympic Peninsula is predicted to increase in annual temperature (+0.6–1.9 °C by the 2020's) and summer potential evapotranspiration (5–18 mm by the 2040's) with climate change – conditions that will likely result in higher fire frequency and size (Halofsky et al., 2011b). The *Tsuga heterophylla* forest zone of the rain shadow region on the Olympic Peninsula experiences fire every 90–150 years and is characterized by a mixed-severity fire regime that experiences 20–70% mortality during a fire event (Agee, 1993; Franklin and Dyrness, 1973; Halofsky et al., 2011a; Weisberg, 2004).

The purpose of the following studies was to assess the *adsorption capacity* of charcoal generated during historical fire events to determine whether adsorption capacity would decrease with time since fire. The effects of formation temperature and oxidation by weathering and adsorption are discernible by advanced analytical techniques yet have an indiscernible interactive effect on adsorption capacity of wildfire-produced charcoal. Therefore, we utilized thermogravimetric analysis (TGA) to determine the mass of volatile organic C, which includes strongly adsorbed organic C theoretically acquired over time, and the mass of thermally stable C, or BC structure produced during the pyrolysis and combustion of charcoal samples. This method quantifies the mass of a sample lost during a thermal ramp under an inert atmosphere followed by combustion and has been used to characterize the chemical composition of OM fractions (Dell'Abate et al., 2003; Plante et al., 2005), differentiate between labile and recalcitrant OM (Lopez-Capel et al., 2005), and quantify charcoal in soils (De la Rosa et al., 2008; Leifeld, 2007; Nguyen et al., 2004).

We hypothesized that (1) the adsorption capacity for phenol in field-collected charcoal will decline with TSF; (2) the adsorption capacity for phenol and the proportion of thermally stable BC in laboratory charcoal will increase with increasing temperature in *P. menziesii* charcoal and provide a frame of reference for the adsorption capacity of field-collected charcoal; and (3) the medium volatile, adsorbed C mass of field-collected charcoal, as measured by TGA, will be negatively correlated to adsorption capacity as this thermal region includes strongly adsorbed organic compounds on charcoal surfaces, which we expect to increase with TSF.

2. Methods

2.1. Field Sites

Wildfire-produced charcoal was collected in the autumn of 2013 and summer of 2014 from the forest floor at nine fire chronosequence sites in the eastern Olympic Peninsula, Washington, USA. The sites, a 250 m² area, were selected in forest stands exposed to historic wildfires (1898_{a,b}, 1922), intermediate wildfires (1977, 1985_{a,b}), and recent wildfires (2006, 2009, 2011) (n = 3, a and b are sites within the same fire perimeter separated by at least 1000 m distance) (Table 1). Sites were selected in the field from pre-designated areas within the North Pacific maritime dry mesic *P. menziesii* *T. heterophylla* potential vegetation zone, between 400 and 600 meters in elevation, and on slopes of less than 20% to avoid erosion effects using ArcGIS maps for reference (Kagan, 2010; USGS, 2009). Where applicable, fire perimeter maps were incorporated to establish the sites within the burned area of BF1, BF2, BG, CF, BH sites only (MTBS, 2013). Sites in the Elwha River Valley (IC, KT, MC, RC) were located with the guidance of fire maps published by Wendel (2009). Soils of the northern and eastern Olympic peninsula are formed on marine deposits of basalt, colluvium, volcanic ash, and glacial till (Henderson et al., 1989; NCRS, 2014). Although there is no formal soil survey of the majority of

the study sites, proximate areas are classified by the US Soil Taxonomy classification as skeletal Typic Haploxerepts (NCRS, 2014), which fits closely with our field observations at all sites. Sites were described by a census of visually estimated understory vegetation species and cover and overstory tree species and diameter (at 130 cm or diameter at breast height [DBH]) within the 250 m² area. Overstory composition at the chronosequence sites was dominated by *P. menziesii* and *T. heterophylla* with a minimal abundance of *Thuja plicata* and *Alnus Rubra* (5% at site RC only) (Table 1). Understory composition was predominantly composed of *Gaultheria shallon*, *Mahonia nervosa*, *Polystichum munitum* in historic and intermediate fire sites and *Chamerion angustifolium* at recent fire sites. Mean annual temperature from 1980–2010 averaged 8.1 ± 0.5 °C and mean annual precipitation was $2,181 \pm 592$ mm across all sites (Wang et al., 2012).

The feedstock for generating laboratory charcoal was collected at recreation sites along the I-90 corridor of the western slope of the Cascade Mountains, Snoqualmie Pass, Washington, USA, in the spring of 2014. Branches were collected in ecosystems similar to the chronosequence field sites where *P. menziesii* dominated the overstory species composition, which had not yet been established.

