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Carbon, biochar and soot black carbon in Yosemite National Park soils: Quantification, characterization and policy implications

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A dissertation submitted in partial satisfaction of the requirements for the degree

Doctor of Philosophy in Environmental Systems

by

Gyami Shrestha

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Gyami Shrestha

DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

ENVIRONMENTAL SYSTEMS

UNIVERSITY OF CALIFORNIA

MERCED

Approved:

Dr. Thomas C. Harmon, Committee Chair

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2011

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Chapter I: Executive Summary

Chapter I

EXECUTIVE SUMMARY

Black carbon in the form of biochar or charcoal has high carbon sequestration potential, i.e. it can store carbon in soils for a long time, diminishing its release to the atmosphere and helping climate change mitigation. Aerosol black carbon, in the form of soot, is the most potent short-term greenhouse-warming particle. Instant decrease in such emission would likely lead to a rapid reduction in temperatures. This doctoral dissertation encompasses a published review paper of all forms of black carbon; an original research paper describing a study of the chemical and radiocarbon properties of soot and biochar forms of black carbon materials deposited in the soil after biomass burning and fossil fuel combustion; and a study of the policy implications of their production from prescribed forest fires as follows:

Paper 1 (Chapter 2): Black Carbon's Properties and Role in the Environment: A Comprehensive Review

Paper 2 (Chapter 3): (a) Potential soil carbon implications of biochar black carbon produced from prescribed forest fires; (b) Age and source of black carbon in surface soils of Yosemite

Paper 3 (Chapter 4): Science Policy aspects of prescribed burns and their effects on carbon, black carbon and air quality impacts

This document is arranged in publication and publication-ready format, with each chapter as a paper with its own study objectives, laboratory analyses and results presented as parts of the overall goal of this research as described here. Chapter II reflects upon the current state of scientific knowledge of soot and biochar black carbon describing its physical and chemical properties, methods of extraction, and its environmental significance. A multidisciplinary review of literature from soil sciences, atmospheric sciences, combustion sciences and climate change science was employed to clarify and distinguish different black carbon types, their formation mechanisms and impacts.

The subsequent chapters delve into the original research conducted for the fulfillment of the requirements of this dissertation, focusing on black carbon recently deposited and accumulated in surface soils of six sites along an elevational gradient in Yosemite National Park in Central California, which also includes the San Joaquin Valley. Below, a summary of these chapters are presented.

1. Black Carbon’s Properties and Role in the Environment: A Comprehensive Review

Depending on its form, condition of origin and storage (from the atmosphere to the geosphere), and surrounding environmental conditions, BC can influence the environment at local, regional and global scales in different ways. In this paper, we review and synthesize recent findings and discussions on the nature of these different forms of BC and their impacts, particularly in relation to pollution and climate change. We start by describing the different types of BCs and their mechanisms of formation. To elucidate their pollutant sorption properties, we present some models involving polycyclic aromatic hydrocarbon species and organic carbon. Subsequently, we discuss the stability of BC in the environment, summarizing the results of studies that showed a lack of chemical degradation of BC in soil and those that exposed BC to severe oxidative reactions to degrade it. After a brief overview of BC extraction and measurement methods and BC use for source attribution studies, we reflect upon its significance in the environment, first by going over a theory that it could represent parts of what is called the 'missing sink' of carbon in global carbon cycle models. Elaborating upon the relationship of BC with polycyclic hydrocarbon species, we show its significance for the sorption and transport of pollutants. A description of pulmonary-respiratory health effects of soot BC inhalation is followed by a discussion on its impact on climate and climate change. We explain how soot BC acts as a global warming agent through light (and heat) absorption and how it reduces the snow's albedo and promotes its uncharacteristic thawing. On a more positive note, we conclude this review by illustrating recent observations and simulations of how pyrolytic processes can stabilize plant carbon stocks in the form of biochar BC that can sequester carbon and can help mitigate climate change, in addition to improving soil fertility.

2. Biochar and soot black carbon in forest soils of Yosemite National Park: age, source, prescribed fire effects and effects on soil carbon concentration

This chapter combines the findings of the two interconnected studies conducted on the same sample sets. First, the effect of prescribed (or controlled) burning on existing carbon and black carbon in surface soils was assessed to illuminate the role of this forest management and wildfire control strategy in the soil carbon cycle and possible implications to the terrestrial carbon budget. Subsequently, the proportional contribution of fossil fuel combustion or radiocarbon dead carbon versus biomass burning sources on these black carbon materials in the soils was analyzed using radiocarbon species to seek the origin of the soot black carbon in the soil, to estimate their ages and to explore possible effects of prescribed burning on the amount of black carbon produced recently as well as historically.

Soil from 0-5 cm depth was collected after prescribed fires in YNP along an elevational gradient ranging from 1148 m to 1992 m. Non-burned sites adjacent to burned sites were sampled as control. Two sites were sampled before and after the fires. In unburned soils, surface litter was collected and in burned soil, charred materials were collected from the surface above the sampled soil.

2.1. Potential soil carbon implications of biochar black carbon produced from prescribed forest fires

Prior to chemical analyses and relative quantification of biochar BC, the samples were treated chemically to remove organic components. The relative amount of BC in the soils was determined using ^{13}C NMR analysis. The carbon analysis results showed a reduction in surface soil organic carbon and total concentration from prescribed fires in 4 of 6 sites. The relative BC biochar concentration from ^{13}C NMR spectroscopy was higher in post-burn soils than controls in five of the six study sites. Biochar was produced in the lab at 222°C and 450°C to mimic prescribed and wildfire flame temperatures. Higher yields of biochar were observed at 222°C than at 450°C independent of source biomass types. The aromaticity of these biochars produced in the laboratory show that prescribed burning in pine species dominated forests may not yield as much refractive and soil carbon-sequestering biochars as in other or mixed vegetation areas, which are found in our study sites. Calculations from this study showed that average potential biochar BC production from biomass in the study sites was 138 gKg^{-1} biomass at 450°C temperatures and 68 g Kg^{-1} biomass at 222°C temperature. Keeping in mind that these quantities are only indicative of ideal natural conditions of burns, they represent significant numbers in terms of potential conversion and preservation of carbon that could otherwise be lost of the atmosphere by degradation and decomposition of dead biomass.

2.2. Age and source of soot black carbon in surface soils of Yosemite

Prior to analysis of soot BC, the samples were treated thermochemically employing the CTO-375 method to remove non-BC carbon components. The relative contribution of radiocarbon (^{14}C) dead carbon on soot BC, litter and biochar BC deposited in the soil was determined using accelerator mass spectrometry. The findings showed that the average soot BC concentrations in the study sites were ranged from 0.52 to 4 g BC Kg^{-1} soil. The radiocarbon concentration results of litter and char samples indicated that all of their carbon is of contemporary origin with turnover rates from 1 to 300 years. However, the samples from both post-burn and control soils in all the sites demonstrated radiocarbon values indicative of a mixture of both contemporary and radiocarbon dead carbon. In average, the radiocarbon dead BC contribution to the soot BC in Yosemite soils was approximately one third of the total of soot BC. All sites showed higher radiocarbon dead BC concentration in the post-burn soil than unburnt (control and pre-burn) soils except for one site. Most of the radiocarbon dead carbon in the surface soils' soot BC was found to be of fossil fuel origin, with mixing of some ancient and modern biomass sources.

3.3. Conclusion

The radiocarbon species analyses point to the modern age of the litter and biochar in the surface soils of Yosemite but indicate that the soot BC in these soils is of 'ancient' age, with approximately a third of the analyzed surface soot BC determined to be ^{14}C-dead. Furthermore, the ^{13}C NMR spectra of the soot BC in these soils suggested an absence of BC from biomass sources. These findings indicate that the majority of the ^{14}C-dead carbon in the soot BC of the surface soil could be of fossil fuel origin with mixing of some ancient and modern biomass sources. This fossil fuel BC in these surface soils could be from historical park traffic and from non-local sources. However, samples taken from > 5 cm depths in these soils could show more soot BC of biomass origin from ancient fires than from recent fossil fuel combustion. However, this study focuses mainly on the recent production of BC and surface soil BC. So, we did not collect and analyze samples from those greater depths.

The average soot BC concentration in the study sites was low, ranging from 0.52 to 4 g BC Kg^{-1} soil. The total average fossil fuel BC comprised a third of this total soot BC contents, suggesting a minimal effect of fossil fuel combustion, and transportation and deposition of such soot BC to these soils from other areas. Hadley et al. (2010) published the first study of soot BC deposition and accumulation in the Central and Northern Sierra Nevada region in California, attributing Asian BC for one quarter to one third of the total soot BC reaching this region and significantly perturbing the snow melt and surface temperature. However, that study did not specify how much of that soot BC was from a fossil fuel source. Findings from our study and subsequent radiocarbon analyses of the soot BC in the snow of the Sierra Nevada could help determining the contribution of fossil fuel BC on the early and/or accelerated melting of snow in these mountain peaks.

4. Science Policy aspects of prescribed burns and their effects on carbon, black carbon and air quality impacts

Prior research findings indicate that PB may be a potential method for forest carbon sequestration in soils of California and the SJV, if implemented adequately under optimum environmental conditions. If ideal conditions are not met, existing pools of non-recalcitrant soil carbon may be lost through volatilization during PB and through leaching and ex-situ transport after PB. For instance, as described above in the summary of Chapter III, our research estimated that average potential biochar BC production from biomass Yosemite National Park sites could be as much as 138 gKg^{-1} biomass for PB temperatures of 450°C and 68 $g\ Kg^{-1}$ biomass for PB temperatures of 222°C. Although the relative biochar BC concentration was observed to increase after PB in five of the six study sites there, four sites showed reduction on surface soil organic carbon and total carbon concentration after PB. With the necessity to conduct PB of higher frequencies in larger areas, there is a clear need to investigate the different scenarios that may evolve as a result of their effect on forest carbon emissions and storage potentials. In this context, this chapter presents the federal and state policies related to prescribed forest fires and black carbon with assessments of past and current bills, acts and regulations that govern the prescribed burns conducted in the San Joaquin Valley of California, with a spatial analysis of prescribed burn sites compared with wildfire affected zones.

We observed that only 0.27% of total burned SJV forest land was affected by both PB and wildfires after the year 1990. The policy analysis showed that some recent federal and state level policies do not address air quality issues. Policies that do mention the need to reduce emissions from PB often do not provide precise scientific guidelines to achieve that goal. Future PB policies will have to evolve and consider these and other issues such as the yield of greenhouse gases and aerosols from PB, particularly in light of new federal regulations and Congressional bills that incorporate the accounting of these emissions from non-mobile sources and which include or could possibly include PB in the near future. This assessment is concluded by discussing smoke reduction strategies and policy recommendations that could improve the efficiency and effectiveness of PB emissions reduction. The alternatives and complements to PB in California, such as the use of forest floor biomass for cogeneration and biochar production are also explored and elaborated upon.

5. Appendix

The appendix includes ancillary information related to chapters III and IV as well as a note on the black carbon properties of surface soils collected from the Virginia Smith Terrace of Merced, California, a conservation site adjacent to the University of California Merced.

5. Publications

The publications and conference presentations that have evolved out of this work are listed below:

1. Shrestha G., Traina S.J. and Swanston C. W. 2010. Black Carbon's Properties and Role in the Environment. Journal of Sustainability 2 (pp. 294-320). In http://www.mdpi.com/2071-1050/2/1/294. (Chapter II)

2. Shrestha G., Berhe A.A., Swanston C.W. and Traina S.J. Prescribed fires in California: black carbon effect. In 1st North American Biochar Conference Proceedings, Boulder, pp. 1-25. (Paper, talk & panelist). 2009. In http://cees.colorado.edu/docs/Shrestha_Production%20Forest%20Systems_%20Paper_%20NABC2009.pdf.

3. Black carbon in central California: soil carbon budget & air quality implications. Eos Transactions 89(53), American Geophysical Union (AGU) Fall Meeting Supplement. (Poster). 2008. In http://www.agu.org/meetings/fm08/waisfm08.html.

4. Recent black carbon emissions: source apportionment. American Association for the Advancement of Science (AAAS) Meeting Proceedings, Boston, Massachusetts. (Poster). 2008.

Chapter II. Black Carbon's Properties and Role in the Environment: A Comprehensive Review

Note: This chapter is a paper that was published in the open access journal Sustainability in 2010 and can be cited as follows:

Shrestha G.[1], Traina S.J. [1] and Swanston C.W.[2] 2010. Black Carbon's Properties and Role in the Environment. Journal of Sustainability 2 (pp. 294-320). In http://www.mdpi.com/2071-1050/2/1/294.

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Black Carbon's Properties and Role in the Environment: A Comprehensive Review

Abstract

Produced from incomplete combustion of biomass and fossil fuel in the absence of oxygen, black carbon (BC) is the collective term for a range of carbonaceous substances encompassing partly charred plant residues to highly graphitized soot. Depending on its form, condition of origin and storage (from the atmosphere to the geosphere), and surrounding environmental conditions, BC can influence the environment at local, regional and global scales in different ways. In this paper, we review and synthesize recent findings and discussions on the nature of these different forms of BC and their impacts, particularly in relation to pollution and climate change. We start by describing the different types of BCs and their mechanisms of formation. To elucidate their pollutant sorption properties, we present some models involving polycyclic aromatic hydrocarbon species and organic carbon. Subsequently, we discuss the stability of BC in the environment, summarizing the results of studies that showed a lack of chemical degradation of BC in soil and those that exposed BC to severe oxidative reactions to degrade it. After a brief overview of BC extraction and measurement methods and BC use for source attribution studies, we reflect upon its significance in the environment, first by going over a theory that it could represent parts of what is called the 'missing sink' of carbon in global carbon cycle models. Elaborating upon the relationship of BC with polycyclic hydrocarbon species, we show its significance for the sorption and transport of pollutants. A description of pulmonary-respiratory health effects of soot BC inhalation is followed by a discussion on its impact on climate and climate change. We explain how soot BC acts as a global warming agent through light (and heat) absorption and how it

reduces the snow's albedo and promotes its uncharacteristic thawing. On a more positive note, we conclude this review by illustrating recent observations and simulations of how pyrolytic processes can stabilize plant carbon stocks in the form of biochar BC that can sequester carbon and can help mitigate climate change, in addition to improving soil fertility.

1. Introduction

As the atmospheric carbon dioxide (CO_2) levels continue to increase from pre-industrial concentrations of 280 ppm (parts per million volume) to an average value of 385 ppm, as reported in 2008 (NOAA/ESRL, 2009), precise investigation and documentation of different carbon (C) forms, pools and sinks is of utmost significance. Carbon dioxide is the most commonly studied form of carbon emissions. Black carbon (BC) in the form of aerosols has received far less consideration, although it is a primary air pollutant produced by combustion activities and has a high global warming potential of 680 on a 100-year basis (Bond, 2005). When BC is buried and incorporated in the pedosphere, its long residence time and tendency to enhance other soil chemical and physical properties can increase the soil's potential to sequester carbon. Such burial is preceded by natural, anthropogenic or a mixture of both kinds of events such as wildfires, prescribed burns, biomass-based cooking and fossil fuel combustion. Subsequent *ex-situ* deposition of BC after aeolian or alluvial transport may occur.

Playing a significant role in the carbon cycle, BC simultaneously influences the quality of air from local to intercontinental distances from its point of origin. Maximizing BC formation (as charcoal and char) during combustion processes can decrease CO_2 emission on one hand, whereas on the other hand, it can increase atmospheric pollution with excess soot BC yield. The global dimming effect is another consequence of aerosol BC emission. The emission and transport of BC in the environment is also associated with the fate of other organic substances, particularly polycyclic aromatic hydrocarbons (PAHs), whose isomers can be utilized to trace the sources of BC in soils and sediments. In this paper, we elaborate upon the above properties of BC, focusing on what they imply for the environment and humans.

2. Properties of Black Carbon

2.1. Origin, Types and Composition

Black carbon originates from biomass and fossil fuels. It comprises a range of carbonaceous materials from char BC, the partially combusted solid residues of plant tissues, to highly graphitized soot BC, the volatile substances formed within flames (Schmidt et al., 2001). At their onset, soot or aerosol BC particles form as hydrophobic primary spherule aggregates with irregular geometry providing active sites for deposition of chemical species (Zhang et al., 2008; Crouzet and Marlow, 1995). With decreasing particle size (particularly with sizes smaller than 2 mm), the ability of these particles to remain airborne in the atmosphere increases, promoting long distance transport (Suman et al., 1997). Immediately after fires, emitted BC particles larger than 1 µm may fail to become airborne or may otherwise quickly drop to the nearest surface (Clark et al., 1997; Masiello, 2004). Precipitation and runoff events may eventually wash such BC particles remaining on the soil surface to rivers and oceans unless deposition occurs further than1 km from significant water bodies (Clark et al., 1997). Larger BC particles and charred materials may not be transported and may instead remain on the soil at, if not close to, the place of production and deposition. Time and natural processes such as bioturbation can mix and accumulate such BC materials with the soil, promoting C sequestration and enhancing nutrient sorption, as described later in this paper.

The size of BC materials spans from a few nanometers for atmospheric aerosols (soot BC) to a few centimeters for charcoal fragments of combusted plant materials. In spite of their common sources and aromatic hydrogen deficient chemical composition, charcoal BC, soot BC and other components of the combustion continuum exhibit significant physical and chemical variations (Massiello, 2004; Hedges et al. 2000). The bulk composition of BC is dominated by condensed aromatic rings and a few functional groups making it resistant to decay (Dai et al. 2005) The extent of polymerization, macromolecular structure (graphitic *vs.* diamond) and surface functional group composition of BC is influenced by the type of combustion precursor (vegetation type), the duration and temperature of combustion in the absence of oxygen and the extent of post-combustion aging or weathering (Goldberg, 1985).

The C: H: N ratio of BC can vary widely but its carbon concentration is on average, over 60% with accessory elements hydrogen, oxygen, nitrogen and sulfur (Goldberg, 1985). Soot BC is more recalcitrant than char BC because of its high formation temperature, low internal microporosity and low O/C ratio (Elmquist et al., 2006 ; Cope, 1979) observed soot BC with H: C ratios of 0.25–0.69 and O: C ratios of 0.08–0.33. Diesel soot (Figure 1) from the US National Institute of Standards and Technology (NIST) has a C: H: N ratio of 1: 0.1: 0.016 with 100% aromaticity. This ratio for BC from Boston Harbor sediments has been observed to be 1: 0.1: 0.07 (Schwarzenbach et al., 2002).

Black carbon *versus* elemental carbon

The term 'black carbon' is often used interchangeably with the term 'elemental carbon' in the atmospheric sciences. Both are light-absorbing carbon compounds, but whereas BC is formed from incomplete combustion in reduced or anoxic environments, the term 'elemental carbon' is used for carbon fractions measured after oxidative combustion in the presence of oxygen above a certain temperature threshold. Another light absorbing carbon is 'brown carbon', which is a non-soot organic carbon aerosol originating from humic like substances (HULIS), bioaerosols and tar (Andrea and Gelencser, 2006; Graber and Rudich, 2006; Lukács et al., 2007).

2.2. Fossil Fuel and Biomass Origins of BC: Attributing Sources of and with BC

Whereas Novakov *et al*. (2000) used the ratio of total C to BC in aerosols to apportion BC sources, Brodowski *et al*. (2005) were able to distinguish source-based differences in shapes, sizes, surface properties and partial oxidation of the surface of soil BC particles for vegetation fire and coal combustion sources. Here, we discuss how BC in aerosols, soils and sediments have been utilized for fossil fuel and biomass source apportionment and how PAHs have been employed for specific BC source attribution.

Radiocarbon species

Soot BC from biomass and fossil fuel combustion are different in properties and adsorbed species (Fitzpatrick et al., 2008). Their physical, chemical and radiocarbon properties can be exploited to examine past and current combustion activities, land fire histories and source apportionment of particulate matters (PMs). For instance, BC derived from fossil fuel is fully depleted in radiocarbon species (^{14}C), whereas BC from combusted biomass reflects approximate atmospheric ^{14}C abundance of the time when the biomass of origin was created, minus decrease through radioactive decay. This property makes BC a good tool to assess emissions from fossil fuel combustion, which may not be identified or quantified adequately through other means. For this reason, sediments, soil and aerosol BC has been used for particulate pollution analysis and emission source apportionment studies with the use of radiocarbon species (Masiello and Druffel, 1998; Reddy et al., 2002).

PAH isomers

The PAH isomer ratios of benzo[a] pyrene to benzo[e]pyrene (b[a]p/b[e]p), benzo[b]fluoranthene to benzo[k]fluoranthene (b[b]f/b[k]f) and benzo[a]anthrancene to chrysene (b[a]a/chry)can provide an indication of the source of BC (Dickhut et al., 2000). More than 50% of PAHs are associated with atmospheric aerosols and distinct isomer ratios exist for combustion sources (Dickhut et al., 2000). Calculation of these ratios at any particular point downstream of a watershed can be used to estimate BC emission from different upstream sources, both point and non-point. Mitra *et al*. (2002) used these ratios from total suspended sediments in the Mississippi river to estimate the contribution of BC from combustion sources into the ocean. Such data from surface and deep river sediments can be correlated with ^{14}C analysis of BC. These ratios can further be used to develop models of combustion events and practices relating to BC emission, deposition, and climate change through time.

PAH isomers can be photolysed during atmospheric transport. Mitra *et al*. (2002) used the following equation (Dickhut *et al*., 2000) for adjustment of PAH in total suspended solids in the Mississippi River:

$$(\text{isomer ratio})_{\text{photoadjusted}} = (\text{isomer ratio})_{\text{TSS}} \times \exp[(\lambda_n - \lambda_d) \times 60 \text{ hours}] \qquad (1)$$

where, λ_n and λ_d are the average photodegradation rate constants per hour of the PAHs. Mitra *et al*. (2002) then utilized the PAH isomer ratios to estimate the contribution of BC from different combustion sources (Table 1).

Particulate matter pollution

Black carbon has been reported as a better marker of total PM sources than standard mass concentration measurements (Jansen et al., 2005) because of its longer lifetime (40 hours to a month) in aerosol form (Ogren and Charlson,1983), a dry deposition rate of 0.1 cm s^{-1} for both hydrophobic and hydrophilic forms (Cooke and Wilson, 1996) and the fact that BC is hydrophobic and chemically inert (Hedges et al., 2000; Cook and Wilson, 1996; Crutzen et al., 1984). In Europe, BC contributes 5–10% to $PM_{2.5}$ and less to PM_{10} (Putaud et al., 2004). Such estimates of BC contribution to PM do not currently exist for the USA. Most studies on particulate pollution in the USA have dealt only with PM_{10} and $PM_{2.5}$, not clearly differentiating between fossil fuel and biomass produced emissions (CARB, 1989; EPA, 2005).

3. Formation Models for BC

Here, we present some models formulated by prior studies to outline the BC formation processes. One such model was initially discussed by Esser *et al.* (1994). They assumed that BC formation in natural environments is proportional to phytomass, respective to the litter pools affected by fires and that all carbon burned by fires goes to the air (cb_{air}), into BC (cb_{BC}) or into litter (cb_L) (Equation 2):

$$cb_{air} + cb_{BC} + c_{bL} = 1 \tag{2}$$

The basic formation model of char BC or biochar (which will be described later) through pyrolysis is shown in Equation 3. The proportions of the final products can be changed by adjusting the set temperature and the rate of heating to reach it. Higher biochar yields occur at low heating rates and temperatures lower than 300 °C due to the dominance of the dehydration step of the cellulose, forming anhydrocellulose, its more stable form. Dehydration is the fourth degradation step in pyrolysis, occurring after depolymerization, hydrolysis and oxidation and preceding decarboxylation. At temperatures >300 °C, depolymerization of cellulose occurs, yielding levoglucosan. When the heating rate is faster, shorter time is allowed for the dehydration step, yielding a higher percentage of unstable products that form primary volatiles (Vigouroux, 2001; Demirbas, 2000; Bridgewater and Peacoke, 2000; Eckstrom and Rensfelt, 1980):

$$\begin{aligned} \text{biomass}_{\text{(solid)}} \xrightarrow{\text{P}\mathit{YROLYSIS}} & \text{ biochar + liquid or oil (tars, water, hydrocarbons)} \\ & + \text{volatile gas } (\text{CO}_2, \text{CO}, \text{H}_2, \text{benzene etc.}) \end{aligned} \tag{3}$$

Kuhlbusch (1993) discussed the BC formation coefficient (K_{bc}) as that part of the charcoal which is produced by vegetation fires and which is biologically not decomposable. This coefficient increases linearly with lower burning efficiency, which depends on factors such as flame or heat temperature, rate of heating or burning and inherent moisture in the biomass. Kuhlbusch and Crutzen (1996) plotted BC as the percentage of total C in the burn residue of experimental forest fires against the CO/CO_2 emission ratio, showing that smoldering combustion produced significantly higher BC than the flaming phase. Pyrolyzing biomass at different temperatures, Dermirbas (2007) formulated the following equation for the amount of 'total carbon' or BC of biochar as a linear function of pyrolysis temperature (T):

$$\text{total carbon} = 0.041\text{T} + 55.21 \tag{4}$$

A very high correlation coefficient (R^2) between T and biochar BC was observed. Dermirbas (2007) further proposed this equation for the biochar formation relation with T:

$$\text{biochar} = 0.00005\text{T}^2 - 0.105\text{T} + 85.08 \tag{5}$$

As shown above and as will be discussed later in this paper, all pyrolysis conditions need to be optimized to maximize the yield of BC residue or biochar with respect to initial biomass and for the BC production process to function as part of an energy efficient carbon sequestration mechanism, as discussed in the later section on carbon sequestration.

In atmospheric sciences, the soot BC formation process from biomass is described as comprising elemental and condensed organic carbon production steps (Fitzpatrick et al., 2008; Penner et al., 1998; Grant et al., 1999; Schaap and van der Gon, 2007) (Equations 6–9):

$$smoke \rightarrow soot + volatiles + ash \tag{6}$$

$$soot \rightarrow black\ soot\,(BC) + OC\,(adsorbed) \tag{7}$$

$$black\ \ soot\,(BC) \rightarrow elemental\ soot + condensed\ organic\ compounds \tag{8}$$

$$OC \rightarrow cell\ wall\ \text{primary pyrolysis products} + \text{ decomposition products} + \text{ PAH} + \text{ oxidized PAH} \tag{9}$$

Soot BC formation from high temperature incomplete combustion of carbonaceous fuels such as hydrocarbons (C_xH_y) or fossil fuels can be explained by Equation 10 (Smith and Chugtai, 1995), where the C on the product side denotes the carbon stock of the yielded soot BC. It is evident from the reaction that higher amounts of oxygen in the process produce higher CO and less soot BC:

$$C_xH_y + zO_2 \rightarrow 2zCO + (y/2)H_2 + (x\text{-}2z)C \tag{10}$$

Fitzpatrick et al. (2008) proposed the following soot formation models for both biomass and fossil fuel sources:

$$\begin{aligned} &biomass\ or\ fossil\ fuel \xrightarrow{PYROLYSIS} CO + H_2 + Ethylene + Benzene\ precursors \\ &\rightarrow aromatics \\ &\rightarrow soot + aromatics \end{aligned} \tag{11}$$

$$\begin{aligned} &biomass\ lignin \xrightarrow{PYROLYSIS} guaiacyl\ units \\ &\rightarrow decomposition\ products \\ &\rightarrow char + aromatics \\ &\rightarrow char + soot \end{aligned} \tag{12}$$

The inherent biomass property affecting the soot yield is the cellulose/lignin ratio (Equations 11 and 12). The soot formation and oxidation of any produced soot is the same for both fossil fuel and biomass in the first reaction steps, with the last step involving soot nucleation forming aggregates which can be as long as 30 nm in diameter (Fitzpatrick et al., 2008). Both types of soot contain oxygen, from oxygen functionality incorporated during soot growth as well as by surface oxidation on reactive sites. The soot precursors themselves comprise small quantities of oxygen, with $C_{25}H_{30}$ as the smallest unit in a seven-ring structure linked to similar structures forming a soot particle (Fitzpatrick et al., 2008; Frenklach, 1994; Frenklach, 2009; Vander Wal and Mueller, 2006; Violi et al., 2004).