2.2. Laboratory and Field-Collected Charcoal

At the chronosequence field sites, we installed a contiguous grid of ten 5 m² plots where we randomly collected three composite OM samples (five composites at BG plot 4 due to sparse OM cover) with a 5 cm diameter ring to the entire depth of the OM, which was recorded as an average of the three or five depths (Table 2). The OM sample included all layers of the O horizon (L, F, H) down to the mineral soil, which was then homogenized and analyzed as a

single organic layer. Charcoal was identified in the OM samples by visual observation on white paper under supplemental light and separated by hand (Table 2).

Laboratory charcoal samples were created from 3 cm³ sections of live *P. menziesii* branches dried for 48 hours at 60 °C. Samples were buried in pure silica sand, in lidded crucibles to reduce O₂ availability, and heated in a muffle oven (Thermo Fisher Scientific 1100 °C box furnace BF 51800 Series) at 300 °C, 500 °C, and 800 °C. The temperature gradient encompassed the probable range of wildfire temperatures in this ecosystem (Bormann et al., 2008; Monsanto and Agee, 2008; Neary et al., 2005; Santín et al., 2016). The muffle oven was programmed to reach the target temperature at 30 minutes, heated at the target temperature for 2 hours, and decreased to 30 °C over a 2 hour period with the high-temperature alarm set at 10 °C above the target temperature. Charcoal samples were heated for 2 hours in order to ensure complete pyrolysis and combustion of the precursor wood material. Individual charcoal samples (3cm³ segments) were ground to a fine powder with a mortar and pestle to pass a 0.2 mm sieve.

2.3. Batch Sorption of Charcoal

Batch adsorption experiments were conducted for laboratory charcoal and field-collected charcoal in 50 mL KIMAX glass centrifuge vials with Teflon-lined lids (Kimax Glass Inc. USA). Approximately 32.0 ± 0.2 mg of pulverized, homogenized charcoal was weighted into glass centrifuge tubes, and allowed to hydrate in 20 mL of distilled H₂O for a 24 hour period (Bornemann et al., 2007; Zhu et al., 2005; Zhu and Pignatello, 2005). Phenolic compounds, condensed and hydrolyzable tannins, are prevalent in forest ecosystems and known to affect substrate quality, decomposition rates, nutrient cycling (Dąbrowski et al., 2005; Hättenschwiler and Vitousek, 2000), and have been shown to increase with TSF in *P. ponderosa* forests of

western Montana (DeLuca et al., 2002; MacKenzie et al., 2004). We chose simple phenol for the adsorption experiment in order to measure the behavior of phenol in the presence of charcoal to provide a baseline of adsorption capacity. The test adsorbate, phenol (Sigma-Aldrich, ACS reagent $\geq 99.0\%$), was added from $1000 \mu\text{g} \cdot \text{phenol mL}^{-1}$ stock solution into three replicate glass vials containing the adsorbate (pulverized charcoal) and distilled water to produce 2, 5, 10, 20, 50, 100, 250, and 500 ppm batch solutions. The vials were placed on a shaker table for 24 hours and allowed to equilibrate at room temperature (20°C). Batch adsorption experiment solutions were neutral to slightly acidic, but well below than the pK_a of phenol (10) and likely to resemble the protonation of OM solution at the chronosequence sites. With the method described below, phenol content was also measured by CaCl_2 extraction in OM samples at each plot in the study sites (Table 2).

Both sorbent free and $0 \mu\text{g} \cdot \text{mL}^{-1}$ controls were analyzed to account for any bottle losses or desorption during the experiment (Sander and Pignatello, 2005). Adsorbate was removed from suspension by vacuum filtration on a vacuum manifold with Whatman #42 filter paper. The initial and equilibrium concentrations of total phenol was determined by colorimetry (Multiskan FC Microplate Photometer, Thermo Scientific) using the Folin & Ciocalteu's reagent and read at 725 nm following Box (1983). The maximum adsorption capacity of field-collected charcoal was quantified by saturating charcoal adsorbate in a solution of $500 \mu\text{g phenol} \cdot \text{mL}^{-1}$ and following the same procedure as laboratory charcoal described above. Previous studies had shown the adsorption of charcoal to be much lower than $500 \mu\text{g} \cdot \text{mL}^{-1}$ (Bornemann et al., 2007); therefore, we expected to exceed saturation and measure the maximum adsorption capacity.

2.4. Adsorption Isotherm Model

The initial concentration of each isotherm was calculated from the charcoal-free 0 $\mu\text{g}\cdot\text{mL}^{-1}$ control samples. Phenol desorbed from field-collected and laboratory charcoal was subtracted from the equilibrium concentration $[\text{Phenol}]_{\text{final}}$.

The adsorbed amount of sorbate q ($\mu\text{g}\cdot\text{mL}^{-1}$) was calculated using the following equation:

$$q \text{ (}\mu\text{g phenol mg charcoal}^{-1}\text{)} = \frac{([\text{Phenol (}\mu\text{g mL}^{-1}\text{)}]_{\text{initial}} - [\text{Phenol (}\mu\text{g mL}^{-1}\text{)}]_{\text{final}}) * \text{volume of solution (mL)}}{\text{charcoal mass (mg)}} \quad (1)$$

The Freundlich isotherm equation is given by $q = KC^n$, where K is the Freundlich empirical constant related to sorption capacity, C is equal to the equilibrium concentration of the sorbate, and n is the Freundlich exponential coefficient indicative of the intensity of adsorption. Data were linearized to fit to the Freundlich model and coefficients were calculated from the linear model.

The disassociation constant, K_d , measures the slope of a line that is represented by the dissociation of large to smaller individuals in the isotherm model at origin and is calculated by:

$$K_d = \left(\frac{C_i - C_f}{C_f} \right) \frac{V}{M} \quad (3)$$

where C_i and C_f are the initial and final sorbate concentrations, V is the volume, and M is the mass of sorbent. The Freundlich adsorption isotherm constants, K_f and n , for phenol were determined by extracting the coefficients of the linearized isotherm model (Langmuir, 1997).

2.5. Thermogravimetric Analysis of Charcoal

Thermogravimetric analysis was performed on a TGA Q50V20, build 39 (TA Instruments). Charcoal samples of 10–12 mg were weighed into alumina sample pans. Samples were heated under N_2 (gas) with a balance purge flow of $40 \text{ mL}\cdot\text{min}^{-1}$ and sample purge flow of 60

$\text{mL}\cdot\text{min}^{-1}$. Starting at an initial temperature of $30 \pm 7\text{ }^{\circ}\text{C}$, the thermal ramp increased at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to $1000\text{ }^{\circ}\text{C}$, followed by an isothermal purge with $\text{O}_{2(\text{gas})}$ for 5 minutes. Thermal decomposition data were compiled using Universal Analysis software (TA Instruments) and treated as a combination of discrete regions within the mass loss range. The segments represent water loss (highly volatile: $T_{\text{initial}}-200\text{ }^{\circ}\text{C}$), lignocellulose material and occluded volatile organic compounds (medium volatile: $200-750\text{ }^{\circ}\text{C}$), carbonization process (low volatile: $750-1000\text{ }^{\circ}\text{C}$), thermally stable BC (combustible: $1000\text{ }^{\circ}\text{C}$ under O_2), and mineral component (ash content: stable at $1000\text{ }^{\circ}\text{C}$ under O_2) (Earnest, 1988).

2.6. Statistical Analysis

Linear regression models were used to determine the relationship between temperature or TSF in charcoal samples to the proportion of mass loss by TGA. In laboratory charcoal samples, we incorporated the effect of individual precursor wood samples as an interaction term with temperature. Similarly, field-collected charcoal models included a plot effect as an interaction with TSF in order to account for the spatial variability within each site. Adsorption capacity of field-collected charcoal (q) did not meet the assumption of homoscedasticity, therefore, we used a one-way Kruskal-Wallis (KW) test to compare non-parametric variances. No more than one outlying replicate of the laboratory charcoal adsorption isotherm data were excluded from the final isotherm data if inclusion increased the coefficient of variation by 20%. At least two of the three replicate data points were used for final analysis of the adsorption isotherms. Pearson's correlation test was used to compare the proportion of medium volatile mass loss from TGA with the maximum adsorption capacity of laboratory charcoal (q) as the independent variable. In order to provide a balanced comparison, we randomly thinned the adsorption observations and used the

excluded data as a validation. All statistical analysis was conducted in the R Statistical Environment (R Core Team, 2015).