4. Sorption Properties

Black carbon surfaces are porous with apolar and aromatic surfaces and can contribute 1–10% of the total fraction of organic matter (f_{oc}) in soils and sediments (Gustafson and Gschwend, 1997). They have a high surface to volume ratio and a strong affinity to nonpolar substances such as polycyclic aromatic hydrocarbons (PAHs), dioxins, furans (PCDD/Fs), PCBs, and PBDEs (Bärring et al., 2002; Mattila and Verta, 2008). They show high affinity for pollutants, particularly planar aromatic compounds (Schwarzenbach et al., 2002). After their release, PAHs are sorbed by both soil and sedimentary organic matter and BC in the environment. High molecular weight PAHs have high affinity to BC (Dachs and Eisenreich, 2000).

Black carbon sorbs organic solutes during mass transport in surface aquatic systems and constitutes approximately 3–38% of total organic carbon mass. Jones et al. (2005) proposed that biomass soot BC contains oxygen as part of the particle structure and that surface oxygenates make it hydrophilic, aiding in the adsorption of many species.

Oen et al. (2006) observed a greater correlation of PAHs with BC ($r^2 = 0.85$) than with OC ($r^2 = 0.15$) in four Norwegian Harbor sediments, regardless of their origin, PAH concentration and size fraction of sediments. The sorption of PAHs by BC was more dominant than by OC partitioning. In three U.S. harbors located in California, Wisconsin and New York , Ghosh and co-workers (2003) found that PAHs sorbed on semisolid coal tar pitch were more bioavailable than those on carbonaceous particles such as coal, coke, charcoal BC.

Gustafsson *et al*. (1996) suggested a model describing the observed distribution coefficient of pyrene, a PAH, as a sum of two isotherms involving the OC fraction and the BC fraction (Accardi-Dey and Gschwend, 2001):

$$K_d = f_{oc} K_{oc} + f_{BC} K_{BC} \tag{13}$$

where, K_d is the solid-water distribution coefficient in L kg^{-1} solid, f_{oc} is the weight fraction of OC in the solid phase representing the organic matter content, K_{oc} is the normalized distribution coefficient in L kg_{oc}^{-1} for the compound of interest, in this case, pyrene.

Accardy-Dey and Gschwend (2001) proposed the mixed models below (involving both linear and Freundlich isotherms) for sorption of PAHs as pyrene on BC in Boston Harbor sediments:

$$C_{is} = f_{oc}K_{oc}C_{iw} + f_{BC}K_{BC}C_{iw} \tag{14}$$

where C_{is} is the concentration of sorbed PAH, f_{oc} is the OC content, K_{oc} for pyrene is $10^{4.7}$, f_{BC} is the BC content, K_{BC} for pyrene (coefficient of BC sorption) and C_{iw} is the concentration of PAH in solution. The Freundlich term ($K_{if}C_{iw}$) dominates the above sorption model at low concentrations PAH. The absorption term ($K_{ip}C_{iw)}$ dominates when the concentration of PAH is very high ($K_{if}C_{iw} >> 1$) (Schwarzenbach et al., 2002). The expected sorbed PAH concentrations in the above case, in the absence of BC, is given by:

$$C_{is} = f_{oc}*K_{oc}*C_{iw} \tag{15}$$

As shown above, the sorption and hence transport process of PAH is enhanced by BC.

5. Stability of Black Carbon in the Environment

The aromatic structure of BC makes it chemically recalcitrant, while its surface functionality and sorption of other minerals and organic compounds facilitate physical protection. These properties increase its lifetime in the environment by rendering it chemically and thermodynamically stable (Brodowski et al., 2005; Forbes et al., 2006). Masiello and Druffel (1998) observed the radiocarbon ages of BC from northeastern Pacific and Southern ocean sediments at 50 cm depth to be 2,400 to 13,900 years before present (BP), respectively. Glaser et al (2002) estimated the radiocarbon based mean residence times of biogenic BC to be 1,000–1,500 years. Below, we summarize different findings on the stability and residence time of different forms of BC in soils and sediments.

While conducting isotopic analyses of graphitic BC samples isolated from pre-industrial marine and terrestrial sediments, Dickens et al. (2004) observed that the BC in oceans was terrestrially derived and almost entirely depleted of radiocarbon, suggesting that it was graphite weathered from rocks, rather than a combustion product. They concluded that the presence of fossil graphitic BC in sediments had led to overestimation of combustion-derived BC in marine sediments and, depending on its susceptibility to oxidation, this recycled carbon may be locked away from the biologically mediated C cycle for many geologic cycles.

Based on proposed BC recalcitrance and production rates (Crutzen and Andrea, 1990; Kuhlbusch 1995; Kuhlbusch and Crutzen, 1996) since the Last Glacial Minimum, BC would be expected to comprise 25–125% of the soil and sediment organic carbon pool

(Forbes et al., 2006; Schmidt and Noack, 2000) . Published values of the proportion of soil C occupied by BC range from 3–7% in South East Asia, less than 35% in Australia and the U.S. to less than 45% in Germany (Rumpel et al., 2006; Skjemstad et al., 2002). Assuming that the rate of intercontinental BC transport is lower than the rate of production, a significant amount of BC appears to be undergoing degradation (Forbes et al., 2006). Soluble products of such degradation have been found to include hydrogen-deficient molecules in dissolved organic matter (DOM) from oceans and rivers (Kim et al., 2004; Hockaday et al., 2007).

5.1. Black Carbon Oxidation and Degradation: Review of Past Experiments

The exact nature of BC surfaces may be a critical feature in the determination of their fate and impact in terrestrial systems. The mechanisms of BC degradation are not yet well known. Both biotic and abiotic transformations could strongly influence the surface properties of BC particles (Lehmann et al., 2005). We present past findings related to such surface reactions, or lack of it, in this section.

During origination, soot BC shows a hydrophobic and aromatic nature (Masiello, 2004). Some studies have indicated that BC can be degraded and mineralized by severe oxidative reactions in soils and sediments (Hamer et al., 2004; Schmidt and Noack, 2000). Earlier, Donnet et al. (1972) used kinetics to demonstrate BC oxidation into carbon dioxide and degradation products such as carboxylic aliphatics and phenols, both based on separate oxidation time dependent rate factors.

Exposure to high concentration of natural substances has shown a potential to influence BC's resistance to degradation. Chughtai et al. (1991) reported that soot could be solubilized in a water solution of 50 ppb of ozone, which creates hydrophilic carboxylic groups on the soot exterior, despite soot's hydrophobic and aromatic nature during formation (Masiello, 2004). Hamer et al. (2004) observed enhanced mineralization of BC after the addition of exogenous C to laboratory microcosms. Mineralization rates increased by 30% and 100% for wheat and wood char, respectively, demonstrating the linkage between BC and the broader C cycle.

Microbial networks are likely primary drivers in the mineralization of BC (Shneour, 1966; Hockaday et al., 2007), though their effectiveness may vary widely between ecosystems. Small decreasees of charcoal were observed from microbial inoculation at 35 °C after 12 days, proving BC refractory nature but indicating that some degree of degradation is possible (Baldock and Smernick, 2002).

Brodowski et al. (2005) with the use of SEM/EDX, observed that soil BC particles varied in shapes and surface properties due to differences in origin (vegetation fires or coal combustion) and due to partial oxidation of rough surface elements. They observed that oxidized elements at edges of BC structures made them prone to interaction with minerals.

Through spatially resolved C-NEXAFS measurements, Lehmann et al. (2005) showed clear differences in the extent of oxidation of bulk, and surface regions of BC particles isolated from Brazilian soils of different ages. Carbon K-edge x-ray spectra indicated that though the interiors of BC particles were highly aromatic, these same particles had high concentrations of phenolic and carboxylic functional groups on their surfaces. More recently, Cheng et al. (2008) observed that compared to newly formed BC incubated for a year, 130 years old BC were significantly oxidized on their surfaces (rather than the entire particle) with increased elemental oxygen, increased carboxylic and phenolic functional groups, disappearance of surface positive charges and evolution of surface negative charges after 12 months of incubation.

Rumpel et al. (2006) did not observe any BC association with the soil mineral phase in slash and burn agriculture exposed tropical soils of northern Laos. However, they observed that BC influenced the $\delta^{13}C$ and the $\delta^{15}N$ stable isotope ratios in the soils and that it was susceptible to erosion downslopes. Hilscher et al. (2006) found that two years was enough for the incorporation of charred BC residues into the Ah horizons while also observing that erosion could remove BC from surface soils in steeper lands.

Clearly more information on what controls the persistence *vs.* degradation of different BC forms is needed before its role in the global C-cycle can be fully understood. Chemical and microbial reactions in the environment may accelerate the conversion of solid BC to gaseous carbon dioxide while physical dislocation by wind, air and water can affect its *in situ* quantification. Black carbon recalcitrance and C budgeting studies need to consider these factors by investigating the chemical and microbial properties of the BC substrates and the watershed scale physical processes of the study sites.

6. Black Carbon Extraction, Detection, Analysis

Studies of BC can be associated with diverse environmental aspects ranging from global C flux to fire histories. Different detection and analysis methods are needed to answer questions related to these different environmental events and BC from different combustion continuums. These methods are based on the definition and type of BC that has to be extracted. Here, we summarize some existing BC extraction and analyses methods, followed by cautionary findings related to their use.

The currently most popular chemical-thermal method of soot BC extraction from soils and sediments (Gustafsson et al., 1996; Lim and Cachier, 1996) is abbreviated as CTO-375. It involves the thermal oxidation and volatilization of OCs at 375 °C, followed by *in situ* acidification of samples to remove inorganic carbonates, leaving soot BC residues to be analyzed for radiocarbon species and other information or to be quantified with carbon elemental analysis. Dichromate oxidation has been employed to separate BC from humin and kerogen in soil and sediments (Jeong et al., 2008; Jeong and Werth, 2005; Knicker et al., 2007; Lim and Cachier, 1996; Rumpel et al., 2007). Simpson and Hatcher (2004) employed sodium chlorite in a chemical oxidation method to remove lignin and non-BC aromatic compounds from organic matter. Cross-polarization magic angle spinning (CP-MAS) ^{13}C-Nuclear Magnetic Resonance (NMR) spectroscopy is used for BC measurement in the residue. This method isolates charcoal, soot and other inert non-oxidizable forms of carbon. The residue for BC analysis in this method should comprise only graphitic black carbon or highly condensed BC (soot) and graphite with no charcoal and kerogen (Dickens et al., 2004). The graphitic BC method developed by Dickens et al. (2004) distinguishes soot in soil and sediments. It involves the selective isolation of only the most condensed BC, generally soot, along with graphite. It destroys charcoal, kerogen (non-BC highly refractory geopolymers), and other non-graphitic BC organic compounds. They used the method of Arnarson and Keil (2001) for density fractionation of sediments with sodium polytungstate solutions of 1.6, 2.0 and 2.5 g cm^{-3}. Microscopic measurements and assessments of BC particles may also be conducted using transmission and scanning electron microscopy (TEM and SEM) (Brodowski et al., 2005) as well as other microscopes. Anderson and Smith (1997) impregnated Sierra meadows sediment samples with epoxy resin to study sediment records of past fires. Charcoal particles at each 1 mm depth increments were measured at 100x with a Reichert microscope.

Masiello (2004) showed that discrepancies in BC measurements were revealed with different analysis methods in the past. For instance, Simpson and Hatcher (2004) observed that relatively BC-free soil samples could create and show BC from thermal oxidative methods, leading to overestimates of refractory carbon and carbon flux studies in the environment. Krull et al. (2006) showed that different oxidation and hydrolysis techniques used to isolate soil BC may in fact isolate different BC pools within a given soil. These pools had differing ^{13}C-NMR spectra and ^{14}C abundances. The NMR showed that residues isolated from some soils were actually dominated by aliphatics, not aryl C. Lignin and other aromatic structures exhibit ^{13}C signals overlapping BC signals in the NMR spectra. Wet and thermal oxidation methods of BC extraction assume that during soil BC isolation, natural organics are totally removed with no effects on BC, to avoid challenges posed by the presence such interfering compounds (Simpson and Hatcher, 2004).

Soil and sediment BC studies have developed a clear understanding of the fraction of incomplete combustion products they extract and refer to as BC. However, studies on aerosol BC have mostly employed thermo-optical methods that often describe BC ambiguously (Chow et al., 1993). This allows for both positive and negative artefacts from sampling and quantification (Novakov et al. 2000; Eatough et al., 1999). The term BC is often used to describe elemental carbon in atmospheric sciences. Owing to differences in definitions, sampling, extraction and analysis methods, this BC is often dissimilar to forms of BC described and studied in soil science and oceanography.

7. The Significance of BC in the Environment

7.1. The 'Missing' Sink of Carbon

Estimates of the global C cycle, including stocks and fluxes, often report a 'missing carbon sink'. It has been calculated to be more than 1 Gt C year^{-1} with minor variations depending on different studies throughout the years (Tables 2 and 3). This missing sink that has been associated with black carbon. Approximately 20% of this missing carbon is hypothesized to remain as charcoal BC after forest fires. The soot BC yielded during such fires eventually falls back down to earth during precipitation (Schmidt, 2005).

Glaser et al. (2001) through their study of Terra Preta soils, described at the end of this paper, concluded that BC can act as a significant C sink. Black carbon formation and deposition in soils and sediments enhances the accumulation of biomass–produced carbon into a slow cycling carbon pool, permitting its storage and transfer from the faster cycling atmosphere-biosphere system (Druffel et al. 1984; Kuhlbusch and Crutzen, 1996; Massielo and Druffel, 1984; Mitra et al. 2002; Dai et al., 2005). It is thus involved in channelization of carbon away from biomass formation and cycling into a refractory pool, which is poorly mineralizable by microbial communities (Haberstroh et al., 2006).

Approximately 12 to 24 Tg C is annually produced as BC from fossil fuel (Penner et al., 1993). Biomass burning produces 50 to 260 Tg of C year^{-1} as BC (1 Tg = 10^{12} g) of which approximately 80% is fire residue (Kuhlbusch, 1995; Kuhlbusch and Crutzen, 1996). Based on experimental burns in the laboratory, Kuhlbusch and Crutzen (1995 and 1996) calculated that 1.4% to 1.7% of carbon exposed to fires is converted to BC. Considering this yield, its recalcitrant properties and its long residence time of 2,400 to 13,900 years in soil and sediments (Masiello, 1998), BC may reduce net CO_2 emission from permanent deforestation by 2–18% and represent part of the missing carbon (Kuhlbusch, 1995; Schmidt, 2004).

The estimated pool of carbon in soils and plants of wetlands is 463 Gigatonnes (Gt) (Table 2). Currently, there is no clear and precise data on BC carbon transfer from wetlands to rivers, oceans, and the atmosphere. The carbon accumulation in peatlands is estimated to be 0.07 Gt per year. Considering the 'missing carbon sink' of 1.4 to 1.6 Gt per year, it is reasonable to say that similar to forest ecosystems, some of it may remain stored in wetlands as BC after natural or prescribed fires and after wet or dry deposition of soot particulates from fossil fuel combustion. Masiello and Druffel (1998) observed that BC comprised 12–31% of the sedimentary organic carbon in two deep oceans sites. This BC radiocarbon (^{14}C) age was thousands of years older than concurrently deposited non-BC SOC.

Differences in environmental turnover times of different BC types are significant, and highlight our lack of knowledge concerning BC decomposition including biotic and abiotic process (Masiello, 2004). Despite its refractory nature, BC may have a more dynamic role in the global carbon cycle than previously thought (Masiello, 2004). Masiello et al. (2002) observed that BC in shelf sediments was affected by oxygen exposure, based on differences between BC and SOC ^{14}C ages with oxidation conditions. They observed that 11 ± 4 % of the sedimentary organic carbon in oxic deposits was BC.

In the anoxic sediments, BC comprised 5.2 ± 1.4 % of the total organic carbon. In spite of clear evidence that BC can be a substantial part of the soil carbon pool, and that it may cycle very differently than much less recalcitrant C, there is still a great deal of uncertainty about its measurement and persistence in terrestrial and aquatic environments.

7.2. Sorption of Pollutants

As described earlier, the role of BC in the sorption of pollutants is significant. Two complementary processes bind persistent organic pollutants (POPs) to BC: occlusion inside BC pores during soot formation as well as during surface adsorption during and after soot formation are the (Koelmans et al., 2006; Mattila et al., 2008). Soot BC emitted to the atmosphere is dry and wet deposited to surface waters and land. The char BC deposited and remaining on the land surface in an unincorporated form is carried to surface waters through precipitation runoff and sedimentation. During origination as well such transports, BC particles sorb xenobiotic and naturally occurring organic pollutants in soils and sediments, controlling their fate and bioavailability (Gustafson and Gschwend, 1997). Use of a nonsteady state spatially resolved mass balance model of chemical transport modified to include BC showed that BC has a higher influence than aquatic biota on the cycling, distribution, total amount, bioavailability, and recovery times of polybrominated diphenyl ethers (PBDEs) in the Baltic sea (Mattila et al., 2008).

7.3. Health Effects

Health effects of particles depend on their sizes and the substances sorbed on their surfaces. Smaller particles such as soot BC, which can vary in size from ultrafine (less than 0.1 μm) to fine (less than 2.5 μm) (Figure 2), can be more detrimental to health than larger ones. Following inhalation, particles larger than 4 μm and below 0.002 μm have a higher tendency to deposit in the mouth and throat, while particles between 0.002 ± 0.2 μm deposit in the alveolar region of the lungs (Lippmann and Albert, 1969; ICRP, 1994) (Figure 3).

The size of particles, including soot, from combustion processes vary depending on the temperature and phase of the wood combustion process. Forsberg et al. (1992) observed an average size of 0.065 μm at the beginning of combustion while the smoldering phase showed average particles sizes of both 0.025 and 0.15 μm. Primary C particles or BC from vehicular exhaust were observed to be 0.024±0.006 μm while those from residential wood smoke were observed to be 0.031±0.007 μm in diameter (Kocbach et al, 2006). Schauer et al. (2001) observed that the average fine particle emission rate of fireplace combustion of pine, oak and Eucalyptus wood was respectively 10, 5 and 9 g kg^{-1} of wood while the elemental carbon contribution to this emission was 3 weight percentage of the fine particulate mass (FPM) for both oak and Eucalyptus and 1.4% FPM for pine wood. The BC contribution can assumed to be close to that of the elemental carbon. Organic carbon contribution was respectively 56, 59 and 44% of FPM for pine, oak and Eucalyptus wood.

Soot BC carries PAHs sorbed to its surface into the lungs. This process is followed by absorption of the PAHs into the bloodstream through the alveolar epithelium. The soot particles themselves can also cause health effects. It may take weeks to years for insoluble particles such as soot to be cleared from the alveolar regions. Mechanisms such as transepithelial passage and phagocytosis by macrophages followed by mucociliary escalation enable such removal. Particles < 0.1 μm can enter the circulatory system through the alveolar-capillary endothelium. Such ultrafine particles can enter extrapulmonary organs such as the liver. As particle loading increases, their transepithelial transport increases (Oberdorster and Yu, 1990; Schlesinger, 2000).

7.4. Climate Impacts

There is an increasing awareness that BC is having a measurable effect on atmospheric and land surface warming, primarily through radiative scattering and absorption in the atmosphere and through changes to system albedo at the land surface. Both of these effects make BC a potent driver of climate change from local to global scales. After CO_2 which exerts a positive radiative forcing of 1.6, BC is the second largest contributor to global warming, causing a net positive radiative forcing (surface warming) of 1 to 1.2 Wm^{-2} (± 0.4 Wm^{-2}) through the following processes (Ramanathan, 2001; Chung et al., 2005; Ramanathan, 2007a): absorption and interception of direct sunlight (negative forcing) contributing to surface dimming and reducing evaporation and rainfall globally; absorption of the solar radiation reflected by the earth and clouds (positive radiative forcing); deposition on sea ice and snow; increasing the absorption of sunlight (positive radiative forcing); and evaporation of low clouds aided by BC caused warming (positive forcing) (Ramanathan, 2007a).

The 100-year global warming potential (GWP) of atmospheric BC has been estimated to be 680 (Bond and Sun, 2005) and 510 (Forster et al., 2007) globally while it is estimate to be 374 for BC of European origin and 677 for African BC (Boucher and Reddy, 2008). It has been called the second greatest greenhouse pollutant as the magnitude of its direct radiative forcing exceeds that due to methane. This, in combination with its short lifetime of a few hours to a few days, could make the control of its emissions from fossil fuel, one of the quickest and the most effective ways of slowing global warming (Jacobson, 2002).

Aerosol BC particles can scatter short wave radiations from the sun before reaching the earth surface (dimming and cooling effect) and can also absorb long wave radiations emitted from the earth back to the atmosphere (warming effect). The surface dimming due to aerosol BC cannot be directly compared with that of greenhouse gas forcings because it does not necessarily cause a cooling effect and it mostly results from increase in atmospheric solar absorption, which can be factor of 3 or larger than the dimming due to reflection of sunlight (cooling effect) by GHGs (Ramanathan, 2007b). The strength of these effects is related to other atmospheric components as well as the location and concentration of the aerosols within the atmosphere. The amount of absorption is measured by the ratio of scattering to extinction (sum of scattering and absorption), the single scattering albedo[(SSA) = (SSA)], which below a certain critical value, causes the earth-aerosol system to reflect less radiation than the earth alone, leading to net warming (Seinfeld, 2008). In regions of highly absorbing aerosols, the radiative impact of aerosols at the top of the atmosphere can change from cooling to warming, particularly over highly reflective surfaces such as snow and clouds (Schuster et al., 2005). Absorption of radiation in the atmosphere occurs mainly by non-organic particulate carbon with optical and physical properties associated with soot BC, at wavelengths less than 4 µm (Schuster et al., 2005). Black carbon exhibits a strong spectral dependence inversely proportional to the incident wavelength across the entire wavelength range, compared to other absorbing aerosols such as OC and soil dust, which show major absorption only at 600 nm (Sato, 2003). The extent to which BC is mixed with primarily scattering aerosol components such as sulfates and reactive organic gases (ROGs) determines the radiative properties of individual aerosol particles (Stier et al., 2007). Another factor that should be considered with respect to BC climate forcings is the source of BC. Fossil fuel BC (as primary emissions) has low OC to elemental carbon ratio, producing an overall warming effect whereas biomass BC has high OC to elemental carbon ratio with the potential of neutralizing the warming effect of the elemental carbon (Penner et al., 1998; Fitzpatrick et al., 2008; Grant et al., 1999; Schaap and van der Gon, 2007).

Prior observational and simulation studies (Meehl et al., 2007; Lau et al., 2008; Ramanathan, 2005) over the Indian Ocean have helped to explain how aerosol BC may be responsible for monsoon rainfall reduction in this region. Interception of sunlight by excess aerosol BCs causes reduction in absorption of solar radiation by the land and sea surface which in turn experience reduced evaporation. Increase in atmospheric stability due to BC caused warming and deceleration of summer monsoonal circulation have also been found to cause Asian summer monsoon rainfall reduction in model simulations.

Solar light and heat absorption by snow and ice is significantly enhanced by soot BC deposited on snow and sea ice (Hansen and Nazarenko, 2004; Clarke and Noone, 1985). This effect, along with that of atmospheric BC, has contributed to the retreat of Arctic Sea ice and increased melting of Himalayan snow and glaciers (Flanner et al., 2007; Ramanathan, 2008). The retreat of the Himalayan-Hindu Kush (HHK) glaciers has accelerated since the 1970s, corresponding with a large warming trend of about 0.25 °C per decade observed over the HHK regions (Thompson, 2003). Atmospheric warming by aerosol BC and deposition of dark soot over bright snow surfaces may be important contributing factors (Ramanathan, 2007b). Employing satellite and ground base observations for over 5 years, and a climate model, Ramanathan (2007a) showed that the contribution of aerosol BC (from the entire Asian continent) to the warming trend of the atmosphere between 1 to 5 km (corresponding to HKK glaciers location) was as much as that of greenhouse gases. These BC particles raised atmospheric solar heating up to 50% between 1 and 3 km. Aerosol BCs cooled the surface over most of the Asian plains at lower elevations above sea level while warming the overlying atmosphere. The model was simulated with the emission history of soot for the last 70 years and Asian climate data from 1930 to 2005 with and without aerosol BCs (Ramanathan, 2007b).

7.5. Sequestration of Carbon and Nutrients in the Pedosphere

Black carbon has a high carbon sequestration potential due to its chemical recalcitrance and long mean decomposition rate, as elaborated upon earlier. Recent examination of this potential has shown that considering soil BC in climate models for high frequency fire affected regions of Australia reduces predicted carbon dioxide emissions estimation by up to 24.4% (Lehmann et al., 2008). The reason is that fires helped in biochar BC production, curtailing emissions that would be expected from degradation of the source biomass. In this section, we discuss biochar as a form of BC that can be employed to sequester carbon at a large scale in regions with high abundance of dead or decaying biomass.

Biochar is the charcoal form of BC, produced through pyrolysis or the low temperature combustion of biomass at less than 600 °C in the absence of oxygen. Biochar is different from charcoal due to its intended use and fate through deliberate incorporation in soils to store plant nutrients and improve soil fertility. In addition to natural production through fires and practices such as slash and char, biochar can be anthopogenically produced from waste biomass in large-scale plants or at a smaller scale such as with the use of cookstoves designed for optimum biochar yield with minimum to no smoke. Terra Preta soils (Portuguese for dark earth), which were created between 450 BC and AD 950 (Neves et al., 2004) are an example of ancient biochar's strong effects on soil carbon and fertility. These rich soils were formed in the Amazon Basin by an indigenous land management practice of slash and char agriculture that involved low temperature and reduced oxygen smoldering of slashed biomass to generate more charcoal than ash on soil in pre-Columbian times. After addition and mixing in soil, over time, after oxidation and charging, these charcoal masses were able to sequester large amounts of soil nutrients on their highly porous surface and generated high microbial activity, allowing for continued high soil fertility for centuries. As much as 70% higher BC, nutrients and organic matter than surrounding unamended soils have been observed in them (Glaser et al., 2001; Lehmann et al., 2003).

The incorporation of biochar in soil can lead to sustainable carbon sequestration. The biochar formation process takes carbon sequestration from afforestation a step further by concentrating and locking, on average, approximately 50% of the original carbon content of standing and rapidly decomposing dead biomass into a more stable form (Lehmann, 2007; Baldock and Smernick, 2002) . The rest of the biomass is released during pyrolysis as gas and oil that can be captured for use as an energy source (Lehmann et al., 2006), further reducing emissions (Lehmann, 2007). Carbon sequestration with biochar points to the possibility of sequestering carbon by biasing biomass pyrolysis practices to yield high proportions of refractory BC char residues from the majority of the initial carbon burnt (Ball, 2008). Essentially, a small decrease in combustion efficiency may increase the yield of biochar, providing greenhouse gas offsets and carbon sequestration. Another significant benefit is the reduction in emissions of particulates and other emissions which harm human respiratory health. The mechanism by which biochar formation could be enhanced during pyrolysis was explained earlier in this paper (section on formation models of BC).

Due to its high surface area, charge density and negative surface charge, biochar BC has very high exchangeable cation sorption and retention capacity (Liang et al., 2006). Over time, carboxylic groups formed on the edges of the aromatic part of BC increases biochar's nutrient holding capacity (Glaser et al., 2001). These properties enable its use for topsoil productivity improvement as well for reducing leaching of pollutants such as dissolved phosphates and nitrates into the groundwater and other water bodies. The pyrolysis temperature has to be above 400 °C for these biochar benefits to be manifested via high pH, cation exchange capacity and surface area (Lehmann, 2007).