3. Results

Field-collected charcoal from chronosequence sites on the Olympic Peninsula measured an average $29.70 (\pm 6.23) \mu\text{g phenol} \cdot \text{mg charcoal}^{-1}$ adsorption capacity (q), which did not differ significantly between TSF sites ($p > 0.1$) (Figure 1). In comparison, the adsorption capacity (q) of laboratory charcoal created from *P. menziesii* wood increased with formation temperature from $61.2 (\pm 5.8) \mu\text{g phenol} \cdot \text{mg charcoal}^{-1}$ (300 °C) to $75.2 (\pm 6.4) \mu\text{g phenol} \cdot \text{mg charcoal}^{-1}$ (500 °C), and $174.8 (\pm 13.7) \mu\text{g phenol} \cdot \text{mg charcoal}^{-1}$ (800 °C) (Figure 2). Laboratory charcoal produced at higher temperatures showed a greater affinity for phenol in batch solution experiments (Figure 2) and greater sorption strength of phenol (Table 3). Adsorption behavior of charcoal produced at 300 °C and 500 °C was indistinguishable after $250 \mu\text{g phenol} \cdot \text{mg charcoal}^{-1}$ (C_i), whereas 800 °C laboratory charcoal reached a maximum adsorption capacity at $\sim 600 \mu\text{g phenol} \cdot \text{mg charcoal}^{-1}$ (C_i) (Figure 2). Similarly, the adsorption capacity increased most rapidly in 800 °C laboratory charcoal compared to that of 500 °C and 300 °C in the lower concentration range, which cover the range of phenol concentration expected in forest floor OM (Figure 3, Table 2). Experimental data from the batch adsorption experiments were fit to both Freundlich and Langmuir isotherm models. Freundlich isotherm model linearization for 300 °C, 500 °C, and 800 °C laboratory charcoals are shown in Figure 4. After the Langmuir linearization by inversion, sorbate concentrations were close to zero, which indicates that the isotherm reduces to a Freundlich model (Langmuir, 1997).

Thermogravimetric results for laboratory and field-collected charcoal are summarized in Figure 5 for each discrete thermal region with formation temperature and TSF, respectively. The

low volatile mass loss (%) between 200 °C–750 °C represents native lignocellulosic material in laboratory charcoal as well as adsorbed organic compounds in field-collected charcoal. The log of mass loss in this region significantly decreases ($r^2 = 0.91$; $p < 0.001$) with increasing temperature in laboratory charcoal while the individual wood sample has a slightly significant interaction with temperature ($p < 0.05$), which suggests % mass loss in this thermal region is a strong indicator of formation temperature (Figure 5). Percent mass of field-collected charcoal samples in the medium volatile region increased slightly with TSF; however, the plot effect (location of charcoal within replicated plots at each site) had a greater contribution to the model than TSF alone, resulting in a significant and positive linear model as a whole ($r^2 = 0.72$; $p < 0.01$). The percent mass loss at 1000°C with oxidative combustion represents the BC structure of laboratory charcoal and increases with formation temperature ($r^2 = 0.82$; $p < 0.01$) without influence from the individual wood sample. The proportion of BC in charcoal samples collected along the fire chronosequence showed a significant negative relationship with TSF and plot effect resulting in a significant and negative linear model ($r^2 = 0.68$; $p < 0.01$).

Thermogravimetric analysis demonstrated a divergence between laboratory and field-collected charcoal in the regions of low volatile loss (750 °C–1000 °C) and residual ash remaining after combustion at 1000 °C (Figure 5). Low volatile loss released by heating of laboratory charcoal increased with increasing temperature, although individual wood sample and the interaction of these factors had a greater influence on the model ($r^2 = 0.83$; $p < 0.01$). Field-collected charcoal showed no significant trend with TSF that incorporated a minimally significant plot effect in the overall model ($r^2 = 0.4$; $p > 0.5$). By contrast, residual ash showed no trend with temperature or individual wood sample ($r^2 = 0.5$; $p > 0.4$) but did significantly increase with TSF despite a significant plot effect ($r^2 = 0.95$; $p < 0.001$). Laboratory charcoal

trends support the hypothesis that as adsorption capacity increases, the percent mass of C compounds in the medium volatile range decreases ($r^2 = 0.69$, $p < 0.05$); however, no correlation was observed for field-collected charcoal ($r^2 = 0.01$, $p > 0.5$) (Figure 6).

4. Discussion

In the current studies, we observed a lower adsorption capacity in field-collected charcoal (Figure 1) compared to laboratory-produced charcoal (Figure 2) and attribute this to the adsorption of organic compounds and oxidation of charcoal surfaces over time, which is supported by TGA results (Figure 5). The average adsorption capacity of field-collected charcoal across all sites was less than 50% of the 300 °C and 17% of the 800 °C laboratory charcoals (Figures 1 and 2) and TGA results show that the proportion BC is generally lower than the 300 °C samples (Figure 5), suggesting that either field-collected charcoal was formed at temperatures below 300 °C or significant oxidative weathering and occlusion with OM occurred *in situ*. Charcoal collected along the fire chronosequence did not demonstrate a significant shift in phenol adsorption with TSF; however, a change in BC structure, ash residue, and mass of volatilized adsorbed compounds (or native lignocellulosic material) was observed with TSF using thermogravimetry (Figures 4 & 5). While the design of this experiment does not allow for direct comparison between adsorption and TGA data, we can use the TGA result to help characterize charcoal material collected along the chronosequence. Field-collected charcoal contained higher proportion of adsorbed compounds or experienced a low temperature pyrolysis in the original wildfire event, as a higher mass was lost at 250 °C–750 °C, and that the proportion of BC, measured as mass loss at 1000 °C with O₂, was much lower than in the laboratory charcoal are both attributes that may reduce total adsorption capacity.

As hypothesized, *P. menziesii* charcoal produced at higher temperatures increased in adsorption capacity for phenol in batch adsorption experiments (Figure 2, Table 3) as well as proportion of BC measured by TGA (Figure 5). Maximum adsorption values reported here are within the scope reported by Bornemann et al. (2007) for benzene and toluene adsorption to *E. camadulensis* charcoal produced over the range of 250 °C–850 °C and about 40-fold higher than catechin adsorption reported by Brimmer (2006) for *P. ponderosa* charcoal produced at 300 °C–750 °C. Single- and bi-solute adsorption experiments using benzene, nitrobenzene, and toluene with 400 °C *Acer spp.* charcoal showed a maximum adsorption capacity of ~ 615 µg nitrobenzene·mg charcoal⁻¹ (Sander and Pignatello, 2005). The experimental adsorption isotherm data from this study showed a predicted non-linear fit to the Freundlich model, despite a slight deviation in the 800 °C charcoal (Figure 4) that is evidenced in TGA results (Figure 5) where higher temperature charcoal displays higher variability in most thermal regions. Sorption behavior of charcoal is reported in literature as highly non-linear – charcoal sorption exhibits molecular sieving and multilayer sorption beyond which may be accurately described by Freundlich and Langmuir models (Pignatello et al., 2015; Sander and Pignatello, 2005). Previous studies of charcoal adsorption describe experimental data with numerous isotherm models and use a variety of charcoal-production parameters, adsorbate solutions, and adsorption techniques, which makes direct comparison of this data difficult to the majority of adsorption research. The experimental data from this study likely fit the Freundlich isotherm model due to multilayer adsorption and heterogeneous distribution of adsorption site energies and functional groups (Langmuir, 1997; Sander and Pignatello, 2005).

Theoretically, the formation temperature of field-collected charcoal can be inferred by the mass loss at combustion (1000° C with O₂), which indicates BC structure (Earnest, 1988). Our

findings showed a decrease in BC structure with TSF, which might indicate that recent fire sites were exposed to higher fire temperatures, although still below 300 °C as compared to laboratory generated charcoal (Figure 5). Alternatively, the observed differences within this TGA region may be due to increased chemical and biochemical oxidation of charcoal particles over time. Abiotic and biotic oxidation of charcoal and biochar in short-term studies ranging 6 months to 1.5 years (Cheng and Lehmann, 2009; Liang et al., 2008; Nguyen et al., 2010; Zimmerman, 2010) and long-term studies of over 100 years (Cheng et al., 2008; Hockaday et al., 2007; Nguyen et al., 2008) shows the importance of these processes in the chemical composition of weathered particles, which results in higher O content, lower C content, and lower adsorption capacity.

Temperature of wildfire events represented in the chronosequence sites is impossible to infer from the existing condition of vegetation structure and composition in historic (over 100 years since fire) and intermediate sites (50–70 years since fire). Satellite data can provide a measure of overstory vegetation mortality after the fire events, which has been used as a proxy for fire temperature (Miller et al., 2009), but we hesitate to extrapolate a direct relationship to understory fire severity due to the limited connection between overstory and understory fire severity and delayed mortality of *T. heterophylla* (Franklin and Dyrness, 1973). Furthermore, fire severity and understory wildfire temperatures are not well correlated to charcoal production and consumption, which may be used to infer combustion conditions (Pingree et al., 2012; Santín et al., 2013). For example, in a temperate forest where understory temperatures during a wildfire were estimated to be > 750 °C, charcoal C formation rates were highly variable and supports the stochastic nature of wildfire events in relation to below-ground effects (Pingree et al., 2012). Charcoal mass across the fire chronosequence sites in this study is weakly, negatively correlated to TSF ($r^2 = 0.21$; $p <$

0.001), which may also support the oxidative decomposition of charcoal samples over time as opposed to wildfire conditions (Table 2).