In the US, Lehman (2007) calculated biochar BC yield from pyrolysis of forest residues (200 million hectares of timber production forests), fast-growing vegetation (30 million hectares of idle cropland) and crop residues (120 million hectares of harvested cropland). They observed that in each case, 1.6 billion tonnes of carbon could be sequestered in the soil (10% of annual fossil fuel emissions for year 2005), if the biochar is returned to the soil and not burned. Globally, estimates have shown that biochar could be used to potentially reduce atmospheric carbon dioxide concentration by 37 ppm through the sequestration of 400 billion tones of carbon over this century (Lenton and Vaughn, 2009).

Assuming that 2.1% of the annual carbon photosynthesized and incorporated into plants would be globally available for production of biochar with 40% carbonization efficiency, the International Biochar Initiative (2009) estimated that 0.5 billion metric tons of atmospheric carbon could be sequestered annually (Figure 4).

Using the energy from the pyrolysis process to replace fossil fuel combustion, this rate would increase to 1.2 billion metric tons per year, offsetting 29% of 2009 annual increase rates of carbon dioxide emissions (Tenenbaum, 2009; International Biochar Initiative, 2009). Due to its carbon sequestration properties, the process of biochar production and integration in soils could be a low-risk and efficient climate change mitigation approach (UNEP, 2009). Carbon offsets and carbon emission reduction schemes such as the clean development mechanism could prove valuable for the successful implementation of biochar production projects around the world. On December 2009, the United Nations Convention of Climate Change and Desertification (UNCCD) determined that biochar would be considered for negotiations as a mitigation strategy for the second Kyoto Protocol commitment period starting in 2013. As interest in this cheap strategy grows, such international consideration is helping to generate more research, testing and evaluation to determine its environmental and commercial value.

8. Conclusions

Although combustion of biomass and fossil fuel are the only forms of BC production, its effects vary distinctively depending on its different forms. It can store carbon for the long terms in soils and sediments but it can also cause severe health problems and contribute to global warming. It is an atmospheric pollutant with high global warming potentials.

However, it is also an integral part of the global carbon budget and, if properly utilized, can play a crucial role in mitigating climate change impacts. Any mechanism targeted toward reducing soot BC should aim at all combustion activities within humankind's control and at large geographic scales since its climate and pollution effects are far reaching. In this context, it would be appropriate to say that the realization of its global influence on climate is very timely, allowing for increased allocation of scientific and monetary resources for research and programs geared towards the alleviation of problems associated with it. For instance, improved cookstove programs in developing countries are now gaining more attention due to their role in reducing soot BC for climate change mitigation, in addition to their prior function of reducing pulmonary-respiratory diseases and improving biomass burning efficiency. Recent developments in biochar cookstoves research and promotion in developing countries is a good sign too. In addition to significant emissions reduction, they also yield biochar for sequestering carbon and improving soil fertility. Both large and small-scale biochar plants are now being established globally. The availability of dead biomass or feedstock, their environmental impacts and the commercial viability of the plants will determine their success. Regardless of the scale of such facilities and projects involving biochar production and application in soils, the direct and indirect reduction in C emissions as estimated and targeted, along with stable net carbon gain in the pedosphere should be verified and ensured. If current findings and projections of biochar's carbon sequestration potential are validated, biochar production could prove to be one of the least costly but most convenient climate change mitigation strategies that could be adopted at any location where there is access to waste biomass. Through linkages with carbon offset based financial mechanisms such as the clean development mechanism, many agricultural communities, particularly in developing countries, would also benefit immensely from this.

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Tables

Table 1: PAH isomer ratios corresponding with combustion source of emissions (adapted from (Dickhut et al., 2000; Mitra et al., 2002).

Sources	**Isomer ratios**		
	b[a]a/chry	**b[b]f/b[k]f**	**b[a]p/b[e]p**
Automobiles	0.53	1.26	0.88
Smelters	0.6	2.69	0.81
Wood	0.79	0.92	1.52
Coal/coke	1.11	3.7	1.48

Table 2: Global carbon stocks and fluxes, incorporating wetland stocks, as reported in the 1990s
(based on Houghton (1999) [1 Gt =1015 g; (–) Inputs; (+) Outputs]).

Carbon Stocks	**Gt Carbon**
Atmosphere	750
Oceans	38,000
Soils	1600 (455 in wetlands)
Land Plants	560 (8 in wetlands)
Carbon Fluxes	**Gt C yr^{-1}**
Inputs	
Fossil Fuels	+5.4
Deforestation and Land Use	+0.9 to +1.6
Plant Respiration	+60
Microbial Respiration	+60
River DOC and DIC Transport	+/–0.8
Outputs	
Photosynthesis	–120
Peatland Accumulation	–0.07
Ocean Sediment Burial	–0.1
Oceanic Carbonate Equilibrium Processes	–2
Accumulation in Atmosphere	–3.4
Missing Sink	**–1.4 to –1.6**

Table 3: Global carbon budget and total missing carbon sinks estimated for different periods

[Adapted from (Lal, 2008; IPCC, 2000). Fossil fuel emissions include those from cement production. Emission of 1 Gt C equals 3.67 Gt CO2. IPCC (2007) uncertainties for land use change emissions exclude interannual variability and are given at 65% interval of confidence.]

Carbon fluxes	**Gt C yr^{-1}**		
Period	1980s	1990s	2000–2005
Known major sources			
Fossil fuel combustion	+5.4	+6.3	+7.6
Land use change	+1.7	+1.6	+1.5
Total sources of carbon	+7.1	+7.9	+9.1
Known major sinks			
Atmospheric increase	–3.1	–3.2	–4.1
Ocean uptake	–1.9	–2.1	–2.2
Terrestrial uptake	–0.2	–1.4	–1.4
Total sinks of carbon	–5.2	–6.7	–7.7
Residual or missing sink of carbon	–1.9	–1.2	–1.4
Terrestrial carbon stock	**Gt C**		
Period	1800–1994	1850–2000	
Residual or missing sink of carbon	–135	–116	

Figures

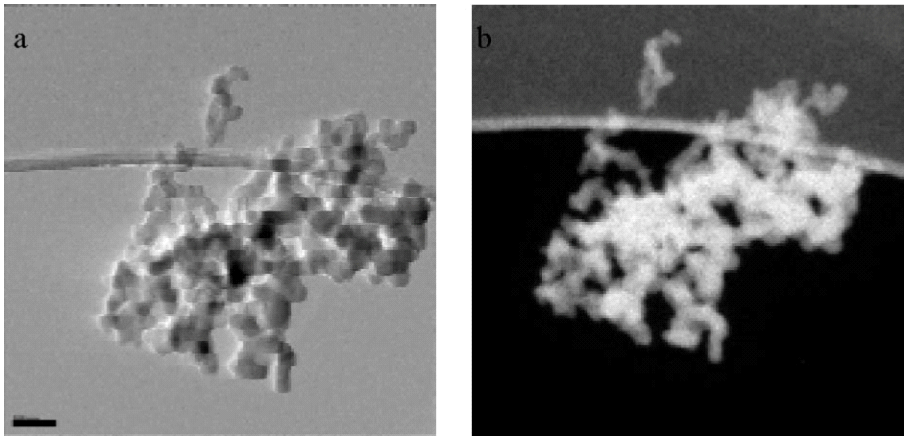

Figure 1: Electron energy loss spectroscopy (EELS) of NIST reference soot material (comprising n-hexane rings).

a. Transmission Electron Microscopy (TEM) image of soot black carbon on a holey carbon film support (above dense transverse line) b. Field emission transmission electron microscopy (FTEM) image of the same, also called the carbon map, with bright portion representing elemental carbon portions in image (a); black color shows absence of carbon in vacuum background (images collected at the University of California Microscopy Facility).

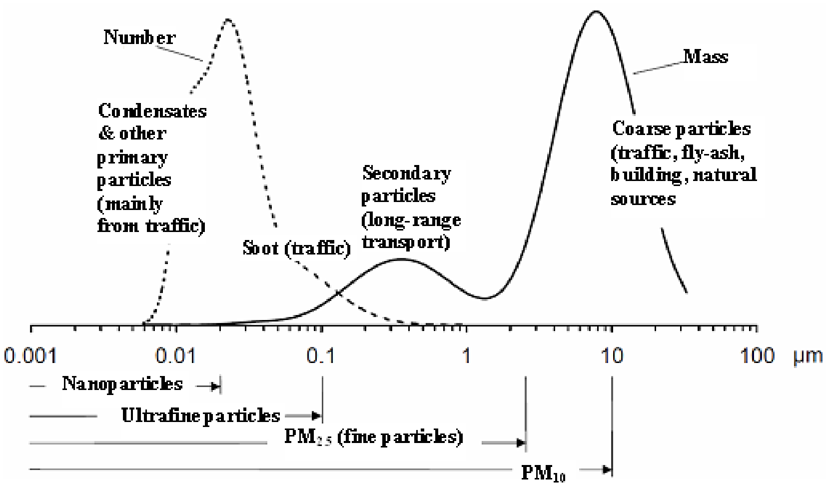

Figure 2: Size distribution of particles emitted from different sources

[Adapted from Danish Environmental Protection Agency data (2008).]

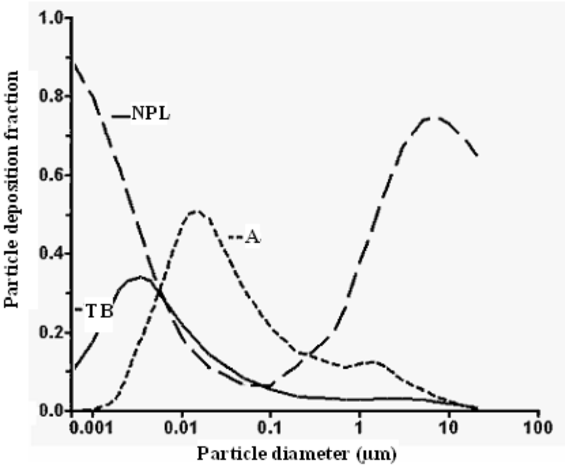

Figure 3: Size based distribution of inhaled particles in the human respiratory tract
[A: Alveolar, TB: Tracheobroncheal, NPL: Nasal, Pharyngeal, Laryngeal) (adapted from Forsberg (ICRP, 1994).]

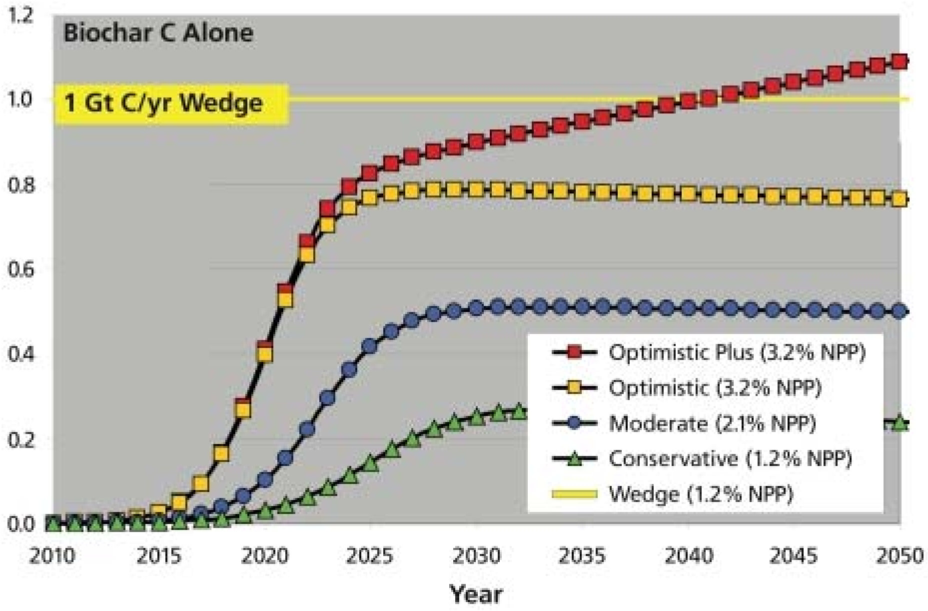

Figure 4: Four Scenarios for potential carbon offsets from biochar between years 2010 and 2050

(International Biochar Initiative, 2009)

Chapter III. Biochar and soot black carbon in forest soils of Yosemite National Park: age, source, prescribed fire effects and soil carbon changes

Biochar and soot black carbon in forest soils of Yosemite National Park: age, source, prescribed fire effects and soil carbon changes

Abstract

This study encompasses two related investigations of the chemical and radiocarbon properties of soot and biochar forms of black carbon materials deposited in the soil after biomass burning and fossil fuel combustion. First, the potential soil carbon implications of biochar black carbon produced from prescribed forest fires in Yosemite National Park (YNP) located in California, USA, was explored. Secondly, the possible age and sources of soot black carbon particles in surface soils of the same site were assessed. For both investigations, soil from 0-5 cm depth was collected after prescribed fires in six YNP sites along an elevational gradient ranging from 1148 m to 1992 m. Non-burned sites adjacent to burned sites were sampled as control. In unburned soils, surface litter was collected and in burned soil, charred materials were collected from the surface above the sampled soil. For the first study, we investigated the possibility of biochar BC from forest fires helping in the accumulation and storage of carbon in the pedosphere of YNP. We also analyzed the carbon content in soil after prescribed (controlled) forest burns and produced biochar in the laboratory to assess how much biochar BC may form from these forest management practices and how such fires influence the carbon budget in the terrestrial system. Reduction in surface soil organic carbon and total concentration from prescribed fires in four of six sites was observed. The relative biochar BC concentration from ^{13}C NMR spectroscopy was observed to be higher in post-burn soils than controls in five of the six study sites. Higher rates of biochar production were noted at 222°C than at 450°C, independent of source biomass types. The aromaticity of these biochars produced

in the laboratory show that prescribed burning in pine species dominated forests may not yield as much refractive and soil carbon-sequestering biochars as in other or mixed vegetation areas, which are found in our study sites. The average potential biochar BC production from biomass in the study sites was calculated to be 138 gKg^{-1} biomass at 450°C temperatures and 68 $g\ Kg^{-1}$ biomass at 222°C temperature. Although these quantities are merely indicative of ideal natural conditions of burns, they represent significant numbers in terms of potential conversion and preservation of carbon that could otherwise be lost of the atmosphere by degradation and decomposition of dead biomass. For the second study, we conducted radiocarbon analyses of soot BC particles in the above YNP surface soils to find out the proportions from burning of modern/ ancient biomass and from the combustion of fossil fuels and to explore possible effects of prescribed burning on the amount of BC produced recently as well as historically. The relative contribution of radiocarbon (^{14}C) dead carbon to soot BC, litter and biochar BC deposited in the soil was determined using accelerator mass spectrometry. The average soot BC concentrations in the study sites were found to range from 0.52 to 4 g BC Kg^{-1} soil. Both post-burn and control soils in all the sites demonstrated radiocarbon values indicative of a mixture of both contemporary and radiocarbon dead carbon. On average, the radiocarbon-dead BC contribution to the soot BC in Yosemite soils was approximately one third of the total of soot BC. All sites showed higher radiocarbon-dead BC content in the post-burn soil than unburnt (control and pre-burn) soils except for one site. This fossil fuel BC in these surface soils could be from historical park traffic and from non-local sources.

1. Introduction

Black carbon in the form of biochar or charcoal has high carbon sequestration potential, i.e. it can store carbon in soils for a long time, diminishing its release to the atmosphere and helping climate change mitigation. Aerosol black carbon, in the form of soot, is the most potent short-term greenhouse-warming particle. Instant decrease in such emission would likely lead to a rapid reduction in temperatures. This study encompasses two related investigations of the chemical and radiocarbon properties of both these forms of black carbon materials deposited in the soil after biomass burning and fossil fuel combustion. First, the potential soil carbon implications of biochar black carbon produced from prescribed forest fires in Yosemite National Park (YNP) located in California, USA, was explored. Secondly, the possible age and sources of soot black carbon particles in surface soils of the same site were assessed.

1.1. Potential soil carbon implications of biochar black carbon produced from prescribed forest fires (Study 1)

The Central Valley of California encompasses forests and rangelands regularly treated with low intensity prescribed burns, which consume forest undergrowth and dead biomass under strictly controlled and monitored conditions. The burned biomass produces black carbon (BC) in the form of aerosol soot emitted to the atmosphere and char (biochar) left on the soil surface as residue. Immediately after such fires, emitted BC particles larger than 1 μm may fail to become airborne or may otherwise quickly drop to the nearest surface (Clark et al. 1997, Masiello 2004). Larger BC particles and charred materials may not be transported and may instead remain on the soil at, if not close to, the place of production and deposition. The C: H: N ratio of BC can vary widely but its carbon concentration is on average, over 60%, with accessory elements hydrogen, oxygen, nitrogen and sulfur (Goldberg 1985).

By enhancing char BC production, prescribed burns could curtail carbon emissions that would be expected from degradation of the source biomass as well as from soot BC emissions biomass fires. Whereas airborne soot from prescribed burns can influence air quality and climate change, time and natural processes can mix and accumulate deposited and residual char BC materials with the soil, promoting C sequestration and enhancing nutrient sorption (Shrestha et al. 2010 and references therein). For such BC production process to function as part of an energy efficient carbon sequestration mechanism with minimization of soot BC emissions from controlled burns and biochar BC productions operations, all pyrolysis conditions need to be optimized to maximize the yield of BC residue or biochar with respect to initial biomass. Carbon sequestration with biochar points to the possibility of sequestering carbon by biasing biomass pyrolysis practices to yield high proportions of refractory BC char residues from the majority of the initial carbon burnt (Ball 2008). Essentially, a small decrease in combustion efficiency may increase the yield of biochar, providing greenhouse gas offsets and carbon sequestration. Another significant benefit is the reduction in emissions of particulates and other emissions which harm human respiratory health. The mechanism by which biochar formation could be enhanced during pyrolysis was explained in the earlier chapter (section on formation models of BC).

To improve our understanding of char BC formation in nature and in controlled environments as well as its carbon sequestration potential, we employed laboratory biochar production, the assessments of the carbon content of char BC and the analyses of the distribution of different carbonaceous materials in prescribed burn exposed soils and biochar. We investigated the ^{13}C NMR composition of such BC in prescribed burns affected areas, the effect of burning on the type and quantity of carbon in surface soils and the actual and potential yield of BC relative to biomass and total C in these sites. We incorporated these BC residue (biochar) and soot data into a soil carbon budget or allocation model for our study sites.

Through this study, we also sought to determine the effect of prescribed fires on soil carbon and BC. If biochar formation could be increased and decrease of organic carbon through volatilization be minimized during prescription burns, carbon enhancement in the soil would be promoted while wildfire hazards are reduced and forest health is maintained. Most carbon budget and emissions studies on forest fires concentrate on non-BC carbon forms and gaseous emissions. This study incorporates BC residues on and in the soil into a carbon mass balance for Yosemite National Park.

1.2. Age and source of black carbon in surface soils of Yosemite (Study 2)

The physical, chemical and radiocarbon properties of BC can be exploited to examine past and current combustion, emissions, and land fire histories. Black carbon derived from fossil fuel is fully depleted in radiocarbon species (^{14}C), whereas BC from combusted biomass reflects approximate atmospheric ^{14}C abundance of the time when the biomass of origin was created, minus decrease through radioactive decay. This property makes BC a good tool to assess emissions from fossil fuel combustion, which may not be identified or quantified adequately through other means. For this reason, BC in sediments, soils and aerosols has been used for paleontology, particulate pollution analysis and emission source apportionment studies with the use of radiocarbon species (Masiello and Druffel 1998; Reddy et al. 2002).

In the Central Valley of California, poor horizontal dispersion of pollutants and high-pressure inversion events caused by topography often exacerbate the effect of emissions from biomass burns and fossil fuel combustion. Measurements of these emissions typically include non-BC carbon forms and particulate matter, often not accounting for BC soot emissions and residues in the soil.

This part of the study investigated the radiocarbon properties of the soot BC in the surface soils of Yosemite National Park in Central California and the effect of prescribed burning on these BC particles. Determining the age of the soot BC, we sought to determine the contribution of fossil fuel versus modern and ancient biomass combustion to these particles in the soil.

2. Materials and methods

Studies of BC can be associated with diverse environmental aspects ranging from global C flux to fire histories. Different detection and analysis methods are needed to answer questions related to these different environmental events and BC from different combustion continuums. These methods are based on the definition and type of BC that has to be extracted. This study focuses on total BC yield and char BC, so, it includes two specific methods: (i) the Simpson and Hatcher (2004b) method and (ii) the CTO-375 method (Gustafsson et al. 1996 and Lim et al. 1996). The Simpson and Hatcher (2004b) method employs sodium chlorite in a chemical oxidation method to remove lignin and non-BC aromatic compounds from organic matter. Cross-polarization magic angle spinning (CP-MAS) ^{13}C-Nuclear Magnetic Resonance (NMR) spectroscopy is used for BC measurement in the residue. This method isolates charcoal, soot and other inert non-oxidizable forms of carbon. The CTO-375 method involves thermal oxidation and volatilization of organic carbons at 375 °C, followed by *in situ* acidification of samples to remove inorganic carbonates, leaving soot BC residues to be analyzed for radiocarbon species and other information or to be quantified with carbon elemental analysis. The field sampling protocol for both methods was common. Below, we describe each of these goal specific analyses separately, starting with experiments associated with the ^{13}C NMR analyses.

2.1 Sampling

In years 2007 and 2008, we collected surface soil (from 0-5 cm depth) and the overlying surface litter (biomass, charred matter) after prescribed fires in Yosemite National Park (YNP) locations along an elevational gradient (Figures 1 and 2). The effect of elevation was not a focus of this paper but simply a convenient approach for sampling and representation of data. Also, the different study sites for sampling were only decided close to or after the time of the prescribed burns, which were implemented by the Yosemite National Park Service based on optimum environmental conditions such as temperature and moisture a short time before the burn. The samples were dug out using metal trowels which were also used to delineate and carve out approximately 10×10 sq.

cm. quadrants for sampling from each point. The treatment for these samples are denoted as ‘post-burn’ in this paper. Non-burnt control sites adjacent to burnt sites were sampled as ‘control’ in the Yosemite Valley-5 (YV-5), Wawona School (WA or WA School), Foresta and Hodgdon (BOF) sites. Only Mariposa Grove (MG) sites, MG10 and MG13 were sampled before (denoted as ‘pre-burn’) and after the fires (denoted as ‘post-burn’). The sampling method within each treatment in each site was random, with three replicates from each post-burn and pre-burn (where applicable) treatment and only two from each control treatment, owing to limited availability of non-burnt area of similar topographic properties close to burnt areas after the prescribed burns. We avoided slopes, and areas close to vehicular traffic. Each replicate sample was collected approximately 100 m apart. Prescribed burns were conducted in these sites by the National Park Service in YNP depending on the optimum environmental conditions, allowing for BC sampling approximately 1-2 weeks after the burns. Precaution was taken to sample in sites exposed to precipitation after the burns. Table 1 shows the frequency of such burns in the past and the year of the last burn, which is also the year we collected the samples for this study. The dominant vegetation type in each site is also listed.

All the collected samples were placed separately in zip lock bags and transported back to the laboratory in coolers. They were all air dried and sieved through a 2mm sieve to remove rocks and litter. Subsamples of equal mass were taken from each sample for lab analyses. In the case of time intensive analyses such as ^{13}C NMR spectroscopy and accelerator mass spectrometry for radiocarbon species, these subsamples were mixed in equal proportions to form composite soil samples reflecting all the samples within a site and treatment equally.

2.2. Chemical oxidation and ^{13}C-NMR analysis

Simpson and Hatcher (2004) employed the sodium chlorite chemical oxidation method to remove lignin and non-BC aromatic compounds from organic matter. Cross-polarization magic angle spinning (CP-MAS) ^{13}C-Nuclear Magnetic Resonance (NMR) spectroscopy is used for BC measurement in the residue. This method isolates charcoal, soot and other inert non-oxidizable forms of carbon, removing non-BC components.

Sodium chlorite (5g), deionized water (200 ml) and acetic acid (5 ml) were mixed with an amount of sample (equivalent to 1 g of total organic carbon), shaken for two hours and centrifuged at 2000g for 5 minutes. The final residue was collected via centrifugation, removing excess salts by repeated deionized water rinses followed by centrifugation. The residue was then treated with 0.3M hydrofluoric acid to remove paramagnetic species (mainly Fe and Mn) in soil minerals that interfere with the NMR signal and increase the resolution of the ^{13}C-NMR spectra (Gelinas et al., 2001; Schmidt et al., 1997; Simpson, 2004) with better signal intensity from mineral dissolution and increased carbon concentration (Baldock et al. 2004). After centrifugation, decantation, one wash with calcium chloride solution for dispersion (additional step, modification from Simpson and Hatcher, 2004b) and 3 washes of deionized water, these samples were freeze dried. This sample preparation technique removes lignin and other oxidizable components in natural organic matter. The residual carbon is assumed resistant to oxidation and falls within the broad definition of BC as charcoal, soot, and other forms of inert and reduced carbon (Simpson and Hatcher 2004b). These samples were sent to Old Dominion University where they were analyzed with CP MAS ^{13}C NMR spectroscopy.

For this method, Cross Polarization Magic Angle Spinning (CPMAS) spectra were recorded on a Bruker AVANCE II 400 spectrometer, operating at a ^{13}C frequency of 100.62 MHz, and a ^{1}H frequency of 400.13 MHz, using a Bruker triple resonance 4mm MAS probe. Approximately 60 mg of each sample was placed in a 4mm zirconium rotor and sealed with a Kel-F cap. The sample was spun at the Magic Angle with a frequency of 13 kHz. The spectra were recorded with a spectral width of 29761.9Hz and the center of the transmitter was at 10061 Hz. A standard single contact time CPMAS pulse was used to obtain the spectra with SPINAL64 proton decoupling and a contact time of 1.5 ms. The ^{13}C and ^{1}H 90^{o} pulses were 4μs and 3μs, respectively. The spectra were externally calibrated with a labeled glycine standard (176.03 ppm for C_1) and were integrated according to the following functional groups: Alkyl (0 - 45 ppm); N-Alkyl/Methoxyl (45 – 60 ppm); O-Alkyl (60 – 95 ppm); Di-O-Alkyl (95 - 110 ppm); Aromatic (110 – 145 ppm); Phenolic (145 – 165 ppm); Amide/Carboxyl (165 – 215 ppm).

The spectra were integrated into the following chemical shift regions: paraffinic carbon (0–50 ppm); substituted aliphatic carbon including alcohols, amines, carbohydrates, ethers, methoxyl and acetal carbon (50–110 ppm); aromatic and phenolic carbon (110–165 ppm); carboxyl and carbonyl carbon (165–215 ppm). The distribution of signal intensity in NMR spectra quantitatively represents the distribution of carbon forms in natural organic materials, with chemical shift values of resonances used to infer the kinds of molecules present (Baldock et al. 2004).

Semi-quantitative estimates of BC concentration are determined from the relative amount of aromatic carbon (aromatic signal at 110–140 ppm in solid-state ^{13}C NMR) and the amount of organic carbon left in the sample after chemical oxidation (equation 1), assuming that the residual aromatic components resistant to oxidation fall within the broad definition of BC as charcoal and soot (Simpson and Hatcher 2004a).

$$\mathrm{BC} = f(\mathrm{aromatic\,C}) \cdot \mathrm{OC}_{\mathrm{oxi}} \quad \text{……………………. (Equation 1)}$$

where, *BC* is BC concentration (g kg^{-1}), *f(aromatic C)* = relative aromatic C fraction; and OC_{oxi} is the OC content after chemical oxidation (g kg^{-1}). We chose to not incorporate the fraction of the original sample mass remaining after chemical oxidation in the above equation because we are only interested in the comparative estimates of BC. We acknowledge that some BC decrease occurs during the multiple chemical and DI washes conducted while preparing the samples for ^{13}C NMR spectroscopy.

Some char samples collected from the forest floor or the surface soil, biochar produced in the lab (at 222°C and 450°C) and samples pre-treated for radiocarbon analysis (CTO-375) were not treated with HF, assuming that they had insignificant aromatics. The aromaticity of char collected from the forest floor was the same regardless of whether it was treated with HCl or not. [1]

---

[1] Note: We observed a small change in aromatic functional group distribution with and without HF treatments. For instance, the aromatic fraction percentage for pre-burn MG10 with no HF treatment was 11.9% whereas as with HF treatment, this decreased to 10.2%.

2.3. Carbon measurement

We conducted Loss on Ignition (LOI) combustion of subsamples to quantify the soil organic carbon contents before any treatment (SOC). Pre- and post-treatment subsamples were analyzed for their total carbon (TC) and nitrogen content using the Fisons NA 1500 Elemental Analyzer. (We were only interested in the C:N ratios.) Post-treatment (implying subsamples after chemothermal and chemical oxidation treatments) samples TC are assumed to represent BC content. Analyses results from non-composited subsamples were statistically analyzed using simple descriptive statistics. Unless specifically stated otherwise, all the results reported in this paper refer to soil from 0-5 cm excluding visible plant materials.

2.4. Lab BC or biochar production

We utilized air dried fresh litter (recognizable mix of leaves, pine), decomposing litter, pine needles and woody biomass (bark, twigs, wood) from the surface samples collected at the study sites in Yosemite for biochar (BC) production on the lab. We combusted these biomass types separately at 222°C and 450°C in a programmable muffle furnace under a continuous flow of liquefied nitrogen (for reduced oxygen environment) for 5 hours. The temperature 222°C was selected based on the average measured temperature 10 cm above the forest floor for prescribed burn with surface fires having flame lengths less than 1 m (Iverson and Hutchinson 2002). The temperature of 450°C was selected to represent a more intense burn, which could be associated with low frequency prescribed burn areas with greater fuel build-up than high frequency prescribed burn exposed sites (Gibson et al. 1990). The biochar yield (BC yield/ fuel biomass) was calculated gravimetrically.

2.5. Comparison of aromatic ^{13}C NMR signals

The ^{13}C NMR for char BC samples from char collected in the study sites and char produced in the lab at 222°C and 450°C were compared. Possible peaks for identification of biomass source versus fossil fuel source and separation of more recalcitrant soot BC from char mass was attempted by plotting the intensity of the peaks against the ppm distribution of the organic functional groups.

2.6. Potential total BC yield per unit source biomass

The BC per unit char was calculated as a product of the aromatic fraction amount obtained from ^{13}C NMR spectroscopy and the total carbon concentration in that char sample, obtained from the total carbon analyzer (Equation 2). The total potential BC per unit source of pyrolized biomass for char produced in the lab was derived from this product and the char yield fraction (Equation 3).

BC per unit char (g Kg^{-1}) = aromatic fraction × total char carbon (g Kg^{-1})……(Equation 2)

Total BC per unit biomass (g Kg^{-1}) = BC per unit char (g Kg^{-1}) × char yield fraction…..…(Equation 3)

Only aromatics proportions were used as multipliers for char BC concentration from ^{13}C NMR spectroscopy and none of the other organic component proportions obtained from ^{13}C NMR spectroscopy were employed for any of the calculations in this paper.

2.7. Carbon mass balance for BC yielding systems

Employing TC and BC data from before and after the chemical oxidation treatment for ^{13}C NMR analysis ($TC_{\text{pre-13C NMR,}}$ $BC_{\text{pre-13CNMR,}}$ $TC_{\text{post-13CNMR}}$ and BC_{13CNM} respectively) as well as BC concentration obtained from radiocarbon data analysis, BC_{CTO375} (described later in this paper), the soil carbon budget was investigated for the 0-5 cm soils in the study sites. An estimate of these soils' inorganic carbon (IC) concentration was derived as the remaining stock of carbon after subtracting the OC and BC from the TC (Equation 4). The IC was assumed to represent carbonates and other non-organic forms of carbon[2]. A distinction between soot BC and char BC as BC_{CTO375} and char BC_{13CNMR} was also made, assuming that all the BC obtained after CTO-375 treatment was from soot and all that obtained after ^{13}C NMR pre-treatment was a combination of both char and soot (Equation 5).

$IC = TC_{\text{pre-treat}} - TC_{\text{post-treat}} - BC_{\text{post13 CNMR}} - BC_{\text{CTO375}}$ ……..(Equation 4)

Assuming that $TC_{\text{post-treat}}$ comprises all and only the organic carbon after chemical oxidation treatment for ^{13}C NMR analyses, including both char and soot BC, and that $TC_{\text{pre-treat}}$ represents all carbon types, including IC.

Char $BC = BC_{\text{post13 CNMR}} - BC_{\text{CTO375}}$ ……. (Equation 5)

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[2] This carbon could potentially be referred to as 'Residual Carbon' instead of 'Inorganic Carbon' as the values are calculated by differences and we did not qualitatively analyze them specifically for inorganic carbon species. However, most these soil samples exhibited effervescence when pre-treated with acidic solutions for both ^{13}C NMR spectroscopy and CTO-375, indicating the presence of inorganic carbonates in the soil matrix. The source of these carbonates could be secondary or pedogenic carbonates as well as the parent materials and carbonate inclusions in them such as calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], sodium carbonate (Na_2CO_3) and/or siderite ($FeCO_3$).

2.8. Chemothermal treatment and radiocarbon analysis for source attribution

The currently most popular chemical-thermal method of soot BC extraction from soils and sediments (Gustafsson et al. 1996; Lim and Cachier 1996) is abbreviated as CTO-375. It involves the thermal oxidation and volatilization of organic carbon (OC) at 375 °C, followed by *in vitro* acidification of samples to remove inorganic carbonates, leaving soot BC residues to be analyzed for radiocarbon species abundance and other properties such as carbon elemental analysis.

Chemothermal oxidation (CTO-375) (Gustafsson et al. 1997, 2001) modified (by adding freeze-drying step at the end) was employed to remove all oxidizable non-soot BC organic matter from the collected soil samples and followed by radiocarbon analysis and source apportionment as described by Reddy et al. (2002). Approximately 200 mg of soil sample was spread across Petri dishes and heated in a programmable muffle furnace at 375 °C for 24 h. The residue was treated with 10% HCl acid and centrifuged. Three washes with deionized water were followed by freeze-drying. These steps ensure removal of organic carbon and inorganic carbonates, leaving only the most recalcitrant carbon form, soot BC as residue in the soil. Standard reference material (SRM 1649a) of diesel soot from the National Institute of Standards and Technology (NIST) as well as n-hexane soot and vertisol SRM from the Black Carbon Ring Trial Group were also treated in the same manner for radiocarbon analysis. No new soot was formed from this method. Due to time and cost constraints associated with Accelerator Mass Spectrometry, composite soil samples as representatives of each site were prepared and used for radiocarbon analysis from the individual pre-treated samples. For comparison, a limited number of individual samples were also analyzed for their radiocarbon properties. Char samples from prescribed burn sites and unburnt litter samples from the control or pre-burn sites were treated with dilute HCl to remove inorganic carbonates but not exposed to CTO-375 due to the oxidative combustion step, which was observed to convert the char and litter to ash in some cases. The treated soil samples were analyzed for total carbon to estimate the total soot BC present per unit mass of soil in the study site (see earlier section on carbon balance).

All the pre-treated samples were transported to Lawrence Livermore National Lab and placed in separate quartz tubes with cupric oxide and elemental silver. These tubes were attached to a vacuum line, evacuated, flame sealed and combusted at 850 °C for 5h. The released CO_2 was isolated through a series of cold traps, and quantified by manometry. Approximately 10% of the CO_2 was separated and analyzed for $\delta^{13}C$. The remainder was reduced to graphite and analyzed for ^{14}C with Accelerator Mass Spectrometry (AMS). Carbon isotope (^{13}C and ^{14}C) composition of the samples was reported as $\delta^{13}C$ and $\Delta^{14}C$ values. The $\delta^{13}C$ data is the fractional deviation of the isotopic ratio of the sample from the same ratio in the international standard Peedee belemnite (PDB) carbonate (Craig, 1957). The $\Delta^{14}C$ data (analogous to $\Delta^{13}C$, with NBS oxalic acid as the standard) is corrected, for isotopic fractionation from photosynthesis, to constant ^{13}C concentration ($\delta^{13}C = -25\%$). Fraction modern (fM) values were obtained from the $\Delta^{14}C$ data. These values provide a quick estimate of the relative radiocarbon concentration and contribution of contemporary or modern carbon (fM = 1) versus radiocarbon dead carbon or fossil fuel source (fM = 0) to a carbonaceous substance. For calculations and corrections, a contemporary atmospheric (background) fM value of 1.053 was used for California for the year 2007 (Riley W., personal comm. 2008) (equation 2 and 3). Pre-nuclear test atmosphere varied a bit with sunspots and fossil fuel combustion and had $\Delta^{14}C$ near 0. Negative $\Delta^{14}C$ values indicate that on average, the ^{14}C has resided in soil organic carbon (SOC) long enough to have undergone radioactive decay. Positive $\Delta^{14}C$ values indicate that the soil must be cycling rapidly enough to have incorporated significant amounts of the elevated ^{14}C from atmospheric nuclear bomb tests (Saleska et al. 2002). Fossil fuel comes from static reservoirs old enough for all of the initially incorporated radiocarbon to have decayed. The $\Delta^{14}C$ values for fossil fuel will therefore approach -1000 ‰ (negative 1000 per mil), indicating essentially no detection of radiocarbon from fossil fuels. New plant matter carries the ^{14}C signal of the CO_2 from which it was formed. Therefore, BC from more recent biomass has young radiocarbon age and low radiocarbon depletion. For the samples, the fc value indicates the fraction of a sample containing radiocarbon species versus the fraction that is radiocarbon-dead (1-fc) (equation1-6).

Since,

$$\Delta^{14}C = \left[fM \cdot \exp(\lambda \cdot [1950 - Y]) - 1\right] \cdot 1000 \qquad \text{Equation 2}$$

Where

$$\lambda = 1 / \left({}^{14}C\right) mean - life \qquad \text{Equation 3}$$

$\lambda = 1/8267 = 0.00012097$; and Y = year of sample collection

$$(fM)_{atm,Y} = \left[\left(\Delta^{14}C/1000\right) + 1\right] / \left[\exp\left(0.00012097 \cdot (1950 - Y_c)\right)\right] \qquad \text{Equation 4}$$

$(fm)_{atm,Y}$= fM of the atmosphere for year Y. Then, for the samples,

$$(fM)_{sample} = R_{sample} = {}^{14}C / {}^{12}C \qquad \text{Equation 5}$$

R_{sample} is calculated as $^{14}C/^{12}C$ of the sample, relative to 0.95 times oxalic acid standard.

The fraction of the contemporary carbon (*f*C) in the sample is calculated using the time-dependent ^{14}C concentration of the (living) biosphere in order to compensate for any bomb-derived ^{14}C from living biomass in that sample using the following equation and method (Reddy et al. 2002, Riley W. and Guilderson T., *personal comm*. 2008)[3]:

$$fC = fM_{sample} / fM_{atm} \qquad \text{Equation 6}$$

where fM_{atm} is the *f*M of the atmosphere at the time of BC formation in this study (the year of sampling or deposition) (Currie et al. 1989), and *f*C and fM_{sample} are the *f*C and *f*M values of the sample. As stated previously, the fM_{atm} employed was 1.053 for the year of sampling.

The radiocarbon-dead[4] fraction of BC is then calculated as $= 1 - fC$ Equation 6 (Reddy et al. 2002).

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[3] We acknoweledge that this calculation may yield some errors for trees and similar perennial vegetation that continuously integrate the fM of the atmosphere into their biomass stocks.

[4] ‘Radiocarbon-dead’ implies absence of radiocarbon species in the samples.

2.9. Quantification of recalcitrant BC

The total carbon concentration in the extracted soot BC was analyzed using the Fisons NA 1500 Elemental Analyzer, as a measure of the total recalcitrant BC (soot) concentration in the samples. Post-treatment (implying subsamples after chemothermal or CTO-375) samples TC were assumed to represent soot BC concentration.

Unless specifically stated otherwise, all the soil sample results reported in this paper refer to soil from 0-5 cm excluding visible plant materials and charcoal pieces (unless present in the soil in naturally pulverized form before the time of sample collection).

2.10. Statistical analyses

Analyses results from were statistically reported analyzed using simple descriptive statistics. Unless stated otherwise, the reported results represent composites of the samples for each treatment within each site. Results for individual (non-composited) samples are also presented where appropriate and when available for comparison. The independent variable used was treatment (control or pre-burn versus post-burn) to focus on the effect of the prescribed burns on the studied parameters. When possible, the standard errors (±1) and the significance difference between treatments were calculated at 95% confidence interval ($\alpha = 0.05$ level of significance). For analysis of overall means within treatments, two-sample t-test was employed. Although elevation is depicted on the x-axis of some graphs, it is not a focus of this study as an independent variable for statistics and is employed here for general information purpose and convenience in graphical representation of the data.

The above mentioned statistics (standard errors and significant differences) are only presented here for analyses in which 3 or more individual results were successfully obtained after the end of the laboratory extraction and analyses of the samples for the desired parameters. In cases when the adequate number of results was not successfully obtained, such as when the analyzed samples were lost during accelerator mass spectrometry or did not produce enough CO_2 due to minimal carbon concentration, such data points could not be included in the statistical analyses. Reasonable efforts were made to repeat the analyses in such cases as much as possible, as the cost and duration of these expensive and time consuming analyses constrained our ability for such iterations.

3. Results

Biochar black carbon produced from prescribed forest fires and associated soil carbon concentration

3.1. Soil Carbon

Total bulk soil carbon and C:N ratios

The total average soil carbon concentration (before chemical pre-treatment) for 0-5 cm soil depths in the Yosemite study sites ranged from 28 g C Kg^{-1} soil (for Foresta-post-burn) to 80 g C Kg^{-1} soil (for YV5 control) (Figure 3). Four of the six study sites showed decrease in total carbon after prescribed burning. Only WA and Hodgdon sites showed higher total bulk soil carbon in post-burn soils compared to control sites. The average total nitrogen concentration for Yosemite soils ranged from 1 g N Kg^{-1} (for Foresta post-burn) soil to 3.5 g N Kg^{-1} soil (for YV5 post-burn). The C:N ratio ranged from 14 (for MG13 post-burn) to 32 (for YV5 control).

Soil organic carbon from LOI

A decrease in SOC was observed in all Yosemite sites except YV-5. Unpaired 2-sample t-tests showed that prescribed burning decreased SOC significantly in Foresta and Hodgdon (or BOF) (Figure 4).

3.2. Lab biochar (BC) production

At 450°C, the biochar yield for different surface biomass types occurred in this order: decomposing litter>woody biomass>fresh litter>pine needles with insignificant effect of pre-burn biomass amount (Figure 5). At 222°C, the yield was not significantly different among the different biomass types. The average yield of 83% biochar at this temperature was higher than the average yield of 33% at 450°C.

3.3. Aromaticity, BC and total C estimates from ^{13}C NMR spectroscopy

Surface soils

The aromatic proportion of the 0-5 cm soils in the study sites varied from 3% (for WA post-burn) to 20% (for MG13 post-burn). This value was lower for post-burn soils than for control soils for all sites except for WA and MG10 (Table 2).

The relative soil BC concentration based on ^{13}C NMR spectroscopy ranged from 0.3 to 6 g kg^{-1} of soil with total C (after oxidation) ranging from 8 to 107 g kg^{-1} (Figure 6). Post-burn BC amounts estimated from ^{13}C NMR spectroscopy was higher than control in all sites except Wawona. Wawona had lower BC concentration in its post-burn soil than it control. These values were low, from 0.3 to 3.5 g kg^{-1} soil.

Forest floor (field) char

The aromaticity of char collected from the forest floor was not affected by HCl pre-treatment but there were differences in total carbon contents. The reason could be the carbonates and other inorganic forms of carbon in the source biomass that were preserved in the charred materials (biochar) during prescribed burn induced pyrolysis. The total relative BC concentration ranged from 75 to 502 g kg^{-1} char (Table 3).

Biochar produced in the lab

The aromaticity of char samples produced in the lab was greater for 450°C than for 222°C, with mean values of 0.7 and 0.2 respectively (Table 4). The type of biomass used to produce biochar at 450°C didn't influence its aromaticity. In comparison, the average aromaticity of char samples from prescribed burns was 0.6, which appears close to that of char produced at 450°C. The 222°C values appear close to that of post-burn soil aromaticity (Table 2). The average concentration of recalcitrant stock BC was calculated to comprise 188 and 393 g Kg^{-1} for biochar generated at 222°C and 450°C respectively (Table 5) compared to 162 g Kg^{-1} for field collected char. Biochar produced at 450°C displayed aromatic proportions in the range of 67 to 70% for all biomass types while it ranged from 13 to 25% for 222°C biochar, with least aromaticity from pine needles and highest from mixed litter.

Total BC per biochar yield at 450°C was higher than at 222°C (Table 5). Aromatic functional groups and total carbon observed at 450°C also appeared higher than at 222°C.

Soot BC from chemical thermal treatment (CTO-375)

The average aromatic concentration of soot BC (as extracted from CTO-375) detected by ^{13}C NMR for 4 sites (MG10 post and pre, MG13 and WA) was 22%, ranging from 18 to 25%. The aromaticity of all those samples was approximately 0.2. These values appear closer to that of the char produced in the lab at 222°C and the post-burn soils, as mentioned above.

Standard Reference Materials

The aromaticity of both Chernozem and Vertisol Standard Reference Materials treated similarly to the soils above was 0.1 with relative BC contents of 1.3 and 2.8 g kg^{-1} soil respectively. This aromaticity value was close to those of all the post-burn surface soils except for Wawona which showed values less than 0.06 for both post-burn and control. That of Diesel Soot (NIST 2975) was 0.5 with relative BC concentration of 389 g kg^{-1} soot. These soot values are comparable with the char from surface soils in the prescribed burn site as well as with biochar produced in the lab at 450°C.

3.4. Total BC yield per unit biomass

The maximum potential BC production per unit mass of forest floor biomass was observed to be 180 g Kg^{-1} for woody biomass pyrolized at 450 °C (Table 8). This amount was the lowest for pine needles (82 g Kg^{-1}). The lower pyrolysis temperature of 222 °C yielded not only lowered total BC per unit mass of biochar but also lower potential BC yield per unit of source biomass.

Prominent peaks in ^{13}C NMR spectra (for biomass derived BC or char identification)

Field char samples

As seen in Figure 7, all the char samples from the field sites as well as the reference standard soot (NIST SRM 2975) showed prominent bands or significant peaking between 126 to 127 ppm, part of the aromatic region. The soot signal peaked at 125.7 ppm and the char samples with 127.4 ppm the highest value. All those samples were pre-treated to remove metallic elements only.

Biochar produced in the lab (effects of charring)

All the char produced at 450°C all demonstrated prominent bands at approximately 125-127 ppm, regardless of source material used (Figure 8). The char produced at 222°C showed prominent bands at 71-72 ppm (MG10 pine needles and Foresta pollen cones) and 218 ppm for (Foresta litter).

Soot BC from chemical thermal treatment (CTO-375)

None of the samples which were pre-treated chemothermally (CTO-375) to remove organic matter for radiocarbon analysis and then analyzed for ^{13}C NMR spectroscopy, showed any prominent peaks at 125-127 ppm, demonstrating an absence of biomass char (Appendix). The signals were not as distinct as those of non-CTO-375 treated soil and char samples.

3.5. Soil carbon and soil BC budgeting or allocation

The allocation of carbon and BC types in the soils of the study sites are shown in Table 6. The non-BC inorganic carbon concentration in the surface soils of the study sites ranged from 4 g Kg^{-1} soil (for MG10 post-burn) to 66 g Kg^{-1} soil (for YV5 control). The non-soot char BC concentration, calculated as the difference between BC_{13CNMR} minus

BC_{CTO375} was zero for all sites and treatments, except for a few cases. This implies that all the BC in these samples chemically oxidized for ^{13}C NMR analysis was soot BC, except for MG10 post burn and YV5 post-burn (non-soot char BC of 1 g Kg^{-1} soil) and Hodgdon post-burn (non-soot char BC of 3 g Kg^{-1} soil). The other sites' negative 1 g Kg^{-1} soil non-soot BC values could indicate decrease of BC during the chemical oxidation and sample DI washes, and also indicate an excess of more recalcitrant soot BC in those samples.

Age and source of black carbon

Composited samples

3.6. Soot BC concentration

The soot BC concentration was low in all the samples, ranging from 0.52 to 4 g BC Kg^{-1} soil (Table 8).

3.7. Radiocarbon analysis - $\Delta^{14}C$ and radiocarbon dead BC

Soot BC in soil samples

Black carbon in four of the five post-burn study sites in Yosemite exhibited more negative $\Delta^{14}C$ (or lower ^{14}C concentration) than control (unburned) or preburn soils (Figure 9). All soils, regardless of treatment showed BC with negative $\Delta^{14}C$ values, implying that the samples contain BC that is > 300 years old (Table 7). Calculation and analysis of relative fraction modern (fC) value of the samples showed higher percentage of ^{14}C dead BC in all post-burn soils than non-burnt soil except in Wawona. The difference was 6, 15, 23 and 58 % of total soot BC concentration in MG 13, MG10, Hodgdon, and Foresta. The radiocarbon dead BC in unburned control soils in the same sites ranged from 8 to 21% of total soot BC. We observed no significant effect of elevation on the ^{14}C -dead BC of post-burn soils. Low correlation between ^{14}C dead BC and elevation was observed in control soils (Figure 10). The total average radiocarbon dead BC contribution to the Yosemite site soil BC was 25% ± 17 of total soot BC.

Litter

All the litter samples exhibited positive Δ^{14}C values of 45 to 116‰ indicating their modern age and origin with carbon turnovers of a few years to less than 300 years (Figure 11). The radiocarbon dead concentration was null.

Char

Similar to the litter sample results, all the char samples collected from the post-burn study sites demonstrated positive Δ^{14}C (Figure 12). These values ranged from 35 to 417‰. The radiocarbon dead BC contribution in the samples was also non-existent, except for very MG13, which showed a 1% contribution.

3.8. $\delta^{13}C$

The vertisol standard reference material (SRM) and the n-hexane soot SRM showed respective δ^{13}C values of approximately -29.4 ‰ and -22.5 ‰. The soil samples' δ^{13}C were approximately -24.8 for MG10 post-burn, –29.7 ‰, for MG13 post-burn, and -29.8 for WA post-burn.. The other samples did not release enough carbon dioxide for δ^{13}C analysis during the AMS sample graphitization. The average δ^{13}C for the litter samples from Yosemite sites was -27.5-‰ ± 0.7 (standard deviation). The char samples' values were highest for YV5 (-28.1 ‰) and the lowest for MG13 (-25.9‰), with the average for all Yosemite sites was -27.1‰ ± 1 (standard error).

Individual samples

Radiocarbon analyses of individual samples (Figures 13 and 14) showed a different pattern than the composite sample results. The average of these samples in each site showed negative values from -11 to -750‰. In contrast to the composited samples above, no distinct trend from the effects of prescribed burning on the Yosemite soils' soot BC was observed. All control or pre-burn soils showed slightly greater (but insignificantly different at 95% confidence interval) negative Δ^{14}C values than post-burn soils except YV5 which showed lower negative values, though the difference was not significant at 95% interval. (For Foresta, the control sample data could not be obtained due to technical reasons at the Accelerator Mass Spectrometer facility at Lawrence Livermore lab). The composite MG10 and MG13 samples that were analyzed simultaneously, however, showed greater negative values than the pre-burn ones. One post-burn sample in the MG10 site exhibited positive Δ^{14}C value of 236 ‰ whereas one pre-burn sample showed a positive value of 39 ‰. The results indicate that the carbon in the soot BC in the former one was fixed between 1 to 35 years before 2009 while the later one's carbon was the mixture of rapid and slow cycling materials.

The average radiocarbon dead BC in control soils of individual soil samples in Yosemite soils except YV5 was greater than in the post-burn soils, although none of these differences were significant at 95% confidence interval (FIGURE 14). These values ranged from 21 to 60%. The composite post-burn soils of MG10 and MG13, however, showed greater radiocarbon dead BC contents of approximately 70%. The total average radiocarbon dead contribution to the total soot BC in all the Yosemite sites was 45% ± 21. Combining the total average radiocarbon-dead contribution to the soot BC of all Yosemite site samples (composite and individual) yielded an average contribution of 36% ± 22.

Averaging the individual sample data, the radiocarbon dead BC of the control samples was (insignificantly) higher than the post-burn for 5 out of 6 Yosemite sites. However, the composited post-burn samples which were run at the same time exhibited greater radiocarbon dead BC concentration than the control ones. (We were unable to determine the p-values or the significance of these differences for this parameter because they were single composites of the individual samples.)

After the CTO375 pre-treatment, most of the individual soil samples yielded very little CO_2 during graphitization compared to the composite ones. These findings also indicate that for radiocarbon analyses of soils for radiocarbon dead soot BC may require the preferential use of composite samples rather than individual samples as representative samples, in addition to consideration of analyses costs and duration.

4. Discussion and Conclusion

4.1. Potential soil carbon implications of biochar black carbon from prescribed burns

Employing ^{13}C NMR and total carbon analyses techniques, observed mixed effects of prescribed burning on the concentrations of carbon and black carbon in surface soils of

Yosemite. Our investigation showed mixed results. In addition to these results, the use of biochar samples collected from the field and those produced in the laboratory under controlled conditions provided some insight into the actual and potential BC yield relative to the original biomass and total C. Some other interesting observations were also noted, such as the estimation of burn temperatures by comparing the aromaticity of field and lab produced biochar. We discuss these findings here.

Soil Carbon, nitrogen and C:N ratios

The YV-5 soils had the highest level of total bulk soil carbon, nitrogen and C:N ratios (before chemical pre-treatment), compared to the other sites, which could be because it is the only valley site and is located at lowest elevation. Foresta soils had the least amount of total soil carbon and nitrogen. Though located at a low elevation, this site appeared to have suffered the most damage from a wildfire in 1998, which could have severely depleted its carbon and nitrogen stocks from volatilization during the wildfire and post-wildfire leaching of released carbon and nitrogen compounds. The ten years after this event may not have been sufficient for replenishment of these stocks. The high C:N ratios associated with all the study sites is indicative of the high carbon and low nitrogen concentration in the soils, the result of high nitrogen immobilization by soil microbial organisms, making it unavailable for plants (Leeper and Uren 1993) and/or presence of highly refractive soil organic matter, which could be attributed to the biochar released and stored in these soils from the forest fires. In spite of high C:N ratios, the bulk of biochars comprise recalcitrant organic carbon, thus, N immobilization by soil microbes is expected to be negligible or transient, and the remaining soil organic carbon does not cause mineralization-immobilization reactions because of high biological recalcitrance (Lehmann and Joseph 2009).