Results from TGA provide a fingerprint of thermal and oxidative characteristics (thermal decomposition under N₂ and oxidative with O₂) for each charcoal specimen and are specific to the heating rate, composition of gases, and flow rate of gases during the thermal ramp (Earnest, 1988). Overall, the TGA results for laboratory-generated charcoal show a clear picture of the relationship between volatile mass loss within each thermal region and the effect of formation temperature. Generally, medium volatile mass loss (250 °C–750 °C) is slightly influenced by the individual wood type but temperature remains a strong indicator of mass loss in this region. Low volatile mass loss (750 °C–1000 °C) of laboratory charcoal is highly influenced by the individual wood chemistry and is a poor indicator of formation temperature. Oppositely, mass loss of combustion at 1000 °C and residual ash provide strong indicators of formation temperature (Figure 5).

Wildfire-produced charcoal in the chronosequence reflects high variability adsorption capacity, which we hypothesized could be explained by the mass loss TGA region where adsorbed compounds are volatilized (medium volatile, 250 °C–750 °C). We also expected the medium volatile mass loss to increase with TSF, which is supported by the TGA results (Figure 4). Although these data do not support the hypothesis that adsorption capacity is negatively correlated to the medium volatile mass loss in field-collected charcoal, laboratory charcoal samples show a significant negative correlation to adsorption capacity ($r^2 = 0.69$; $p < 0.05$) (Figure 6). Field-collected charcoal shows high adsorption variability both within and between TSF sites that may be attributed to temperature and oxidation conditions during the fire event and as a result of subsequent weathering. This high variability is reflected by the strong site

effect in TGA results for most thermal regions of field-collected charcoal. For example, the effect of TSF on the combustive mass loss region, which represents BC structure, equates to a 0.3% decrease per year – the effect of plot is worth 100 years of TSF.

The adsorption capacity of field-collected charcoal represents the site-specific acquired characteristics of abiotic and biotic conditions since the wildfire event (Tables 1 & 2, Figure 1). The presence of natural OM in soil solution can significantly reduce charcoal adsorption capacity of hydrophobic organic C compounds (Cornelissen and Gustafsson, 2004; Pignatello et al., 2006) by physical occlusion of macropores that may be alleviated over time (Braidia et al., 2003; Hale et al., 2009). The occlusion of adsorption sites by mineral or organic particles could explain the decreased adsorption capacity of field-collected charcoal compared to laboratory charcoal and be further supported by the high ash content in some field-collected charcoal (Figure 5). Existing studies suggest a decrease in charcoal sorption capacity over time (Brimmer, 2006; DeLuca et al., 2006; Zackrisson et al., 1996), which is not supported by our direct measurement of phenol adsorption in field-collected charcoal over a 115-year fire chronosequence (Figure 1). In our studies, overwhelming site effects and limited recent fire sites may have negated the potential for observing the previously documented trend of adsorption capacity decreasing with TSF in the field-collected charcoal (Zackrisson et al., 1996) (Table 1). Our studies provide a direct quantification of charcoal adsorption capacity (Figure 1) and behavior (Figures 2 and 3, Table 3) with batch adsorption experiments. Phenol in solution clearly does not replicate the complexity of dissolved soil OM in forests soils, yet this research provides a controlled, mechanistic evaluation of adsorption behavior *in vivo*, setting the stage for future investigations for OM adsorption to wildfire-produced charcoal in forest soils (Blum, 1996; Blum et al., 1999).

Charcoal and its adsorption capacity may play an important role in post-fire recovery through the adsorption of compounds that might otherwise interfere with seedling germination and growth (Pluchon et al., 2016; Wardle et al., 1998). The prevalence of charcoal after wildfires is documented in recent literature (Buma et al., 2014; DeLuca and Aplet, 2008; Pingree et al., 2012; Santín et al., 2015), yet the implications of this highly active C-rich material in forest soils remains poorly understood in temperate forests where fire conditions are predicted to become more frequent and extensive. The findings of this research reiterate the importance of separating the acquired effects of weathering and adsorption of organic compounds from intrinsic formation temperature in order to accurately measure adsorption capacity and define the function of charcoal in forest soils. This study suggests that charcoal adsorption capacity may influence dissolved organic C flux in post-fire soils of the Olympic Peninsula, which is likely derived from formation temperature or oxidative decomposition rather than with TSF. Despite the low adsorption capacity of field-collected charcoal compared to laboratory charcoal (Figures 1, 2, and 3), field-collected charcoal from the chronosequence sites yielded 0.09 ± 0.04 $\mu\text{g phenol} \cdot \text{mg charcoal}^{-1}$ (n=10) (Table 2). The adsorption capacity of field-collected charcoal will likely reduce solution concentrations of phenolic compounds in forest soils; however, we expect the capacity to be highest immediately after charcoal formation in a fire event. Due to a lack of chronosequence sites that had been recently exposed to fire (the most recent fire site was 3 years post-fire), we were unable to sample within the time frame when field-collected charcoal is likely highest. Mixed-severity fire regime and micro-site environmental conditions of the eastern Olympic Peninsula forests added an additional layer of spatial and temporal complexity observed in this study. Future studies would benefit from a larger number of study sites across the

429 chronosequence and a wider range of TSF values. This would allow us to overcome some of the inherent spatial variability and allow fire effects to overcome site variation effects.