Prescribed burning did not appear to affect the bulk soil's C:N ratios in the study sites. However, it had the effect of significantly reducing total carbon and SOC concentration in 2 out of our 6 study sites in Yosemite, with another 2 indicating some reduction. Similar reduction in forest floor carbon and nitrogen was observed after prescribed fires in the Eastern Sierra Nevada Mountains by Murphy et al. (2006) and in the Central Sierra Nevada Mountains by Moghaddas and Stephens (2007) who calculated a decrease of up to 25 Mg C ha^{-1} from more than 80% consumption of forest floor mass and depth. Decrease in SOC and resultant total carbon could have been observed due to reasons already mentioned previously - volatilization of organic components during burning and leaching of organic acids released from burning into lower depths of the soil and eventually the ground water system. Soot BC that is transported and deposited ex-situ would also cause additional deficit in the original terrestrial system's total carbon budget. These processes and decreases occur despite the preservation of a portion of initial biomass during the production of biochar deposited in-situ. This production is dependent on a number of factors, including temperature of the burn. This was also shown by our lab biochar production experimental results discussed below. However, the increase in biochar BC in spite of decrease in total carbon (owing to loss of organic carbon from volatilization/leaching during or after the prescribed burns) is important because of the positive gain in the soil's recalcitrant carbon stock versus the loss of more readily decomposable or volatile carbon forms.

Laboratory biochar yield

Prior studies have found that higher biochar yields occur at low heating rates and temperatures lower than 300 °C due to the dominance of the dehydration step of cellulose, forming anhydrocellulose, its more stable form as explained here (Eckstrom and Rensfelt 1980, Bridgewater and Peacoke 2000, Dermibas 2000 and Vigouroux 2001). Dehydration is the fourth degradation step in pyrolysis, occurring after depolymerization, hydrolysis and oxidation and preceding decarboxylation. At temperatures >300 °C, depolymerization of cellulose occurs, yielding levoglucosan. When the heating rate is faster, shorter time is allowed for the dehydration step, yielding a higher percentage of unstable products that form primary volatile. In agreement with the above, the lab biochar BC production experiments from our study showed higher yield rates at 222°C than at 450C°. The yields from 222°C were independent of biomass types whereas those from 450C° showed the least yields from fresh litter and pine needles. However, the lower pyrolysis temperature also lowered the total relative BC per unit mass of biochar as well as the potential BC yield per unit of source biomass. The higher char yield rate at this temperature compared to that at 450 °C, could not compensate for the lower relative BC content per unit mass of char. These results may help answer the question of prescribed fires temperatures and initial biomass mixtures required to produce more biochar per biomass fuel. The total BC concentration and aromaticity deduced from ^{13}C NMR spectroscopy, indicative of refractive properties, in forest floor chars and soil samples as inferred from this study shed some more light on this aspect.

The laboratory-produced biochar results also indicate that the dominance of pine needles on the soil surface may diminish the aromaticity and recalcitrant property of the produced biochar. Prescribed burning in pine species dominated forests may not yield as much refractive and soil carbon-sequestering biochar as in other or mixed vegetation areas, which are found in our study sites.

Field biochar BC from ^{13}C NMR spectroscopy

The relative concentration of BC biochar from ^{13}C NMR spectroscopy was higher in post-burn soils than controls in all the study sites except Wawona, as would be expected due to the new biochar production from previously unburnt biomass. The reason for this slightly higher relative biochar BC could be attributed to differences in prescribed burn temperatures and residues from previous burns in the control site.

Biochar aromaticity and burn temperature estimation

Heating and burning of biomass forces the rapid conversion of biomass carbohydrates and proteins into highly aromatic residues (Almendros et al. 2003). The bulk composition of BC produced in these residues is dominated by condensed aromatic rings and a few functional groups making it resistant to decay (Dai et al. 2005). The extent of aromatization, macromolecular structure (graphitic vs. diamond) and surface functional group composition of BC is influenced by the type of combustion precursor (vegetation type), the duration and temperature of combustion in the absence of oxygen and the extent of post-combustion aging or weathering (Goldberg 1985). Based on our findings (comparing field and lab produced biochar), the average burn temperatures of the most prescribed burns before sampling in the study sites may have been closer to 450°C than 222°C, if the aromaticity of the field char samples is used as proxy. However, using the same assumption, and using the aromaticity data of BC stored in the surface soils, the previous prescribed burns in the sites may have reached temperatures of approximately

200°C, as reaffirmed by the observed similar aromaticity of the soot BC extracted using the CTO-375 method. Biochar produced around 200°C from prior burns may have been physically broken into much smaller soot particles over long periods due to natural and human factors. The carbon budgeting and allocation analysis of the soil samples also revealed that all of BC in the soils of 3 sampled sites consisted of soot BC.

The laboratory-produced biochar results also indicate that the dominance of pine needles on the soil surface may diminish the aromaticity and recalcitrant property of the produced biochar. Prescribed burning in pine species dominated forests may not yield as much refractive and soil carbon-sequestering biochar as in other or mixed vegetation areas, which are found in our study sites.

The differences among some of the results such as with the total BC concentration in the forest floor field char could be due to the differences in vegetation, source material, frequency of previous burns, and burning conditions such as temperature, airflow and soil and biomass water concentration. Wawona was the only site that showed results that were a bit different compared to the other sites in all measured parameters. In addition to the reasons already mentioned, this sample site was the only one in which was closer to daily human traffic than the others. The presence of an elementary school and associated entities close to the site may have slightly altered the condition and amount of old and newly deposited BC in the area owing to their local emissions and anthropogenic activities. The aromaticity of the soil and the surface char from this site was also the lowest compared to the other sites.

The ^{13}C NMR spectra prominent peaks of the field char and soil samples affirm the absence of any biomass char lost during treatment (Appendix). However, it appears that a presence of a peak in the 126-127 ppm band proves the presence of biomass char but does not prove the absence of fossil fuel soot BC, as this peak was manifested in the standard reference diesel soot spectra as well as in the 450°C lab char samples. In a prior study, this peak, more particularly like 128 ppm band spectra of graphene carbon atoms in well-charred biochar, has been attributed to biochar spectra (Weshaw et al. 2009).

Comparison of prominent bands or peaks between field char and char produced in the lab show possible indication of fire or field temperatures during prescribed burning. The spectra of biochar samples produced at 450°C showed the closest resemblance to the char samples collected from the study sites. This further strengthens our prior observations about the possible temperature of the latest prescribed burns in the study sites derived from the aromatic properties earlier.

Soil BC and carbon mass balance

The soil BC mass balance analysis showed that the valley site (YV5) had the highest concentration of non-BC inorganic carbon, which could be the result of higher initial lithogenic and pedogenic carbonates and sequestration of secondary carbonates compared to the higher elevation sites where erosion may have led to decrease of exposed carbonates through release of CO_2 (Lal, Hassan and Dumanski, 1999) The soil carbon and soil BC concentration is significant because of their implication for carbon sequestration. After char is produced from recent fires, physical and chemical alterations are induced by natural and human causes, and the parts of the initial char that remains mixed and stored in the soil instead of decomposing further or being translocated by wind and water represent the most recalcitrant forms of BC in that soil. Our study sites showed the dominance of soot BC bearing close resemblance to the type of BC that could have originated from prior fires of lower temperatures around 222°C. However, as already mentioned above, it cannot be ruled out that some portions of this soot BC in the soils could contain BC of fossil fuel origin. The analysis of the radiocarbon properties of these soot BC particles from the same study sites investigate and elaborates these possibilities further, as discussed in the subsequent section of paper.

In the US, Lehman (2007) calculated biochar BC yield from pyrolysis of forest residues (200 million hectares of timber production forests), fast-growing vegetation (30 million hectares of idle cropland) and crop residues (120 million hectares of harvested cropland). They observed that in each case, 1.6 billion tonnes of carbon could be sequestered in the soil (10% of annual fossil fuel emissions for year 2005), if the biochar is returned to the soil and not burned. Globally, estimates have shown that biochar could be used to potentially reduce atmospheric carbon dioxide concentration by 37 ppm through the sequestration of 400 billion tones of carbon over this century (Lenton and Vaughan 2009). Findings from our study could help reinforce the importance of such estimates of of biochar production and their emissions reduction potential. Based on experimental burns in the laboratory, Kuhlbusch and Crutzen (1995, 1996) calculated that 1.4% to 1.7% of carbon exposed to fires is converted to BC. Considering this yield, its recalcitrant properties and its long residence time of 2,400 to 13,900 years in soil and sediments (Masiello and Druffel 1998), BC may reduce net CO_2 emission from permanent deforestation by 2–18% (Kuhlbusch and Crutzen 1995 and Schmidt 2004). Similar to

Kuhlbusch and Crutzen, calculations from our study showed that average biochar BC production potential from biomass in our study sites was 138 gKg^{-1} biomass at 450°C temperatures and 68 $g\ Kg^{-1}$ biomass at 222°C temperature. Keeping in mind that these quantities are only indicative of ideal natural conditions of burns, they represent significant numbers in terms of potential conversion and preservation of carbon that could otherwise be lost of the atmosphere by degradation and decomposition of dead biomass.

4.2. Age and source of black carbon in surface soils of Yosemite

The radiocarbon properties of soot BC from the study sites helped us estimate not only their possible ages but also the relative contribution of the radiocarbon-dead sources (fossil fuel or old biomass) versus modern sources (young biomass) to the BC stock in those soils. The results from this study point to the following possibilities, which are discussed subsequently:

- Recent deposition and accumulation of fossil fuel soot BC in these soils is high and/or

- The prescribed fires induced the exposure of old (>300 years), physically protected biomass soot BC and/or

- A high amount of old biomass carbon from the control (unburned) soils was destroyed by the CTO-375 pre-treatment process, compared to the conversion of biomass to soot BC by prescribed burning in the post-burn soils.

Litter , char and soot BC

The radiocarbon concentration of litter and char samples indicate that all of their carbon is of contemporary origin with turnover rates from 1 to 300 years. However, the soil samples from both post-burn and control Yosemite sites demonstrated radiocarbon values indicative of a mixture of both contemporary and radiocarbon dead carbon. In average, the radiocarbon dead BC contribution to the soot BC in Yosemite soils was approximately one third of the total of soot BC. All sites showed higher radiocarbon dead BC concentration in the post-burn soil than unburnt (control and pre-burn) soils except for the Wawona site. In addition to the sampling procedures, the time of the year and the physical location of the sampling impacting the ^{14}C signatures (Klinedinst and Currie 1999), the heterogeneity of the soil, its surface litter or char cover, laboratory conditions, pre-treatment steps and accelerometer mass spectrometry procedures may have caused some differences in the radiocarbon results.

The soil soot BC radiocarbon results point to two possibilities: a high deposition and accumulation of fossil fuel BC in the soils of Yosemite National Park and/or exposure of old (>300 year) physically protected biomass soot BC induced by prescribed burning. Assuming that the radiocarbon dead BC in the samples should comprise a mixture of both old biomass (> 50,000 years) and fossil fuel BC, we could attribute the higher radiocarbon dead BC in the (composite) prescribed burn soils to combustion of old biomass charcoal material or disruption of physical protection of old BC. The CTO-375 method isolates soot BC. So, ancient soot formation and deposition from ancient charcoal or exposure of ancient soot during prescribed fire could have occurred in the study sites. We employed ^{13}C NMR findings to elucidate these findings, as described below.

Freshly produced charcoal exhibits $\delta^{13}C$ values representative of their biomass source. The $\delta^{13}C$ values that were obtained for soil, litter and char samples point to their origin from C3 vegetation which have average $\delta^{13}C$ values of 26‰. Turney et al. (2006) recorded significant isotopic depletion by up to 1.3‰ for temperatures typically reached in natural fires (<450°C), advising for the cautious use of $\delta^{13}C$ for reconstruction of paleoenvironmental and paleoclimatic changes from sedimentary charcoal. This is not the purpose of our study and both the char and ground biomass samples analyzed also were clearly of modern origins. Our results also suggest that the information from these values for the soil samples may also be insufficient for determination of origin (fossil fuel vs. biomass) of the soot BC in the soils and maybe unnecessary when $\Delta^{14}C$ data is available. Furthermore, Bush et al. (2006) observed a high degree of both spatial and temporal variability in the isotopic composition of fossil fuel emissions (up to 3 ‰) which could influence the characterization of carbon sources and sinks when using $\delta^{13}C$ values. If effects of prescribed burns were not considered and if this study extended beyond BC to include fossil fuel CO_2, however, these values could be employed for study of fossil fuel contribution. For instance, Lichtfouse et al. (2003) demonstrated that urban grasses could assimilate as much as 29.1% of fossil fuel derived carbon in their tissues based on their findings of depleted $\delta^{13}C$ values of -35.08 ‰ for urban grass versus -30.59 ‰ for rural grass in Paris. (The global average atmospheric $\delta^{13}C$ is approximately −8‰ and that of fossil fuel derived CO_2 is -20 to -27‰.)

Source and proportion of radiocarbon-dead fraction of BC

The ^{13}C NMR spectra of CTO-375 soil soot BC samples from the Yosemite sites compared to biomass derived spectra, indicated the absence of BC from biomass origin in them (earlier section on ^{13}C NMR and carbon balance). This, in addition to the modern age of the litter and char samples in contrast to the 'ancient' age of the soot BC in the soil samples, indicates that most of the radiocarbon dead carbon in the surface soils' soot BC is of fossil fuel origin, with mixing of some ancient and modern biomass sources. Fossil fuel BC deposition and accumulation from historical park traffic and from non-local sources could have been the cause of this high contribution of fossil fuel soot to the soot BC in the soils, compared to biomass soot BC. Another important inference from this study is how the recalcitrant form of soot BC extracted using the CTO-375 method from these sites are not predominantly of biomass origin, in spite of frequent prescribed burns in recent years and the natural wildfires in the past. Collecting samples from depths below 5 cm may have revealed more soot of biomass origin formed from ancient fires than recent fossil fuel emissions. However, this study was focused on recent production of BC, not ancient ones. The soot BC extraction procedures that we employed may have caused the destruction of some biomass derived soot BC. (The CTO-375 method allows for normal flow of air for oxidative combustion of non-BC organic carbon but does not specifically target the removal of biomass carbon already converted to soot BC.) Two of our individual soil samples, however, contradicted these findings, as their soot BC even after the CTO-375 pre-treatment, showed predominantly modern radiocarbon ages with only 0-1 % fossil fuel contribution. The other samples also showed, on average, more than 50% of biomass-derived soot BC.

Considering that the average soot BC concentration determined from this study were found to be as low as 0.52 to 4 g BC Kg^{-1} soil and the total average fossil fuel BC contribution was estimated to be approximately one third of this total soot BC in the

Yosemite sites, the effect of fossil fuel combustion, transportation and deposition in Yosemite soils should be minimal but studies on how and how much of these particles travel, circulate and deposit in Yosemite National Park should be investigated further. Though this study observed no altitudinal dependence on fossil fuel soot BC concentration accumulation in the soils, its deposition and impact in higher altitudes, particularly the snow covered areas of Western Sierra Nevada facing Yosemite National Park needs to be investigated. Hadley et al. (2010) published the first study of soot BC deposition and accumulation in the Central and Northern Sierra Nevada region in California, attributing Asian BC for one quarter to one third of the total soot BC reaching this region and significantly perturbing the snow melt and surface temperature. However, that study did not specify how much of that soot BC was from a fossil fuel source. Findings from our study and subsequent radiocarbon analyses of the soot BC in the snow of the Sierra Nevada could help determining the contribution of fossil fuel BC on the early and/or accelerated melting of snow in these mountain peaks.

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Tables

Table 1: Frequency of prescribed burns in study sites

[Data shown for years since implementation of prescribed burn policies in Yosemite, and the year of the last burn, which is also the year we collected the samples for this study. Year(s) of prior burn is also shown.]

Site	Last burn	Frequency of burns	Prior burn year(s)	Elevation (m)	Vegetation
YV5	2007	27	1980	1203	incense cedar association ,black oak
WA	2007	7-10	1990, 1997	1472	incense cedar, ponderosa, black & canyon live oak-mountain misery greenleaf & white leaf manzanita
FORE	2008	None reported before 2008. Large wildfire in 1998.	1263		Ponderosa pine and manzanita
Hodgdon	2007	10	1997	1461	incense cedar association, ponderosa pine, white fir association
MG10	2008	3,4, 10	1990, 1993, 1997	1755	incense cedar, white fir, ponderosa pine, giant sequoia
MG13	2008	11	1989	1955	incense cedar, white fir, ponderosa pine, giant sequoia

Table 2: ^{13}NMR based percentage distribution of carbon among functional groups in 0-5 cm soils from the study sites (after 13C NMR oxidation pretreatment). (Sample numbers and standard errors are not shown as these results represent composited samples.)

Site	Treatment	Total Carbon	Total Percentage Carbon In This Form (Fraction ×100%)						
		g kg^{-1} soil	Paraffinic 0-50 ppm	Aliphatic 50-110 ppm	Aromatic 110-140 ppm	O-Subst aromatics 140-160 ppm	Carboxyl & Carbonyl 165-215 ppm	Total BC = Aromatic Fraction × Total Carbon g kg^{-1} soil	Aromaticity
YV5	control	1.1	46.88	40.72	6.52	5.71	0.17	0.72	0.07
	post-burn	2.28	43.34	28.15	10.05	7.25	11.21	2.30	0.10
WA	control	2.43	34.86	45.31	5.34	4.67	9.81	1.29	0.05
	post-burn	1.84	38.76	48.44	3.42	4.22	5.17	0.63	0.03
FORE	control	0.96	49.67	39.32	5.8	4.41	0.8	0.56	0.06
	post-burn	0.84	52.61	33.57	10.58	3.13	0.1	0.88	0.11
Hodgdon	control	0.81	41.36	50.57	4.11	2.84	1.12	0.33	0.04
	post-burn	3.24	39.98	36.2	18.39	4.7	0.72	5.95	0.18
MG10	pre-burn	2.23	63.29	20.79	10.2	5.58	0.15	2.27	0.10
	post-burn	2.29	56.16	28.88	10.5	3.87	0.58	2.41	0.11
MG13	pre-burn	2.30	46.63	41.33	5.04	4.78	2.21	1.16	0.05
	post-burn	1.7	39.22	32.01	20.45	5.76	2.56	3.48	0.20
SRM	Vertisol	2.9	39.6	37.12	9.68	4.21	9.38	2.81	0.10
	Chernozem	1.18	54.91	25.92	11.35	5.59	2.22	1.34	0.11
SRM	Diesel particulate soot NIST 2975	770	18.64	20.72	50.48	8.75	1.41	388.70	0.5

Table 3: ^{13}C NMR based percentage distribution of carbon among functional groups in char produced from prescribed fires in the study sites (after ^{13}C NMR oxidation pretreatment)

Site	depth	comment	Total percentage carbon in this form (fraction ×100%)					Total carbon g kg^{-1} biochar	Total BC = aromatic fraction × total carbon g kg^{-1} biochar
			Paraffinic 0-50 ppm	Aliphatic 50-110 ppm	Aromatic 110-140 ppm	O-substituted aromatics 140-160 ppm	carboxyl & carbonyl 165-215 ppm		
YV5	surface	no HCl	8.48	12.53	52.27	19.47	7.26	145	76
Wawona School	surface	no HCl	24.95	22.71	34.74	11.27	6.32	470	163
Foresta	surface	no HCl	4.12	9.15	69.54	11.95	5.24	491	342
Foresta	surface	HCl	4.46	10.87	69.95	11.37	3.34	337	236
Hodgdon	surface	no HCl	17.43	11.68	48.69	11.05	11.14	154	75
MG 10	surface	no HCl	6.25	11.64	66.9	13.56	1.65	259	173
MG 10	surface	HCl	6.25	11.64	66.9	13.56	1.65	751	502
MG 13	surface	no HCl	9.48	15.25	61.42	9.95	3.9	219	135
MG 13	0-5 cm	HCl	20.47	13.38	51.51	11.73	2.91	580	299

Table 4: Percentage distribution of carbon among functional groups in biochars produced at 222 °C and 450 °C from different source biomass collected at the field sites' control (non-burnt) areas.

			Total percentage carbon in this form (fraction ×100%)				
Site	Source biomass	Pyrolysis temperature (°C)	Paraffinic	Aliphatic	Aromatic	O-substituted aromatics	carboxyl & carbonyl
			0-50 ppm	50-110 ppm	110-140 ppm	140-160 ppm	165-215 ppm
WA	Mixed litter	450	6	11	67	13	3
WA	Pine needles		2	9	71	14	4
Foresta	Wood		4	9	69	15	3
Foresta	Twigs		4	14	68	13	2
Foresta	Pollen cones		3	11	70	13	3
Hodgdon	Mixed litter		3	10	71	13	2
Foresta	Pollen cones	222	29	25	22	14	10
Foresta	Mixed litter		23	26	25	15	11
MG10	Pine needles		24	50`	13	8	6
Diesel soot	SRM 2975	NA	19	21	50	9	1

Table 5: Total BC production potential per unit mass of source biomass pyrolized at 450°C and 222°C

(Where applicable, standard errors are shown. In cases involving aromatic fractions, standard errors are not shown as the multiplier, aromatic fraction, was derived from composite of replicate samples which yielded only one value per type of source biomass.)

Site	Source biomass	Pyrolysis temperature	Total carbon	Total BC in char = aromatic fraction × total carbon	Char yield in lab	Potential BC from biomass = Char yield fraction × BC
		°C	g Kg^{-1} biochar	g Kg^{-1} biochar	% of source biomass	g Kg^{-1} biomass
WA	Decomposing litter	450	509	342	46 ± 5.1	157
WA	Pine needles		556	393	21 ± 4.5	82
Foresta	Wood		740	512	35 ± 13.3	180
Foresta	Twigs		658	444	35	156
Foresta	Pollen cones		560	393	32	125
Hodgdon	Mixed litter		617	438	29 ± 4	129
Average		450				138 ± 56.4
Foresta	Pollen cones	222	592	128	76	98
Foresta	Mixed litter		269	66	86 ± 3.9	57
MG10	Pine needles		488	61	82 ± 4.7	50
Average		222				68 ± 39.4

Table 6: Soil and soil BC carbon mass balance in the study sites.

Shown: estimated contents of inorganic carbon (IC), total carbon (TC) before and after 13C NMR pre-treatment, BC from ^{13}C NMR analysis and from chemothermal oxidation pre-treatment (CTO-365). All samples are from 0-5 cm soils. (Assumption: IC = $TC_{pre\text{-}treat}$ - $TC_{post\text{-}treat}$ – BC_{13CNMR} - BC_{CTO375})

Site	treatment	$TC_{pre\text{-}treat}$ g Kg^{-1} soil	$TC_{post\text{-}treat}$ g Kg^{-1} soil	BC_{13CNMR} g Kg^{-1} soil	BC_{CTO375} g Kg^{-1} soil	IC g Kg^{-1} soil	BC_{13CNMR} minus BC_{CTO375} g Kg^{-1} soil
MG10	pre-burn	43.3	22.27	2.27	2.06	16.7	0
	post-burn	30.4	22.9	2.41	1.22	3.87	1
MG13	pre-burn	46.8	23.04	1.16	1.56	21.04	0
	post-burn	29.7	17	3.48	3.97	5.25	0
WA	control	46.4	24.25	1.29	1.72	19.13	0
	post-burn	58.8	18.37	0.63	1.04	38.77	0
YV5	control	79.8	11.04	0.72	1.79	66.25	-1
	post-burn	63.1	22.84	2.3	1.21	36.75	1
Foresta	control	44.8	9.59	0.56	0.52	34.14	0
	post-burn	30.1	8.36	0.88	1.4	19.45	-1
Hodgdon	control	48.9	8.10	0.33	1.23	39.23	-1
	post-burn	60.6	32.37	5.95	2.97	19.31	3
Merced	control	77.9	56.81	1.12	0.73	19.24	0
	no-burn	134.1	106.9	2.12	3.31	21.78	-1
SRM	Vertisol	31.1	29.03	2.81	4	- 4.74	-1

Table 7: Age or turnover of soil C reflected by $\Delta^{14}C$ (based on Trumbore 2000).

$\Delta^{14}C$	Soil carbon type or turnover
> 100‰	C fixed between 1 to 35 years BP
0 to 100‰	C turnover of decades to centuries or a mix of rapid ($\Delta14C$ > 100‰) and slow ($\Delta14C$ > 0‰) cycling materials
0‰ to - 1000‰	SOC >300 yr
~ - 1000‰	fossil fuel C or extremely old BC

Table 8: Soot BC concentration

(based on total carbon concentration in thermochemically treated surface soil samples)

Site	treatment	BC_{CTO375} g Kg^{-1} soil
MG10	pre-burn	2.06
	post-burn	1.22
MG13	pre-burn	1.56
	post-burn	3.97
WA	control	1.72
	post-burn	1.04
YV5	control	1.79
	post-burn	1.21
Foresta	control	0.52
	post-burn	1.4
Hodgdon	control	1.23
	post-burn	2.97
Merced	control	0.73
	no-burn	3.31
SRM	Vertisol	4

Figures

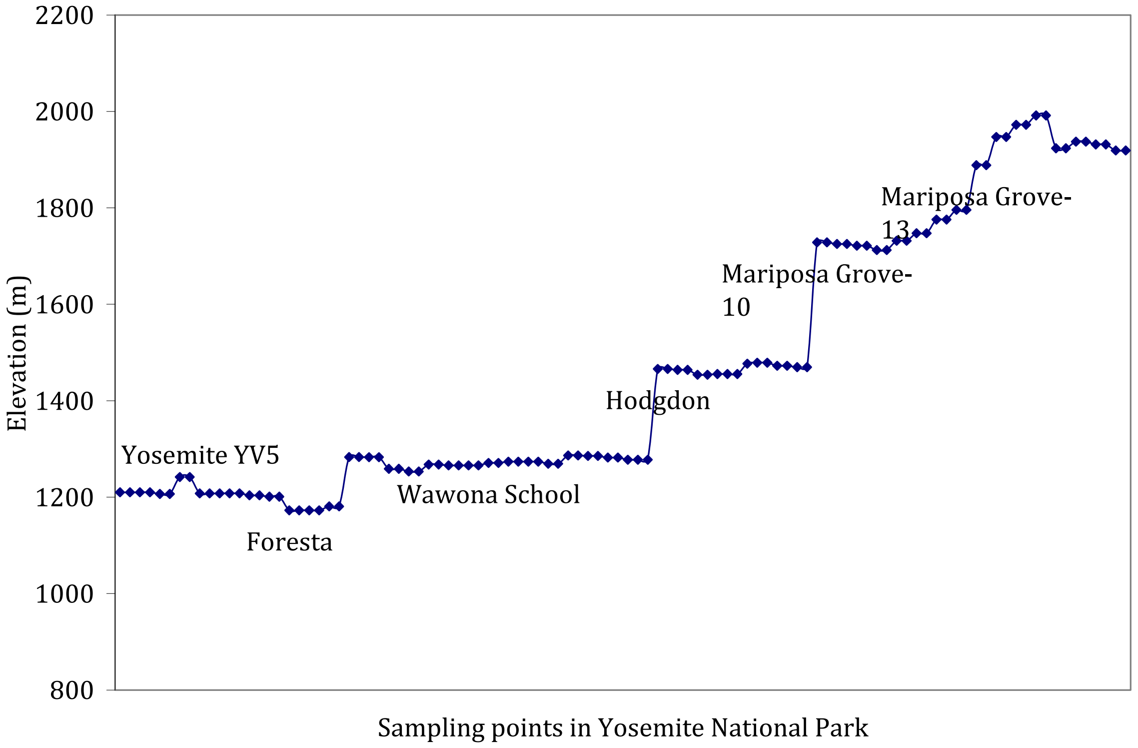

Figure 1: Distribution of sampling points along elevation gradient of the study sites in Yosemite National Park forests.

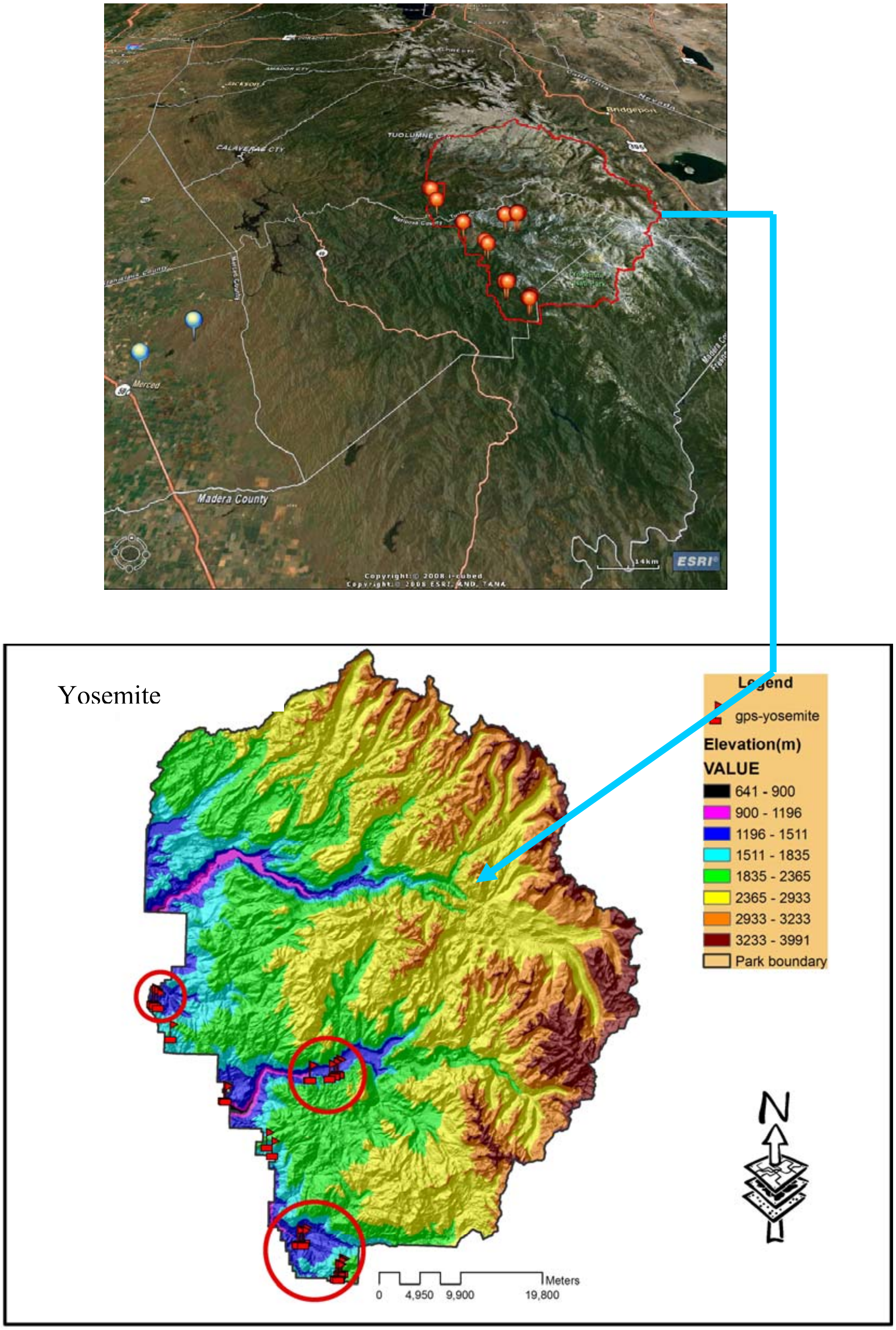

Figure 2: Spatial representation of study site locations with sampling points circled in red.

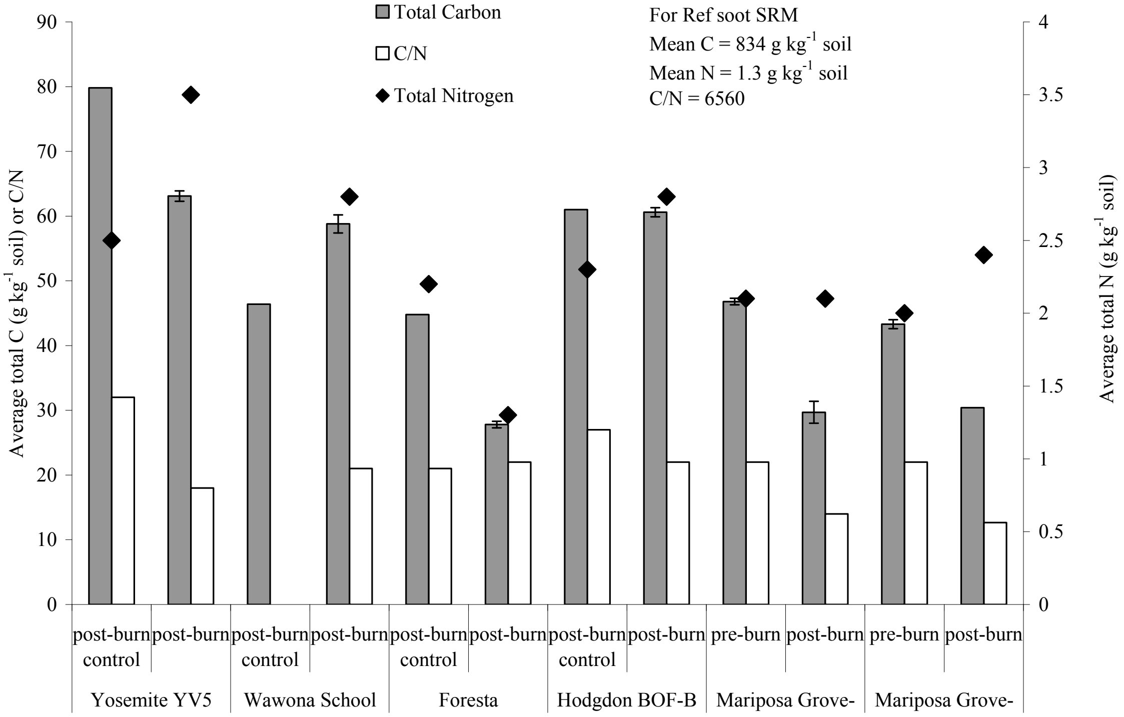

Figure 3: Average total carbon, total nitrogen and C/N ratios of 0-5 cm soils from study sites

[Error bars denote standard errors (SE ± 1). Except for MG sites, n = 3 for post-burn sites, n = 1 for control. For MG10, n for post-burn = 1, pre-burn n = 6. For MG10, n for post-burn = 3 and for pre-burn, n = 6. Error bars only shown for total carbon data as they are the focus of this study.]

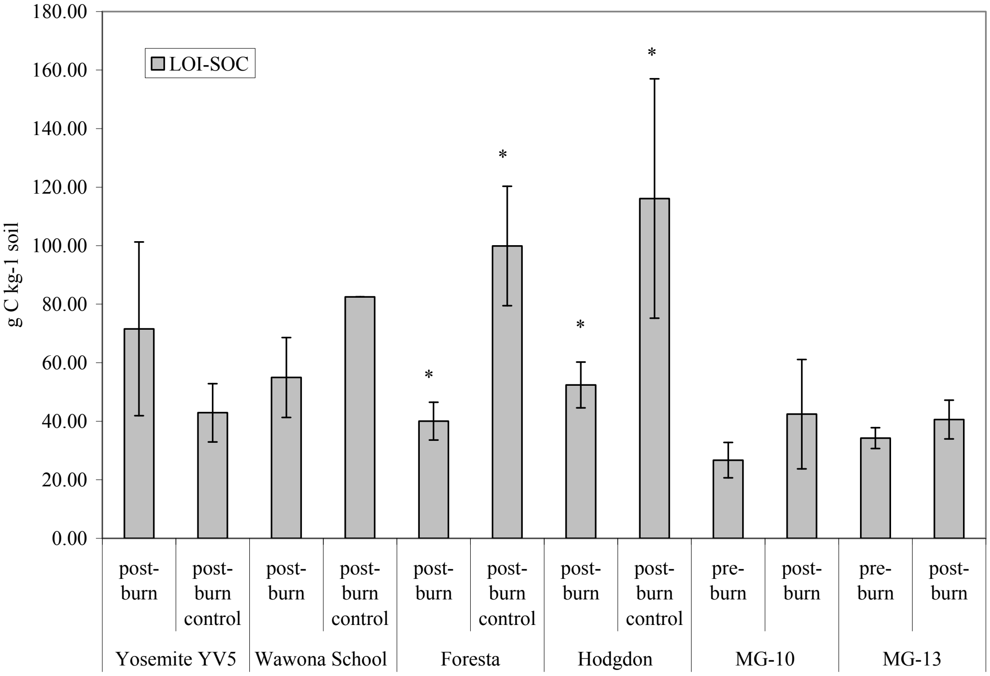

Figure 4: LOI SOC in Yosemite pre-burn, post-burn and adjacent control sites
Error bars denote standard errors (SE ± 1). The symbol * indicates significant difference at α = 0.05 within a site. All data points are from 0-5 cm soils.

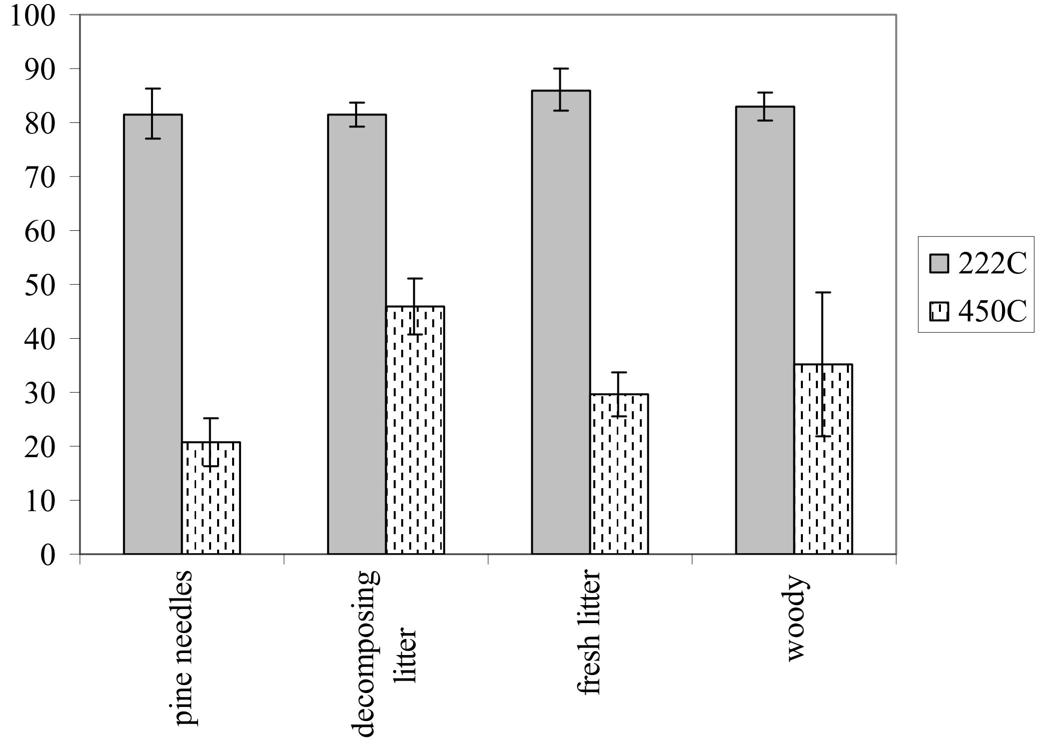

Figure 5: Yield (%) of BC in lab from combustion of different biomass types at 222°C and 450°C for 5 hours in oxygen-reduced atmosphere. Error bars denote standard error (S.E. ± 1)

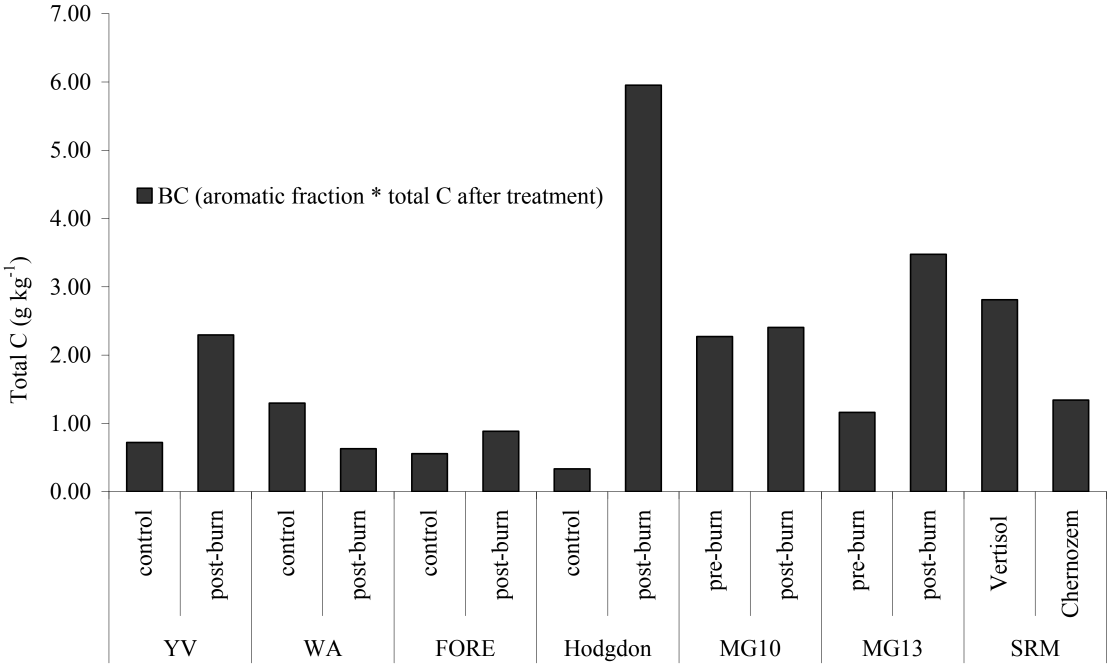

Figure 6: Comparison of relative BC concentration by site and treatment before and after chemical oxidation treatment for ^{13}C NMR analyses (Results are for composited samples, so, standard errors were not calculated)

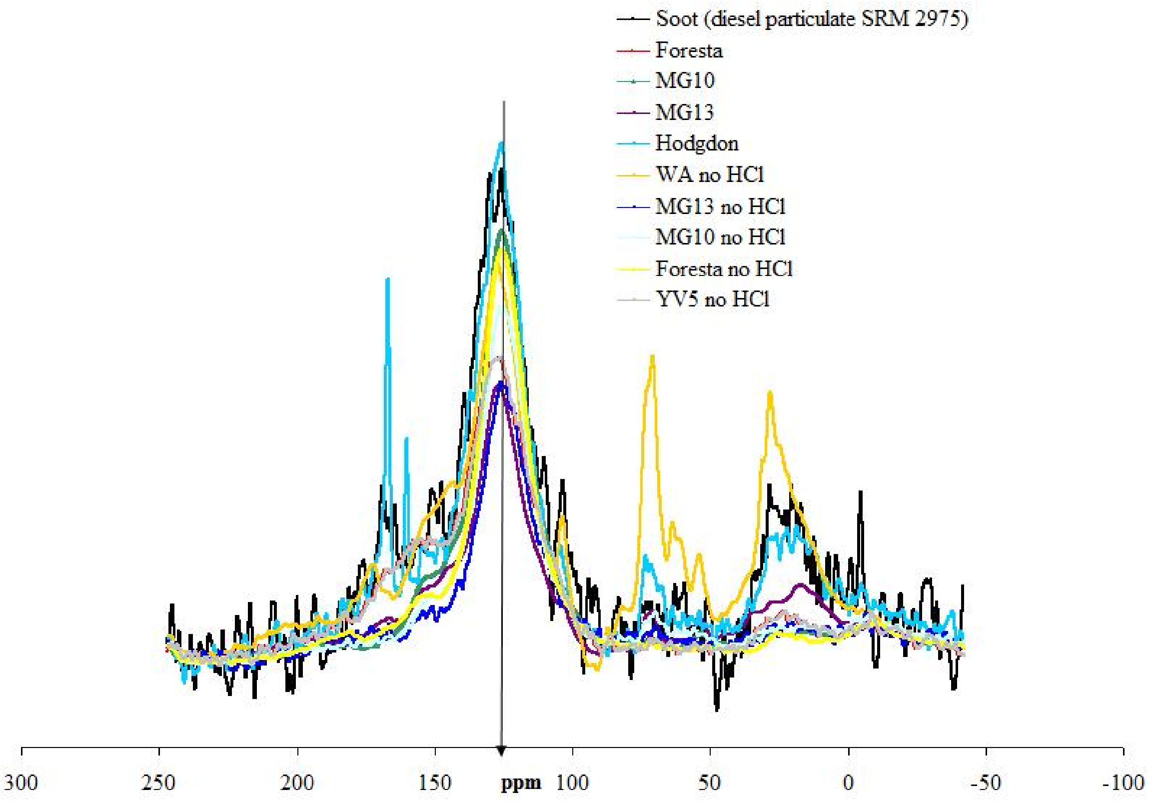

Figure 7: ^{13}C NMR spectra of surface char samples from field sites
(Suffix ‘no HCl’ refers to sample not treated with HCl for inorganic carbon removal. Arrow showing maximum intensity or peak for all samples at 126 to 127 ppm.)

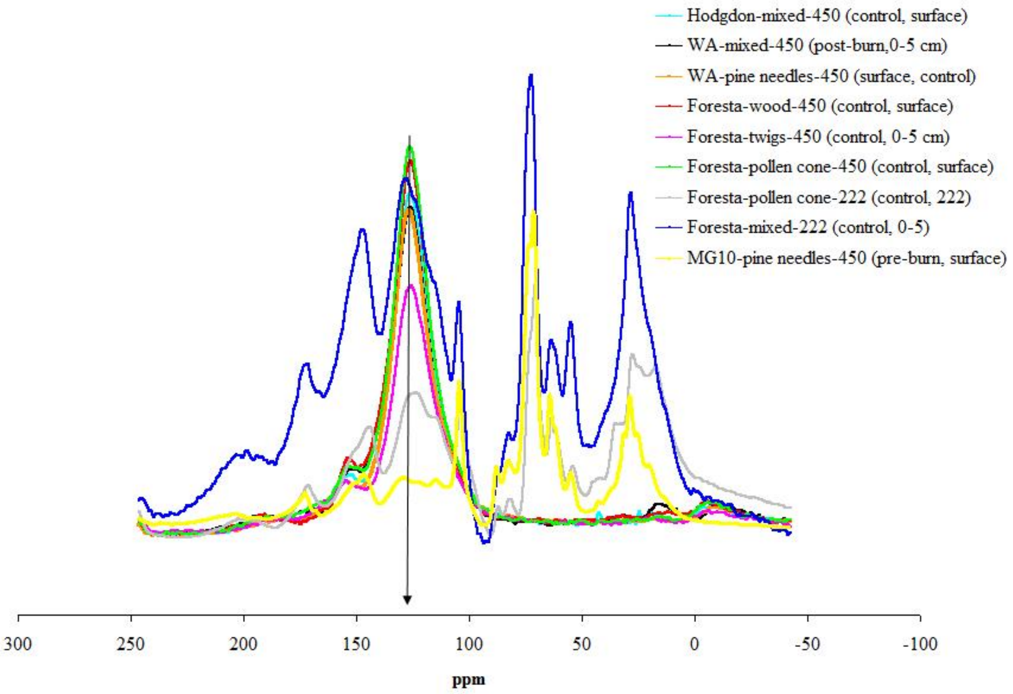

Figure 8: ^{13}C NMR spectra of char produced in the lab at 222C and 450C. 'Mixed' denotes mixed litter.

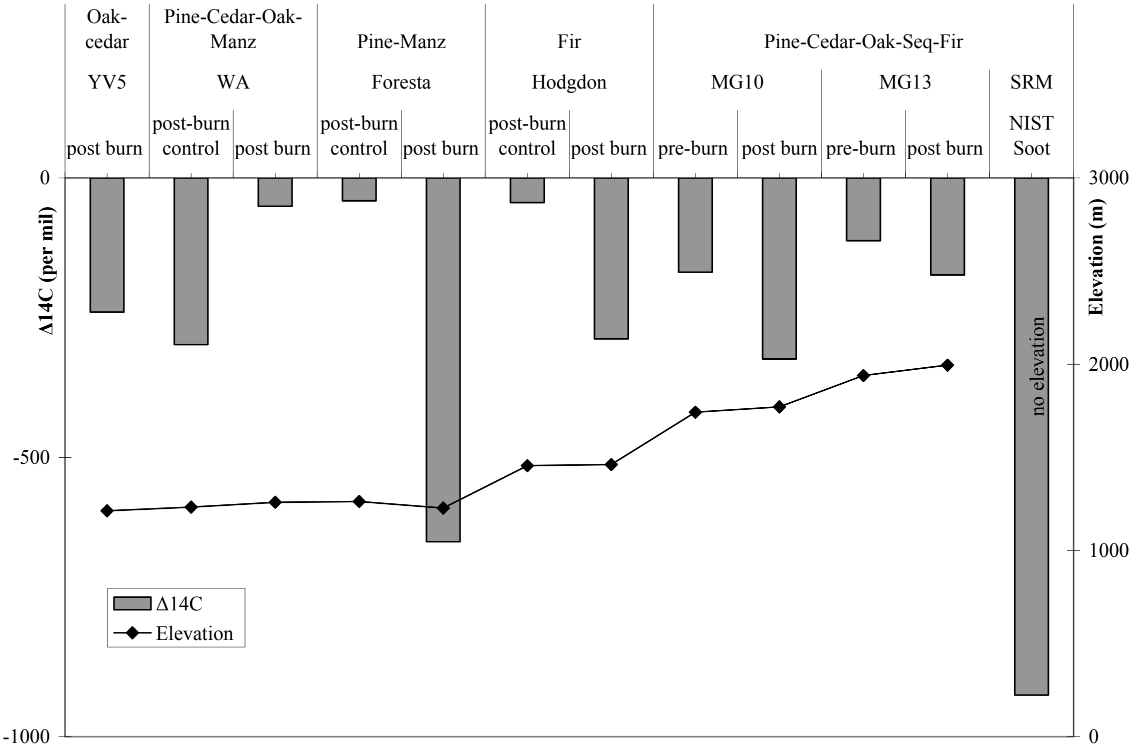

Figure 9: $\Delta^{14}C$ of soil BC for each site, burn treatments and dominant vegetation for composited soil BC samples
(Samples treated with CTO-375 method and AMS)

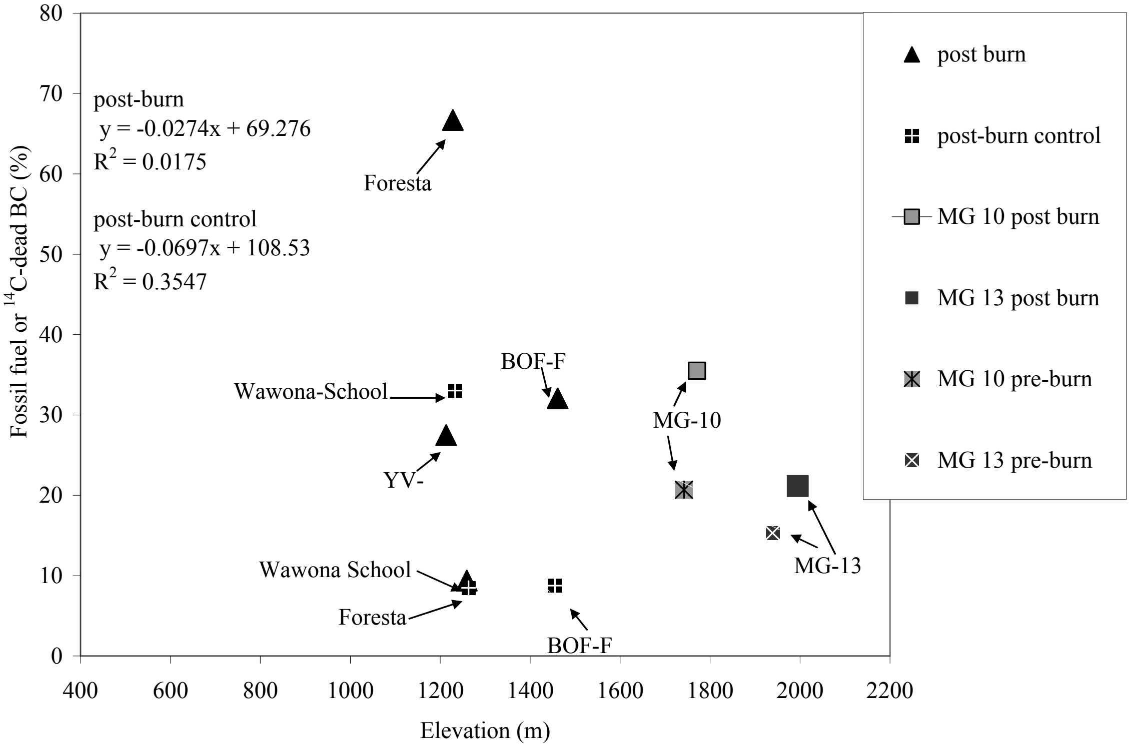

Figure 10: Percentage of radiocarbon dead BC in Yosemite soils
(Percent of total soot BC in the composite samples)