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Tables

Table 1: Fire chronosequence site attributes for study sites on the Olympic Peninsula, Washington. Sites are dated from establishment and organic matter collection (IC, KT, MC, RC in 2013 and remaining sites in 2014). Number of fires since 1568 was determined by Wendel (2009) for sites IC, KT, MC, RC, and with fire history maps provided by the USDA Forest Service for remaining sites. Basal area is calculated with only live standing trees > 9 cm in diameter. Saplings qualify as trees taller than 130 cm and < 9 cm in diameter.

Fire History	Site	Time since fire (years)	Number of fires since 1568	Basal area (m ² ha ⁻¹)	% Basal area of <i>P. menziesii</i>	% Basal area of <i>T. heterophylla</i>	% Basal area of <i>T. plicata</i>	Saplings ha ⁻¹
Historic	Idaho Creek (IC)	115	4	65	29	68	<1	1200
	Krause Top (KT)	115	5	71	100	0	0	80
	Michael's Cabin (MC)	86	7	85	100	0	0	80
Intermediate	Rica Canyon	36	6	38	83	0	4	6720

	(RC)							
	Beaver Fire 1 (BF1)	29	2	97	87	1	11	7120
	Beaver Fire 2 (BF2)	29	2	82	97	<1	11	2720
Recent	Bear Gulch II (BG)	8	4	100	89	0	<1	0
	Constance Fire (CF)	5	2	51	100	0	0	0
	Big Hump (BH)	3	2	21	76	24	10	0

Table 2: Organic horizon soil and charcoal characteristics for the Olympic Peninsula fire

chronosequence sites. Depth of organic horizon (OM) is an average of three composite samples and chemical composition is an average of ten samples. Charcoal mass was quantified from ten replicate plots. Charcoal elemental composition is an average of 9 individual samples. Standard error is given in parenthesis.

	Organic Horizon Soil Characteristics					Charcoal Composition		
Site	OM depth (cm)	Total C (mg·g ⁻¹)	Total N (mg·g ⁻¹)	Charcoal mass (kg·ha ⁻¹)	Phenol content (mg·kg ⁻¹)	Total C (mg·g ⁻¹)	Total N (mg·g ⁻¹)	Total H (mg·g ⁻¹)
IC	3.2	332.63 (18.78)	7.56 (0.45)	406 (160)	48.92 (14.27)	512.65 (15.46)	4.91 (0.40)	37.08 (1.22)
KT	4.0	364.46 (16.74)	9.72 (0.55)	139 (49)	28.72 (5.46)	570.53 (25.67)	3.82 (0.29)	38.86 (1.17)
MC	2.5	318.15 (15.32)	7.90 (0.39)	105 (59)	42.71 (9.79)	504.84 (7.34)	5.26 (0.37)	42.66 (1.03)
RC	4.2	373.69 (21.51)	10.43 (0.67)	129 (63)	66.31 (11.32)	546.05 (9.26)	4.66 (0.27)	40.18 (2.98)
BF1	2.8	335.89 (26.27)	7.12 (0.65)	535 (127)	23.39 (3.02)	628.23 (17.79)	4.43 (0.26)	29.90 (1.88)
BF2	2.3	321.14 (23.97)	5.00 (0.41)	380 (93)	26.02 (2.71)	582.77 (10.42)	4.46 (0.36)	39.41 (0.82)
BG	3.3	196.66 (18.33)	5.72 (0.56)	1,063 (212)	5.74 (1.47)	583.79 (9.88)	6.44 (0.32)	29.88 (0.51)
CF	2.2	321.00 (25.14)	11.23 (0.96)	610 (135)	16.13 (3.16)	572.48 (17.12)	9.76 (0.36)	26.44 (0.59)
BH	2.5	229.52 (14.91)	6.83 (0.42)	1,180 (251)	5.85 (1.36)	579.95 (17.75)	7.39 (0.56)	30.07 (0.33)

Table 3: Isotherm coefficients (K_f) , sorption strength (n) , and elemental composition of laboratory charcoal samples ($n = 3$, standard error in brackets). K_d reported at 50 mL·mg charcoal⁻¹ initial concentration. Model fit parameters are provided in Figure 3.