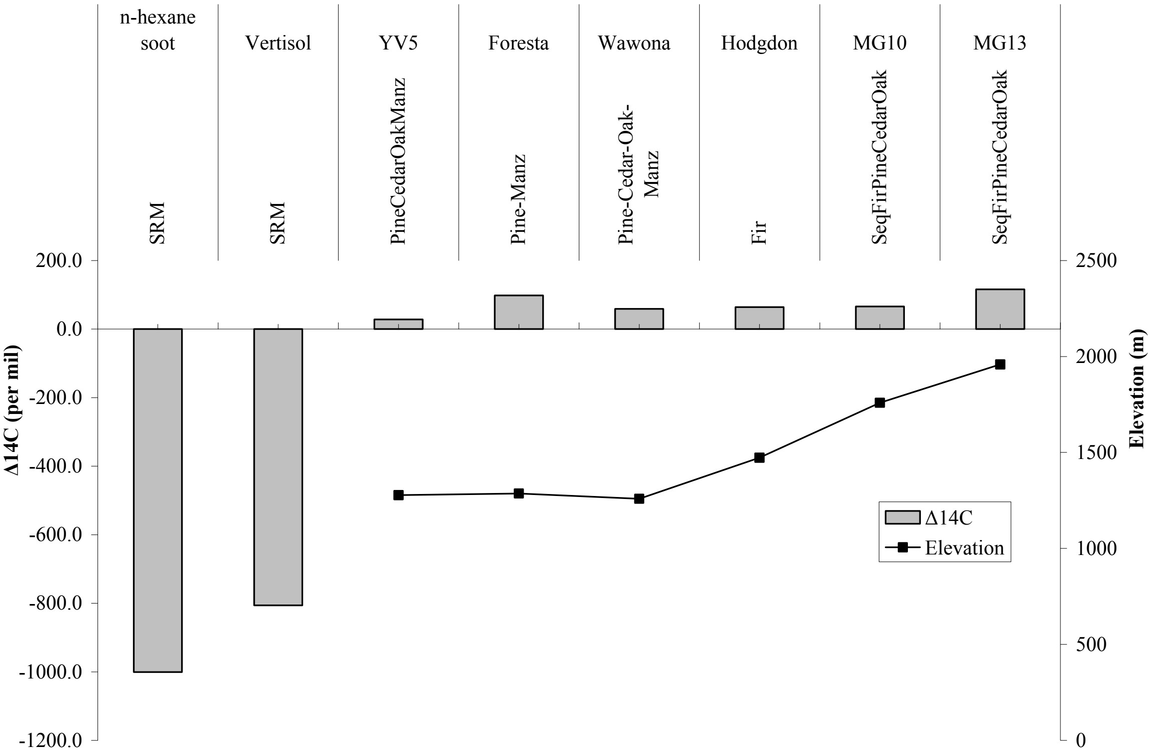

Figure 11: Average $\Delta^{14}C$ of litter from the study sites

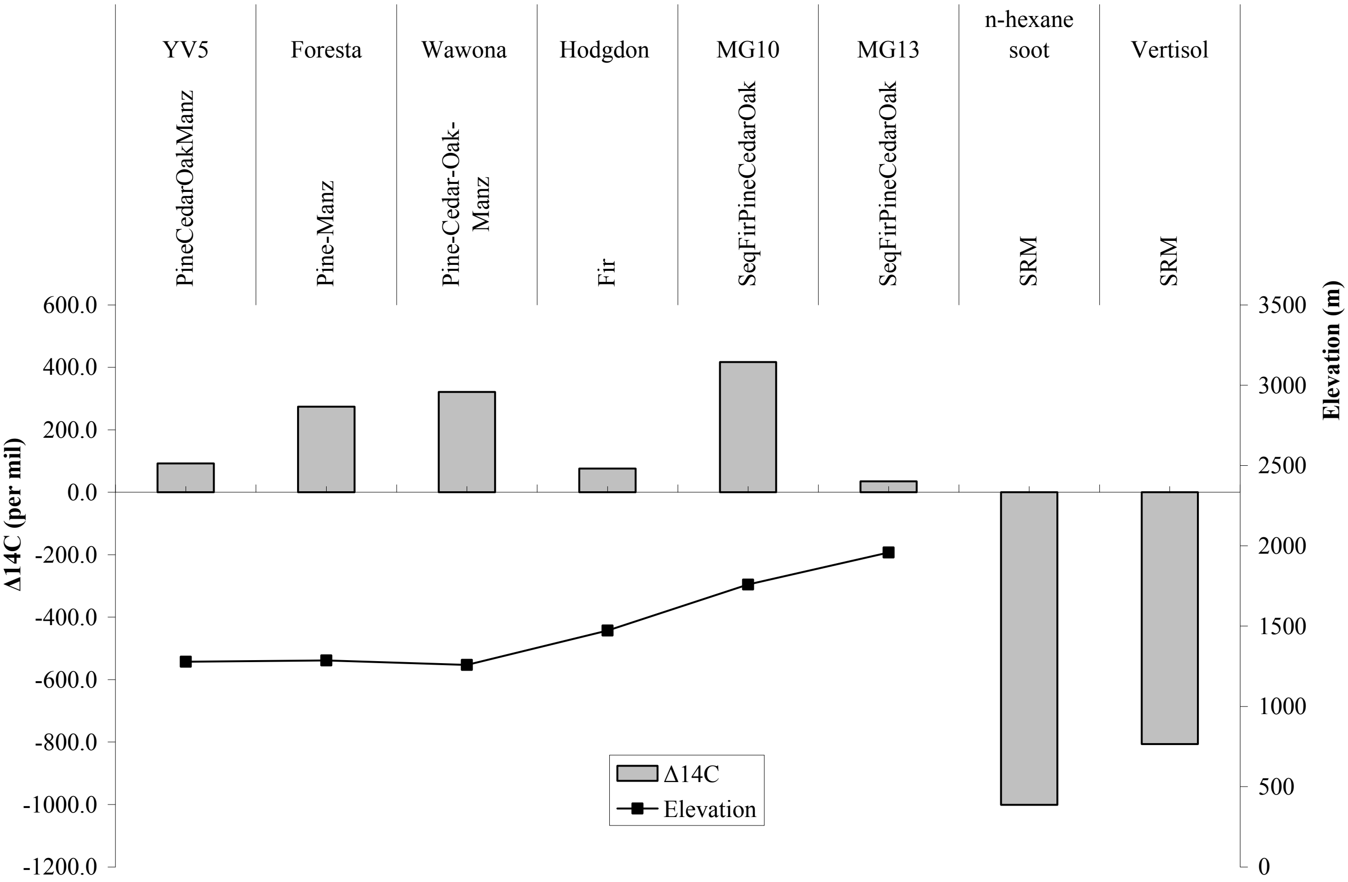

Figure 12. Average Δ^{14}C of char from the study sites

Individual samples

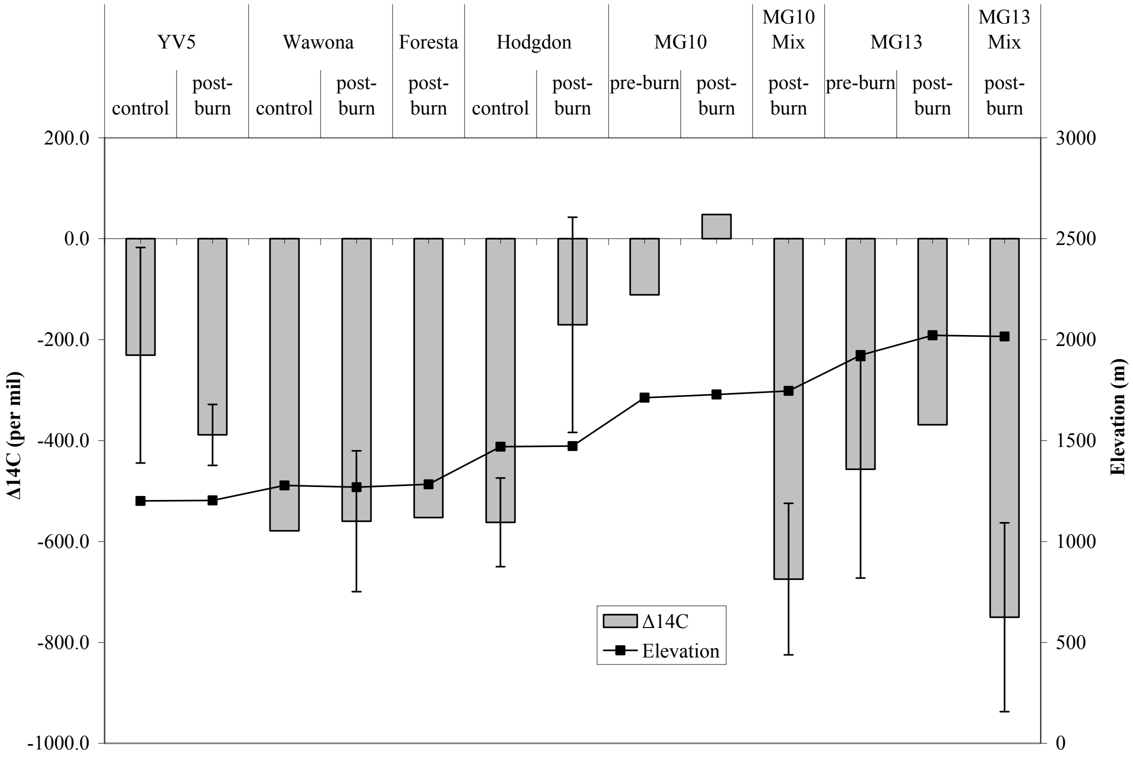

Figure 13: Average $\Delta^{14}C$ of soil BC against sites and treatments for individual soil BC samples

[(Samples treated with CTO-375 method and AMS). Error bars represent standard errors. Where applicable, n = 3 for post-burn and pre-burn treatments and n < 3 for control treatment within a site).]

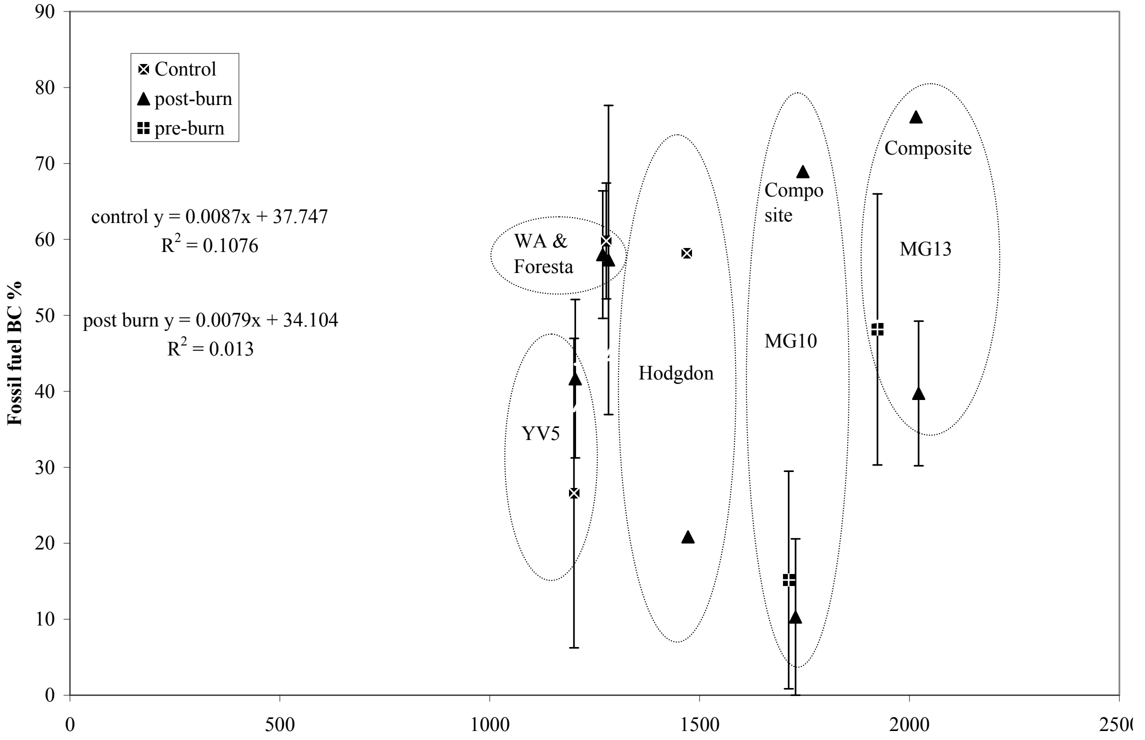

Figure 14: Average radiocarbon dead percentage of soil BC against sites and treatments for individual soil BC samples

[(Samples treated with CTO-375 method and AMS). Error bars denote standard errors. Where applicable, n = 3 for post-burn and pre-burn treatment within a site and n < 3 for control treatment within a site.]

Chapter IV. Prescribed fires in California: trends, policy recommendations and alternatives for emissions reduction

Note: This chapter was prepared as a manuscript for publication in 2010. The co-authors listed in it were Samuel J. Traina[1], Ricardo Cisneros[2],Yihsu Chen[1], Suraj Ahuja[2], and Trent Procter[2]

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Prescribed fires in California: trends, policy recommendations and alternatives for emissions reduction

Abstract

The historical status of prescribed burning (PB) policies with respect to air quality in the United States was assessed, focusing on the San Joaquin Valley (SJV) of California, which regularly experiences some of the poorest air quality days in the nation. Analyzing PB spatial coverage trends and emissions compared to wildfires, PB policies at federal, state and SJV levels were evaluated for their consideration of air quality, stakeholder involvement, forest health and alternatives to burning during formulation. We observed that only 0.27% of total burned SJV forest land was affected by both PB and wildfires after the year 1990. We estimated that in the year 2006, PB in the SJV air district annually yielded an average of 2 metric tons/day of $PM_{2.5}$ and 25 metric tons/day of carbon dioxide compared to wildfires, which produced approximately 30 metric tons/day of $PM_{2.5}$ and more than 300 metric tons/day of carbon dioxide. The policy analysis showed that some recent federal and state level policies do not address air quality issues. Policies that do mention the need to reduce emissions from PB often do not provide precise scientific guidelines to achieve that goal. Future PB policies will have to evolve and consider these and other issues such as the yield of greenhouse gases and aerosols from PB, particularly in light of new federal regulations and Congressional bills that incorporate the accounting of these emissions from non-mobile sources and which include or could possibly include PB in the near future. This assessment is concluded by discussing smoke reduction strategies and policy recommendations that could improve the efficiency and effectiveness of PB emissions reduction. The alternatives and

complements to PB in California, such as the use of forest floor biomass for cogeneration and biochar production are also explored and elaborated upon.

1. Introduction

Many ecosystems in the United States have evolved with fires, relying on their periodic recurrence to remain healthy. However, the adoption of fire suppression as the prevailing forest management policy from post-European settlement times till a few decades ago led to conditions favoring catastrophic wildfires (WFs) which severely deteriorate air quality while destroying forests, and affecting the hydrology, species habitat, soil fertility and soil stability. Prescribed fires or burns (PB) which are implemented and managed to consume forest undergrowth and dead biomass under strictly controlled and monitored conditions, can reduce the severity and risk of such events and provide many ecosystem benefits. Even though the concentration and quantity of emissions from PBs may not be as temporally and spatially detrimental compared to WFs due to their differences in coverage, intensity and fuel consumption capacity, they can still influence the air quality within smaller airsheds if not implemented appropriately. The extent of these effects depends on fire size, fuel composition, moisture and physical and chemical characteristics of the events (Kasischke and Penner, 2004). For instance, the $PM_{2.5}$ and ozone precursor emissions from PB depend on the season of the year: higher fuel moisture causes lower fuel consumption and higher incomplete combustion with subsequent higher emission (and emission factors) (Tian et al. 2008). The proportion of aerosol black carbon (soot) yield, which influences air quality and climate change versus residual charcoal which can help sequester carbon from burnt forest biomass, would also depend on similar parameters (Shrestha et al. 2010 and references therein).

The planning, implementation and management of PBs is influenced by policies set in place by regulatory and land management agencies (LMAs) at federal, state and local levels. With the mounting threats of potential WFs from rising temperatures (Westerling et al. 2007) and the consequently higher demand or need for PB from these agencies, the practice of treating land with PB may potentially increase. The implementation of the Federal Fire Guide (Fire Executive Council 2009) will also lead to quantitative and spatial expansion of PB. The preservation of air quality and protection of human health, in such current and predicted future scenarios, should always remain the primary goal of all regulators and LMAs. In this context, this paper addresses the implications of the development and implementation of PB policies on air quality, focusing on California and SJV. Assessing the historical coverage of PBs and their estimated average emissions compared to WFs, we investigated the mechanisms by which past, existing and newly formulated multi-level PB policies and plans handle the issue of emissions from these fires. We sought answers to the following questions:

- What are the trends in the coverage of PB in the SJV, compared to WFs? Can PB reduce the risks of WF and WF associated air quality impacts?
- How does PB contribute to emissions of criteria pollutants in SJV?
- How have past and current policies, regulations and regulatory mechanisms affected PB and its impact on air quality?
- How can existing policies be improved to decrease the impact of PB on the SJV air quality and maximize benefits to all stakeholders? How are new legislations handling this?

The San Joaquin Valley was selected for this study because (i) it is recognized as one the most polluted areas in the United States (American Lung Association, 2002, EPA 2011), (ii) it encompasses vast expanses of forested lands with multi-agency operated PB regimes as shown later in this paper, and (iii) it may face a rising need for forest management practices such as PB to combat increased WF risks in the near future. The SJV is upwind of the southern Sierra Nevada. The topographic features of the SJV Air Basin (SJVAB) restrict air movement out of the basin. Most of the mountains surrounding it are above the normal height of summer inversion layers (500 to 915 meters). Poor horizontal dispersion of pollutants and high-pressure event inversions frequently occur in the SJVAB. In a region like this, where topography and meteorological conditions favor the concentration and weak outflow of polluted air masses, PBs' actual, potential and perceived contribution to poor air quality, in addition their ecosystem and WF prevention benefits, is of a great scientific and management importance. However, the exact magnitude of the contribution of PB to the SJV air quality has still not yet been determined.

Prior studies that address the effects of PB on air quality (Cofer et al. 1988, Hobbs et al. 1996, Lee et al. 2005 and 2008, Tian et al. 2008) and analyze the related policies at the federal (Franklin and Agee 2003, Stephens and Ruth 2005) and state levels exist. However, there are no studies that dissect such policies from federal to local levels simultaneously and specifically with respect to air quality in California. To our knowledge, this kind of study (i) strictly focused on PB policies, (ii) scrutinizing the emphasis on air quality in North American PB policies from federal to local scales, (iii) analyzing the effect of such policies on air quality, and (iv) and spatially assessing the potential of PB in the reduction of WF coverage and WF associated air pollution, has not been conducted for forest ecosystems in SJV, California.

2. Methodology

Employing literature reviews, spatial (GIS) analyses, descriptive statistics and policy evaluation methods, the coverage of PBs and WFs in the past throughout California and SJV, the emissions from PB vs. WF, policies and implementation strategies, and possible amendments to policy and strategies for air quality improvement were investigated (Figure 1). The regulatory agencies included in this study include the U.S. Environmental Protection Agency (EPA), California Air Resources Board (CARB) and the San Joaquin Air Pollution Control District (SJVAPCD). The LMAs include U.S. Forest Service (USFS), the National Park Service (NPS), the Bureau of Land Management (BLM), the Bureau of Indian Affairs (BIA), some state agencies and private groups (including industries such as Southern California Edison, PG&E and private landowners). The LMAs' duty is to control and extinguish WFs while also conducting PB to achieve natural resources benefits and protect property. The regulators regulate sources of emissions, including those from agriculture and PBs and the associated LMA activities. With the understanding that both LMAs and regulators accept PB as essential for healthy forest ecosystems, our assessments are based on the fact that PBs produce pollutants that are detrimental to air quality and human health, depending on temporal, meteorological and spatial factors; and that their emissions can be controlled to minimize impacts on human welfare.

2.1. Prescribed burn and wildfire area comparison

Spatial and statistical analyses of the Fire and Resource Assessment Program (FRAP 2008) geodatabase for PB and WF affected area information using ArcGIS 9.3.1. (ESRI 2009) were conducted. We analyzed historical coverage of forest fires in California and SJV Air District for years 1900 through 2007. Mariposa County, Yosemite National Park and Sequoia National Forest, parts of which are either within SJV or within adjoining to it, were also studied. Geospatial base maps of the state and counties were downloaded from the California Geospatial Clearing House (State of California 2010), in the form developed by the Teale Data Center GIS Lab and updated by the California Air Resources Board to be aligned with air basins and California air districts' polygon boundary shape files. The total burn areas for different periods in the past were estimated by investigating coverage trends of PBs and WFs in the SJV was estimated. For particular areas, we obtained estimates of areas affected or not affected by both or either types of fires on the past. For coverage calculations, we assumed no overlap of WF events in the same area, i.e. that the there was no recurrence of a WF in the same area. Given the short history of PB implementation in Federal and State owned land, we assumed that each PB was implemented only once in a given area. However, given the reality that PB treatments may be undertaken more than once in the same area within the same decade, we accept that our estimates of PB area may not adequately represent PB practices in some cases.

Publicly available geospatial information on forest fires (such as FRAP 2008) has some conflicting and inconsistently reported field entries that could be related to different measurement protocols and unit conversions of burn coverage. Data from more than one source had to be compiled and analyzed for comprehensive understanding of the actual coverage and status of PB in the US, California and SJV. For instance, to assess the contribution of different LMAs to both PB and mechanical thinning, we used a different set of data from www.forestandrangelands.gov (USDA and DOI 2009) for years 2003 through 2008.

2.2. Average annual emissions

Emissions data from the Almanac Emission Projection Database (CARB 2007) was employed for estimating the average annual forest fire emissions per day for the year 2006. During this study, 2006 was the most recent year for which such emissions data for SJV was available. Comparative quantification with the impacts of other combustion sources on the air quality of the SJV Air District was conducted with these estimates. To complement the PB information from prior studies and from the FRAP (2008) data sets, we utilized additional sources of burn area and emissions data, as shown in the section 3. Unless stated otherwise, we assumed that the boundaries for SJV were the same for all these sources.

2.3. Policy evaluation and comparison matrix

Two types of policies and policy implementation strategies regarding PB at the federal, state and local levels were evaluated: those developed by the regulatory agencies and those adopted the by LMAs (Table 1). A qualitative matrix approach to comparative analysis of environmental policies as adapted from Ragin (1987) by Day (2002) was modified and employed as described below. Hypothesizing that there is a correlation between policy outcomes and the degree of involvement by non-governmental actors in the design, implementation, enforcement and evaluation phases of the policy cycle, Day (2002) proposed a Boolean methodology for discerning the effectiveness and efficiency of policy regimes. We prepared a matrix table following the same approach, assigning 1s (if present) and 0s (if absent) for different metrics of evaluation as follows: air (focus on air quality and measures for its protection); other stakeholder involvement in sub-criteria D (design phase), I (implementation phase), C (cooperation and communication with other stakeholders); scientific basis; ease of access to documents (via the internet and agency website); comprehension level (readability and clarity of document and process); diffusibility (vertical and horizontal transfer of information, rights and authority across federal to local/public and regulatory to LMA levels); space for improvement/flexibility; forest health (ecosystem and fire functions); alternatives (methods to be evaluated instead of or before burning); overall impression (subjective assessment of the authors).

3. Findings and Discussion

3.1. Spatial analysis of burned area

Spatial analysis of data from the FRAP (2008) geodatabase revealed the total area of California land area burned by at least one WF from 1878 to 2007 to be approximately 10,650,928 ha or 26% of California's land area. From year 1900 to 2007, total land treated with PB was 528,907 ha, approximately 1% of California land (Figure 2). Between 1950 and 2007, 108,377 ha of total SJV land was burned by PBs. This constitutes 20.5% of total PB area in the state. Between year 1900 and 2007, WFs burned 945,467 ha of land in SJV, constituting 9% of the total WF affected land in California (Table 2). Since the turn of the century, the annual average land area of approximately

2724 ha was treated with PB in SJV. This area has not varied significantly from year to year, with 2300 ha burned in 2000 versus 2200 ha in 2007.

High density of PB was observed in northeastern parts of the SJV and its adjoining areas in the air basin, Mariposa county and Yosemite National Park (Figure 2). Approximately 68% of Mariposa County has been exposed to WFs, as reported since the last century, while 31% of its land area has also been treated with PBs. Yosemite National Park, which stretches to the east side of Mariposa, has 34% of its land affected by WFs and 13% treated with PB. Sequoia National Forest, located in southeast SJV, has had only 3% of land treated with PB so far but an area with an order of magnitude higher, 89% has been burned by WFs (Table 2).

The proportion of post-1990 PB area also exposed to WFs is low (equal or less than 3%) in all the analyzed cases (Table 3). This proportion, compared to total combined burn area of WFs and PB (WF+PB) in each unit is less than 2% except Yosemite, which has a slightly higher proportion of 6.5%. Assuming that the recorded PB occurrences in FRAP (2008) were in locations not recorded as WF affected areas before the PB, these numbers are low and, with further analyses, could be indicators of PB as an effective tool for WF prevention, reduction and control in this region. This would be further validated if the reported PB locations overlapping with those of WF did not suffer the WF event(s) within a few years after the PBs. In most cases, the reported WFs occurred years before the PBs. In some cases, such as in Sequoia National Forest, some WFs occurred in areas pre-treated with PB.

Employing satellite data, Finney et al. (2005) observed that time since PB directly influenced WF severity and that under extreme weather conditions, PB in conjunction with thinning and timber harvesting reduced both fire growth and fire severity of large WFs in Ponderoa Pine forests. Future studies in our study sites should incorporate similar correlation analysis of PB with WF severity and growth under normal and extreme conditions.

3.2. Comparing annual PB area in SJV with CA and the US

Analysis of data sets from FRAP (2008), NIFC (2007) and CARB (2006) between the years 2001 and 2007 showed that the annual PB area has been increasing gradually in CA and the rest of the country. However, SJV has not seen a similar rate of increase in its PB area (Table 4).

3.3. Coverage of PB and mechanical thinning: Distribution by LMAs

Since the inception of the Healthy Forest Restoration Act or HRFA (2003), LMAs have been reporting the area of both PB and mechanical thinning in forests and rangelands located in wildland interfaces and other places. Calculation based on data from the DOI and USDA database (2009) showed that total PB area in California is low compared to that of mechanical thinning which is considerably larger and it has not changed much from 2003 to 2007 (Figure 3). The difference in total PB area between the year the act was initiated, 2003, and year 2007 was observed to be just 6.5%. However, compared to the year 2007, a decrease of 29% was observed in total area burned in 2008. Unfavorable weather conditions and large deployments of fire crews and forest personnel for WF mitigation in that year may have caused this. Some gaps in data accumulation and reporting may also have been partly responsible for this. The agencies conducting the greatest amount of PB are, in decreasing order, USFS, FWS and NPS.

3.4. Emissions Estimation

Using the CARB Almanac Projection database, we estimated that in 2007, PB annual average production of $PM_{2.5}$ in the SJV air district was approximately 2 tons/day while both WFs and agricultural burns produced approximately 30 tons/day of the same pollutant. Emission of carbon dioxide at an average of 27 tons/day was the highest among the analyzed emissions from PB (Figure 4 and Table 5).

3.5. Fire management and policy development in the United States

In the 20th century, dramatic reduction natural burn areas, compared to in the pre-settlement times, contributed to conditions that favor high severity fires (USDA, 2001), causing the destruction of hundreds of thousands of hectares of forested land (Figure 5A). Although the state and local rangers used to implement PB in the 1940s and 1950s, a gradual rise in PB in forests started in 1968 with the large-scale change in LMAs' fire policies from suppression to management and prescription (Figure 5B). In the 1990s, PB was eventually implemented and adopted as a policy by the federal government. Since then, PB in federal and state lands have been implemented to alleviate the catastrophic impact of WFs in fire prone forest areas of the country. Whereas a sharp increase in PB has been observed across the US and California since 2002, PB coverage in SJV has not changed significantly. During the same period, a sharp rise in WFs has also been observed nationwide and in California (Figure 5C). Regulators and land management agencies at the federal, state, and local levels have developed, adopted and implemented various policies related to such burns. These major rules and policies related to PBs (Table 6 and Table 7) are discussed in this section.

3.5.1. Air quality in PB policies in the SJV

Review of policies related to PB showed a gradual evolution of attention toward air quality from the early years of forest fire policy development. Federally, the Environmental Protection Agency's Interim Air Quality Policy on Wildland and Prescribed Fires (EPA 1998) and, for California, the California Air Resource Board's Title 17 Smoke Management Guideline for Prescribed and Agricultural Burning (CARB 2001), were landmark documents for PB in relation to human health (Table 7). They made the consideration and maintenance of air quality standards a compulsory requirement for PB planning and implementation by all LMAs. Title 17 was developed from the EPA Interim Air Quality Policy. In the San Joaquin Valley, the San Joaquin Valley Air Pollution Control District (SJVUAPCD) has been implementing Title 17, which requires it to develop Smoke Management Programs (SMPs). This agency has been regulating all PB based on air quality conditions. The SVAPCD developed Rule 4106 (2002) based on Title 17. Land management agencies such as the United States Forest Service (USFS) and the National Park Service (NPS) can conduct PB on their lands only when the forecasted post-burn air quality levels will not exceed established standards for human health. In the attached Supplementary Materials (See Appendix), we scrutinize the development and the impact of these federal and LMA policies on PB and air quality considerations in the U.S., California and SJV.

3.5.2. Effectiveness of major policies

We observed that the 1998 EPA policy, the 2001 CARB Title 17 and the 2001 SJVAPCD Rule 4106 were well-balanced, in spite of some areas requiring ameliorations (Table 8). These policies scored the highest total points while the 2003 HRFA scored the least. Based on these findings, we formulated the following recommendations to improve existing PB policies.

3.3. Policy implications and recommendations

With the United States' acceptance of prescribed burning as a valuable forest management practice in the 20th century, multi-tiered regulatory and land management agencies have developed PB policies incorporating different scopes and objectives based on their own mandates. We observed that the complexity of forest fires and their impacts on air quality, particularly at wildland interfaces, has been underestimated in such PB policies. As amendments to such policies, innovative ideas and policies that can scientifically and holistically manage PB for both social and ecological benefits should be envisaged and devised by policy-makers.