Formation Temperature	K_f	n	Average sorption strength (K_d)	C g·kg ⁻¹	H g·kg ⁻¹	N g·kg ⁻¹	Average H/C
300 °C	1.72	0.88	0.08	625.02 (9.82)	40.74 (1.13)	2.99 (0.21)	0.065
500 °C	0.76	1.02	0.36	761.88 (3.26)	26.32 (0.39)	2.87 (0.04)	0.03
800 °C	0.24	1.18	1.64	822.11 (2.86)	6.51 (0.30)	4.39 (0.14)	0.008

Figure Headings

Figure 1: Adsorption of phenol by field-collected charcoal (q µg phenol·mg charcoal⁻¹) from a chronosequence of nine sites varying in time since fire on the Olympic Peninsula in western Washington. Boxplots of each plot show the median values (middle black line), the largest and smallest observations (vertical lines), and the 25th and 75th percentile (lower and upper bounds of boxes, respectively) ($n = 3$ except for year 36, where $n = 2$).

Figure 2: Experimental adsorption isotherms for laboratory charcoal generated from *Pseudotsuga menziesii* wood at 300 °C (in light grey), 500 °C (in dark grey), and 800°C (in black) from 2 mg L⁻¹ phenol to over 800 mg L⁻¹ ($n = 2$ or 3).

Figure 3: Experimental adsorption isotherms for laboratory charcoal generated from *Pseudotsuga menziesii* wood at 300 °C (in light grey), 500 °C (in dark grey), and 800 °C (in black) from 2 mg·L⁻¹ phenol to 25 mg·L⁻¹ (n = 2 or 3).

Figure 4: Freundlich linearization of laboratory charcoal, phenol adsorption isotherms. a) Charcoal produced at 300 °C (r²=0.98), b) 500 °C (r²=0.99), and c) 800 °C charcoal (r²=0.93).

Figure 5: Percent mass loss from T_i-1000 °C with N₂, at combustion with O₂, and ash residue after combustion for laboratory *Pseudotsuga menziesii* (left) and field-collected charcoal (right) from nine sites varying in time since fire on the Olympic Peninsula in western Washington. Linear models incorporate temperature and variation of individual charcoal samples (x-axis represents temperature of laboratory-charcoal combustion). Field-collected charcoal linear models incorporate time since fire in years and the plot effect (x-axis represents TSF in years). Model fit parameters for laboratory charcoal medium volatile and ash content are for logarithmic models, but displayed as linear for visual ease.

Figure 6: Correlation results for adsorption capacity in relation to a) medium volatile mass loss for laboratory charcoal (n = 2 for 300 °C and 500 °C, n=3 for 800 °C) and b) field-collected charcoal from nine sites varying in time since fire on the Olympic Peninsula in western Washington (n = 3).

Figure 1: Adsorption of phenol by field-collected charcoal (q $\mu\text{g phenol}\cdot\text{mg charcoal}^{-1}$) from a chronosequence of nine sites varying in time since fire on the Olympic Peninsula in western Washington. Boxplots of each plot show the median values (middle black line), the largest and smallest observations (vertical lines), and the 25th and 75th percentile (lower and upper bounds of boxes, respectively) ($n = 3$ except for year 36, where $n = 2$).

Figure 2: Experimental adsorption isotherms for laboratory charcoal generated from *Pseudotsuga menziesii* wood at 300 °C (in light grey), 500 °C (in dark grey), and 800 °C (in black) from 2 mg L⁻¹ phenol to over 800 mg L⁻¹ (n = 2 or 3).

Figure 3: Experimental adsorption isotherms for laboratory charcoal generated from *Pseudotsuga menziesii* wood at 300 °C (in light grey), 500 °C (in dark grey), and 800 °C (in black) from 2 mg·L⁻¹ phenol to 25 mg·L⁻¹ (n = 2 or 3).

Figure 4: Freundlich linearization of laboratory charcoal, phenol adsorption isotherms. a) Charcoal produced at 300 °C ($r^2 = 0.98$), b) 500 °C ($r^2 = 0.99$), and c) 800 °C charcoal ($r^2 = 0.93$).

Figure 5: Percent mass loss from T_i –1000 °C with N_2 , at combustion with O_2 , and ash residue after combustion for laboratory *Pseudotsuga menziesii* (left) and field-collected charcoal (right) from nine sites varying in time since fire on the Olympic Peninsula in western Washington. Linear models incorporate temperature and variation of individual charcoal samples (x-axis represents temperature of laboratory-charcoal combustion). Field-collected charcoal linear models incorporate time since fire in years and the plot effect (x-axis represents TSF in years). Model fit parameters for laboratory charcoal medium volatile and ash content are for logarithmic models, but displayed as linear for visual ease.

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