Fire policies at different levels is that PB and air quality impacts associated with PB are often at the lowest hierarchical echelon. This may understandably be the least chaotic way to manage related rules, regulations and plans, considering that PB was initiated only at later stages of policy development of different LMAs. However, there has been a gradual increase in new scientific evidence supporting the need for treatments such as PB to counteract increasing risks of disastrous fires from warmer temperatures (Westerling et al. 2006). In this context, there might be a need to revisit some of the hierarchies in forest management policies and strategies. Below, we discuss the implications of some PB policies with specific recommendations.

(i) The policies created by the LMAs, specifically the Federal Land Management Agencies (FLMAs) such as the such as those of USDA/USDOI National Fire Plan and Wildland Fire Plan and Program Review (1995), dictate the way these agencies will manage fire. Increasing catastrophic fires, decreasing budgets and rising costs of managing such catastrophic fires have led to the changes and evolution of the FLMA policies over time. The main objectives of these policies are to reduce the risk of catastrophic fires; protect, maintain, and enhance forest resources and ecosystems; allow fires to function in their natural ecological roles; and to protect the Wildland Urban Interface zone. They reflect the objectives and nature of the FLMAs but do not include the protection of human health. They do not include the need to conduct fires without harming the air quality. This is a major flaw of the FLMA policies. They do not consider that many US forests are located within areas of non-attainment where air quality is the main reason for no burn days. The FLMA policies should include the need to monitor and mitigate air quality impacts in already affected areas. Agreements on how and when to burn, particularly in wildland-interface zones, should be reached between all LMAs and regulators by always keeping in mind the air quality and avoiding the potential health impacts of PB on the public.

(ii) Smoke from PBs can be as polluting and unhealthy as that from WF. Regulatory efforts should aim to minimize smoke from the sum of all types of forest fires. Ceasing PB does not prevent WFs. It just changes the timing, magnitude and condition, at which the WF occurs, which can be catastrophic in nature. Prescribed fires can be controlled easily whereas WF is far less manageable. Air quality impairments from PBs are smaller in magnitude and short-lived and may be preferable over restrictions that lead to an increased risk of air pollution, and ecosystem and resource damage from WFs. The PB policies need to allow state agencies like CARB to assess whether the regulatory efforts developed to manage PB will not result in an increased risk to health created by the impacts of WF on air quality. In addition to PB, the state regulatory agencies should provide incentives and encourage the use of alternative treatments of combustible forest biomass, such as for co-power generation (cogeneration) and cellulosic ethanol production as discussed further in Section 4. However, this should be done only where ecologically feasible, as thinning can impair regeneration of some fire dependent species.

(iii) A common theme in PB policies is that they do not talk about specific burning periods for specific ecosystem types. For instance, Title 17 requires smoke reduction from PB. In order to prevent adverse dispersion of smoke, it offers detailed meteorological descriptions such as differences in 'expected' temperature required between the soil surface and 3000 ft elevation for PB. However, it does not offer other ecosystem specifics such as the condition of burning material and soil moisture, which have an impact on the quantity and kind of pollutants produced during the burn. Climate change related alterations in the advent of spring and other seasonal and climatic patterns (Westerling, 2007) are influencing living and dead plant biomass and physical parameters like temperature and moisture that determine optimum PB opportunity. Climatic parameters and the 'expected' temperatures at different levels may change with changes in the onset of seasons, particularly in western states such as California. We suggest that different ecosystems of California and their optimum litter/duff conditions, depending on the time of the year, be included in PB criteria listed in policy documents. We propose that specific guidelines on simple measurable environmental parameters like soil moisture be designed for specific ecological zones and rural-urban settings or interfaces be provided by the policy documents like Title 17. A better definition, with scientific explanations, of ‘expected’ temperatures (range, model emission scenarios, downscale techniques) for different air basins would also be needed. In response to changes in climatic and seasonal onset patterns, the air quality dispersion conditions required by regulators like SJVAPCD may have to be re-examined in coordination with the ecosystem conditions required by the LMAs for burning during specific periods of the year. These additions would help the burn implementing agencies and workers while judging prescription burn conditions.

(iv) Most policy documents are flexible enough to carefully give guidelines as ‘the minimal’ standard to be followed. They also provide considerable leeway for managers and implementers to follow their own professional judgments based on given criteria and forecasts. We recommend scientific or statistical documentation (in policies and plans) of the certainty, precision and effectiveness of professional judgment in PB case scenarios and on the role of such judgments in promoting PB and reducing impacts on air quality from such burns.

(v) Scientists have used models to determine susceptible high WF periods and areas based on regional and global phenomena like Pacific Decadal Oscillation and Atlantic Multidecadal Oscillation as well as based on global warming simulations. Forest managers and agencies in control of fire management plans tend to rely a lot on their own experience-based knowledge and local environmental and weather data to determine timing and frequency of PB in particular forests. The revision and update of PB policy and implementation plan documents using (a) newly developed robust forecasting models of higher spatial and temporal scales and (b) environmental and meteorological data of higher resolution and quality than current ones is recommended.

(vi) Air quality data from before, during and after PB events and policy documents assumed to be important to complete this study were not available and/or readily accessible in some cases. In may cases, the data are available but not easily accessible to people not affiliated with related regulatory agencies or LMAs. We highly recommend a two-way approach to PB policymaking where amendments are made regularly (every 2-3 years), based on regulators' experience, LMAs' feedback, changing environmental and social conditions including air quality data and their associated human impacts. There would be issues with time and effort concentrated in preparing these amendments and in broadcasting them to all the stakeholders. However, as all PB managers and LMAs workers now have access to the internet, information may be easier to disseminate than the late 1990s and early 2000s, when most of the PB policies were created. The Prescribed Fire Information Reporting System (PFIRS development) and utilization can simplify tracking of all current burns. A similar system with tracking of burns and air quality data accessible to laypeople should be in place. An easily accessible and understandable interactive online repository of policy documents from all levels and databases related to PB and air quality impacts should be created. We urge the regulators and LMAs to work together to create one common easily accessible web portal/website with information on PB and policies (including updates and amendments). This website should also contain real time, average and long-term data on air quality before and after

PB. It would help stakeholders, including members of the public who may be misinformed about the health risks and ecological benefits of PB.

(vii) Primary and secondary aerosols such as CO_2, CO, CH_4, NMHC (non-methane hydrocarbon), $PM_{2.5}$, PM_{10}, black carbon and NOx emitted from forest fires, in addition to polluting the air, also have greenhouse effects (IPCC 2007). Black carbon, an air pollutant and residue of incomplete combustion, is persistent in the environment and may constitute a significant portion of the total carbon emissions from forest fires in California and SJV basin systems. Data on the average amount of soot black carbon produced for SJV have been documented in any sort of publication. In combination with assessments of char residue formation from prescribed and WFs, such data would aid in refining what we know about air quality, carbon emissions and pedospheric carbon sequestration from these fire events, as elaborated on under the 'New research needs' section below. We attempted to fill this void in knowledge in regards to char residue as discussed therein. Future amendments in PB policies will have to consider scientific evidences and account for greenhouse gas and particles emissions. We recommend that emissions of carbon dioxide, black carbon and other global warming enhancing gases and particles also be targeted for reduction in PB policies, particularly in view of recent publication of the EPA's Endangerment Findings (2009) which authorizes the EPA to regulate greenhouse gases, as discussed toward the end of this paper. Consultation and information sharing with the evolving carbon offsets sector within and beyond the United States might become a necessity for PB regulators and LMAs, considering that PB is an anthropogenic process of carbon emissions, and could prove to be part of a significant potential carbon sequestration mechanism. We recommend that regulators and LMAs in

California improve the PB and air quality rules and policies in association with the Regional Greenhouse Gas Initiative (RGGI) and the California Greenhouse Gas Vehicle Standards (CGGVS). Such an effort would be particularly useful for the SJVAPCD and LMAs in the future when the mechanisms for carbon trading will be better established.

3.4. Recommendations for PB implementation

Prescribed forest burns should be conducted to meet all of the following (equally significant) goals -- reduction of excess forest fire prone fuels, improvement and, in some cases, restoration of forest ecosystem health, and protection of human health from air quality impacts of fire. Regulators and LMAs at federal, state and local levels should not omit any of these requirements from their PB policies, reviews and implementation plans. In this section, we present recommendations that could improve the ability of LMAs to perform PB for the accomplishment of these goals. The recommendations presented here do not suggest the relaxing of air quality standards but rather better management of PB for the maintenance of these standards.

The composition and quantity of smoke produced during a PB depends on the chemistry and condition of the fuel, the amount and arrangement of fuel layers and on the behavior of the fire and weather conditions (Ward, 1990) and the phase of combustion. For instance, smoldering combustion produces more CO, NH_3 and particulates than flaming combustion (Griffith, 1991; Ward, 1999). The smoldering phase is the least efficient due to incomplete combustion and yield of the highest pollutant to consumed fuel ratio. The higher the fuel moisture, a greater proportion of consumption occurs in the smoldering phase of the fire, and the lower the combustion efficiency. Air quality impacts of PBs during the smoldering phase are larger than in the flaming phase at night (Tian et al. 2008). Because PBs are spatially and temporally limited, their air quality impact can be reduced by implementing smoke reduction strategies that include minimization of burned area and fuel consumption while increasing the fire combustion efficiency. In agreement with Tian et al (2008), we recommend mechanical and chemical thinning, pre-precipitation burning, rapid mop-up and keeping high moisture in large woody fuel to promote the flaming phase of burning because air quality impacts from PB during smoldering are larger than in the flaming phase.

The frequency of PB is inversely proportional to the amount of emissions (Tian et al. 2008). When the burn frequency (fire return interval or FRI) is low, more fuel is burned in each fire, leading to larger emissions and air quality impacts per fire. In addition, more fuels in larger sizes, which usually cannot be consumed completely during flaming, contribute significantly to smoldering emissions. With the warm weather induced increase in such WF risks in Western US (Westerling et al. 2006), LMAs will have to conduct PB of higher frequency and spatial coverage to protect overstocked forests from a catastrophic WFs. Improved understanding of this need for prescription fires and ways to minimize smoke hazards will have to be generated by both regulators and LMAs among themselves as well as the public and other stakeholders. We recommend an increase in PB frequency in the SJV, depending on the remoteness of the site, the availability of optimum burning conditions and the predicted impact on local air quality and surrounding human population.

3.5. New research needs and recent legislative developments

In this section, we elucidate the need for research on different forms of carbon emissions and stocks related to PB, along with a discussion on federal regulations and legislations that have recently been promulgated and that may influence PB policies down to the air district level in the near future.

(i) Wiedinmyer and Neff (2007) calculated that for the period 2002-2006, Western and Southeastern US needle leaf forests were dominant contributors to total yearly US fire CO_2 emissions which amounted to 293 Tg CO_2 yr^{-1} (1 Tg or teragram= 10^{12} g). California contributed a significant annual average emission of CO_2 from fires, 24 Tg yr^{-1}, equivalent to 6% of fossil fuel combustion estimates. Prescribed forest burns were observed to constitute an insignificant percentage of this emission. A study by CARB (CARB, 2006) estimated CO_2 emissions from PBs in California to be 0.12 Tg yr^{-1} in 2002. Further scrutiny of the overall carbon budget for specific ecosystems may reveal that reduction or exclusion of fires to promote forests carbon sink properties may not necessarily be effective. Fellows and Goulden (2008) showed that due to fire exclusion between the 1930s and the 1990s, US mid-montane conifer forests underwent pest and disease induced net decrease of big trees while forest stem density (small tree numbers) increased. This effect caused a noteworthy net decline of above ground carbon biomass (storage). In another study, the inclusion of biochar black carbon stocks in accounting of high frequency fire affected regions of Australia was found to reduce the predicted carbon dioxide emissions estimation by up to 24.4% (Lehmann et al. 2008). The fires helped in biochar BC production, curtailing emissions that would be expected from degradation of the source biomass. Such findings indicate PB may be a potential method for forest carbon sequestration in California and the SJV, if implemented adequately under optimum environmental conditions. If ideal conditions are not met, existing pools of non-recalcitrant soil carbon may be lost through volatilization during PB and through leaching and ex-situ transport after PB. For instance, Shrestha et al. (in prep., chapter III), estimated that average potential biochar BC production from biomass Yosemite National Park sites could be as much as 138 gKg^{-1} biomass for PB temperatures of 450°C and 68 $g Kg^{-1}$ biomass for PB temperatures of 222°C. Although the relative biochar BC concentration was observed to increase after PB in five of the six study sites there, four sites showed reduction on surface soil organic carbon and total carbon concentration after PB. Similar reduction in forest floor carbon and nitrogen was observed after prescribed fires in the Eastern Sierra Nevada Mountains by Murphy et al. (2006) and in the Central Sierra Nevada Mountains by Moghaddas and Stephens (2007). Meta analysis of global data by Johnson and Curtis (2000) showed on average, a decrease in total soil C following prescribed burns and an increase following wildfires. With the necessity to conduct PB of higher frequencies in larger areas, there is a clear need to investigate the different scenarios that may evolve as a result of their effect on forest carbon emissions and storage potentials.

(ii) The Endangerment Findings (EPA 2009) recognize that greenhouse gas emissions from fossil fuel combustion are subject to regulation under the Clean Air Act because they endanger human welfare by increasing the likelihood of global warming induced diseases and extreme events such as WFs. However, it reiterates that some WFs are and will be designated as ‘exceptional events’ and will not fall under the Clean Air Act regulations because they are beyond control or prevention, although their emissions are also harmful for human health. Prescribed burns are not mentioned in this document. However, due to the fact they are not natural and cannot be considered exceptional events under current definitions, there could be future ramifications for PBs. The Department of the Interior, Environment, and Related Agencies Appropriations Act of 2010 (HR 2996 2010), which became public law on October 30, 2009, requires the DOI and related agencies to submit a WF management strategy providing for the allocation of a hazardous fuels reduction fund and assessing the climate change impacts of WFs. This and similar future acts and funds will facilitate research on PB and associated emissions reductions as well as PB potential in assuaging WF risks.

(Update: the final EPA rule on the Prevention of Significant Deterioration and Title V Greenhouse Gas Tailoring, which became effective on August 2, 2011, did not include black carbon to the list of greenhouse gases.)

(iii) Black carbon emissions have entered the recent U.S. national policy formulation platform. Whereas the Endangerment Finding (EPA 2009) recognizes black carbon as a component of PM influencing climate change and air pollution, it falls short of calling it a hazard to human health (i.e. an 'Endangerment Finding'). However, it clearly acknowledges the possibility of regulating black carbon emissions in the future, upon further evaluations. In addition to this rule, there are some other pending policies and legislation such as the Black Carbon Reduction Act (HR1760, 2009) introduced on March 26, 2009, that could have implications on the incorporation of black carbon in PB policies down to the local air districts such as the SJVAPCD. More significantly, the 2009 American Clean Energy and Security Act (H.R. 2454, 2009) which passed by the house on June 26, 2009 includes an amendment to the Clean Air Act. If this bill is passed by the Senate in its current or improved form or combined with another similar bill, the EPA will be required to mandate the reduction of black carbon or issue a finding for existing PM regulations to also include such reduction. In collaboration with other Federal Agencies, the EPA will also be required to prepare an emissions inventory of black carbon and programs addressing their emissions from PB. The aforementioned 2010 Department of the Interior and Environment Appropriations Act (H.R. 2996) which became law in late 2009 authorized the EPA to implement and submit to Congress a study on emissions of black carbon from all national and international sources, its effects and public health benefits of its reduction compared to carbon dioxide and other greenhouse gases.

4. Conclusion and Alternatives

In this study, spatial analysis of all forest fires showed that forests treated with PB in SJV were only minimally affected by WFs, which could be an indication of their potential to reduce WF occurrence. In SJV, emissions from PB were estimated to be significantly lower than for both WF and agricultural burning. The difference was an order of magnitude for all emission types. This assessment of the coverage and emissions of PB, followed by the impacts of PB policies and implementation on emissions reduction, revealed several opportunities for improvements and alternatives for emissions reduction from PB and forest biomass, as discussed in this section.

All rules and regulations specified for air pollution control during PB by different federal, state and local agencies have a common theme: allowing PB only when appropriate environmental conditions develop. In California and the SJV, the regulators have been involved in several ways to ensure the appropriate implementation of PB without elevating air pollution to levels beyond established standards for human health protection. The LMAs and regulators regularly meet as working groups to devise appropriate policies to maximize the PB objectives of all parties. Such vertical and horizontal pathways of candid and respectful communication and cooperation among all levels and agencies need to always remain open.

Well-justified concerns over the impacts of PB on air quality prevail, particularly in wildland-urban interfaces. However, wildfires and the subsequent need for PB have increased nationally and will continue to increase under the predicted increases in temperature and drought due to climatic changes. Corresponding fire management policies are evolving, and the way the LMAs manage fire will continue to change. Such changes are also occurring in the regulatory agencies and their policies. In light of the observations from this study and recent legislations, it is clear that detailed long-term scientific monitoring, research and documentation of PB implementation, management and emissions of all types, including greenhouse gases and particles, are in high need. Prescribed burns are required for healthy forests and WF prevention but the smoke produced from them are harmful to humans, particularly firefighters, employees and residents around and downwind of the lands used for PB. We would like to emphasize the necessity for assessments of short- and long-term smoke related health of the people living and employed in, around and downwind of PB treated forests. The relationship between the above and changes on short and long-term air quality from PBs; the effects of the frequency and intensity of PB with the air quality and incidence of smoke related diseases; and the role and potential of PB in reducing WF occurrence, intensity and frequency should also be investigated and considered at all levels of PB policy formulation, decision making and implementation.

4.1. Alternative treatments of forest fuel

Prescribed fires, WFs and emissions from both, could be reduced immensely by increasing the use of forest floor biomass for less air polluting purposes such as cogeneration and biochar (Figure 6) production, which have exhibited a potential for carbon negative bioenergy production (Figure 7). Such use could serve as complements to PB. We recommend that regulators and LMAs mandate the consideration and use of such alternatives, when possible, in all their forest biomass reduction related documents, if they have not already done so. This would also assure the success of the targets set in the Executive Order S-06-06 of California Governor Schwarzenegger (2006), according to which the State should produce a minimum of 20%, 40% and 75% of its bioenergy by 2010, 2020 and 2050 respectively through an interagency collaborative effort including the Department of Forestry and Fire Protection and CARB.

Of the 90 million tons of biomass produced annually in California, only 30 to 40 million tons are technically feasible for renewable electricity, fuels, and biomass-based products. Only 40% of this total amount is from forestry (Moller, 2005). Biomass cogeneration plants can produce biofuels, bio-products, heat and power from biomass with minimal emissions to the atmosphere. These and other potentially carbon neutral means of combustible forest biomass reduction such as biochar and cellulosic ethanol production should be carried out only when resource use and the emissions from transportation, processing, field activities and plant operations are lower than from other means of disposal and PB.

In California, 78 power plants (operated by Pacific Gas and Electric, its chief utility company) with 2,512,987 kW of total operating capacity use cogeneration but none of them use biomass as their primary energy source. As of January 2008, 35 biomass power plants (not cogeneration plants) with a total capacity of 447,100 kW were functional. Wood waste is utilized by 33 of them. Three of those 33 woody biomass plants are located in SJV (based on data from Pacific Gas and Electric, 2008). We strongly recommend that incentives for the establishment and perennial use of biorefineries and cogeneration plants be provided to federal, state and local LMAs and private parties, particularly in SJV, which has large amounts of forest and agricultural biomass waste. The permitting processes for big and small-scale biomass utilizing facilities near the sources of combustive biomass should be streamlined and facilitated.

A recent study by Campbell et al. (2009) showed that the use of electricity from biomass could lead to 81% more transportation distance and 108% more emission offsets per unit of land than the combustion of cellulosic ethanol. Through life-cycle analysis calculations, Roberts et al. (2009) observed that the greenhouse reduction, soil carbon sequestration and economic potential of biochar production from waste biomass is dependent on transportation distance to the biochar facility, the market value of C offsets, the pyrolysis process variables and the cost of production. Such scientific findings should be followed for the development of biofuels and biochar production methods and strategies aimed at effective management of forest fuels with minimization of air pollutants and carbon emissions.

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Tables

Table 1. Agencies involved in prescribed burning and their current burning goals

Agency type	Example	PB Goal
Regulatory	EPA, CARB, SJVAPCD	Protect public health from air quality problems created by fires while allowing fires to function for ecological benefits.
LMAs	USDA/DOI (USFS), NPS, BLM, BIA, state agencies and private groups (industry such as Southern California Edison, PGE and land owners)	Allow fire to function. Restore forests to fire adapted ecosystems.

Table 2: Total areas of prescribed burns (PB) and widlfire affected sites

[Representing the SJV air district which includes Yosemite National Park, Mariposa County and Sequoia National Forest till end of the year 2007 (based on FRAP 2008 geospatial information, as reported by LMAs).]

Unit		Area (ha)	Proportion of unit area (%)	Total burnt PB+WF (ha)	Main LMAs
SJV Air District	Total area	6,131,769.97			NPS, USFS, BLM, CDF
	PB (1950-2007)	108,376.52	1.8		
	WF (1900-2007)	945,466.99	15.4	1,053,843.52	
Yosemite National Park	Total area	302,550.38			NPS
	PB (1970-2007)	40717	13.5		
	WF (1908-2007)	102,336.51	33.8	143,053.93	
Mariposa County	CA land	378,373.60			NPS, USFS, BLM, CDF
	PB (1946-2007)	119,172.19	31.5		
	WF (1909-2007)	255,943.29	67.6	375,115.48	
Sequoia National Forest	Total area	480,169.08			USFS
	PB (1950-2007)	14,428.12	3		
	WF (1900-2007)	425,852.11	88.7	440,280.23	

Table 3: Area of PB land also affected by wildfires (WF) between years 1990 and year 2007.

Unit	**Area affected (PB∩WF) (ha)**	**Proportion of unit area (%)**	**Proportion with respect to total burnt area (WF+PB) in all years per unit (1900s-2007) (%)**
SJV	16, 809.83	0.27	1.60
Yosemite	9286.80	3.07	6.49
Mariposa	5066.05	1.34	1.35
Sequoia	5983.93	1.25	1.36

Table 4: Estimated total area annually affected by prescribed burning in the US, CA and SJV from 2001 to 2007 (based on data from FRAP 2008, NIFC 2007 and CARB 2006)

Year	**Area burned by prescribed fires (ha)**		
	US	**CA**	**SJV**
2001	667,946	7,527	2,293
2002	1,087,346	5,888	2,036
2003	1,148,585	6,605	2,805
2004	997,226	8,764	2,791
2005	935,690	19,733	2,034
2006	1,101,821	55,840	4,215
2007	1,275,372	40,205	2,205

Table 5: Annual average emissions from forest fires and agricultural burning in the San Joaquin Valley Air Pollution Control District for the year 2006 (calculated from annual average CARB Almanac Emission Projection Data, 2007)

	Prescribed burning	**Wildfires**	**Total agricultural burning**
Emissions	**--------------(Metric Tons/day)--------------------**		
ROG	1.53	21.95	23.49
CO_2	24.52	315.26	339.78
NO_X	0.75	9.63	10.38
PM	2.59	33.19	35.78
PM_{10}	2.49	31.91	34.39
$PM_{2.5}$	2.20	27.07	29.27

Table 6. Summary of major policies and rules related to PB (pre-1998)

(The year 1998 is used as a major year due to the implementation of the EPA Interim Air Quality Policy on Wildland & Prescribed Fire.)

Agency/Policy	Level	Fire Policy	Year	Amendment/ Comments
USFS	Federal	Exclusion	1910	1974, 1978
USFS - Clarke McNary Act (CM-2 Program)	Federal/ State	Suppression	1924	Federal legislation and funding for states
NPS	Federal	Suppression	1916	1968
NPS	Federal	Prescription	1968	For resources and fuel management
USFS	Federal	Management	1974	Change from control to management
EPA: Clean Air Act	Federal	NA	1977	Protection of visual air quality in Class I federal areas such as National Parks
USFS	Federal	Prescription	1978	New prescription burn policy: 10 am policy abandoned
USDA & DOI : Wildland Fire Management Policy and Program Review	Federal	Management	1995	First interagency effort for risk and cost management from forest fire. Amended in 2001.
NPS: DO-18	Federal	Prescription/ Suppression	1996	Suppress wildfire not meeting prescribed fire resource management objectives with firefighter and public safety.
Grand Canyon Commission (Congress)	Federal	Prescription with smoke reduction	1996	Recommendation only.
USFS	Federal	Prescription	1998	Fund for PB from Federal Emergency Firefighting Fund.

Table 7. Major policies and rules related to prescribed burning (post-1998)

Agency/Policy	Level	Fire Policy	Year	Amendments/ Comments
EPA Interim Air Quality Policy on Wildland & Prescribed Fire	Regulator Federal/ State/ Local	Prescription/ Suppression/ Smoke Management	1998	(i)First legislation on PB air quality. (ii)State and tribal LMAs and wildland owners urged to collaborate for air quality impact mitigation from prescribed fires. (iii) Measures for emission reduction
EPA Regional Haze Rule	Federal	Prescription with smoke management	1999	Interagency collaboration.
USDA/DOI National Fire Plan	Federal	Prescription	2000	Local collaboration on thinning, planned burns and forest restoration projects
CARB Title 17 Section 80145(o)	Regulator State	Prescription	2001	Fulfill the policy set by EPA Interim Policy 1998 for protection of air quality at the state level.
SJVAPCD Rule 4106 Prescribed burning & hazard reduction burning	Regulator Local	Prescription	2001	Fulfills Title 17 policy at the local level.
SJVAPCD Smoke management program	Local	Prescription	2002	Complies with Title 17. Requires District forecasters to study PM and Ozone before prescribed burn.
USDA/DOI Healthy Forests Restoration Act	Federal	Prescription/ Thinning	2003	(i) From 2002 Healthy Forest Initiative (ii) Allows USFS and BLM forest fuel reduction to prevent wildfires and for forest health.
NIFC Interagency Prescribed Fire Planning and Procedures Reference Guide	Federal	Prescription	2006	(i) Guidance from Federal Wildland Fire Management Policy and Program Review. (ii) Appropriate Management Response (AMR)
EPA Exceptional Events	Federal/ State	Prescription	2008	Section 319 of the CAA, as amended by section 6013 of the Safe Accountable Flexible Efficient Transportation Safety Act of 2005

Table 8. Policy evaluation matrix for landmark prescribed burning and forest resource management policies

(1= present; 0 = absent; D = design; I = Implementation; C = Cooperation)

Policy document	Level	Air Quality consideration	Other stakeholder involvement			Accessibility	Comprehensibility	Diffusibility	Scientific basis	Space for improvement/ flexibility	Forest Health	Alternatives	Total
			D	I	C								
EPA 1998: Interim Air Quality Policy on Wildland & Prescribed Fire	Federal/ Regulator	1	1	1	1	1	1	1	1	1	1	1	**11**
CARB 2001: Title 17 Section 80145(o)	State/ Regulator	1	1	1	1	1	1	1	1	1	1	1	**11**
SJVAPCD 2001- Rule 4106 Prescribed burning & hazard reduction burning	Local/ Regulator	1	1	1	1	1	1	1	1	1	1	1	**11**
USDA/DOI 2003: Healthy Forests Restoration Act/National Fire Plan	Federal/ LMA	0	1	1	1	1	1	1	1	1	1	1	**10**
NIFC 2006: Interagency Prescribed Fire Planning and Procedures Reference Guide	Interagency/ LMA	1	1	1	1	1	1	1	1	1	1	0	**10**

Figures

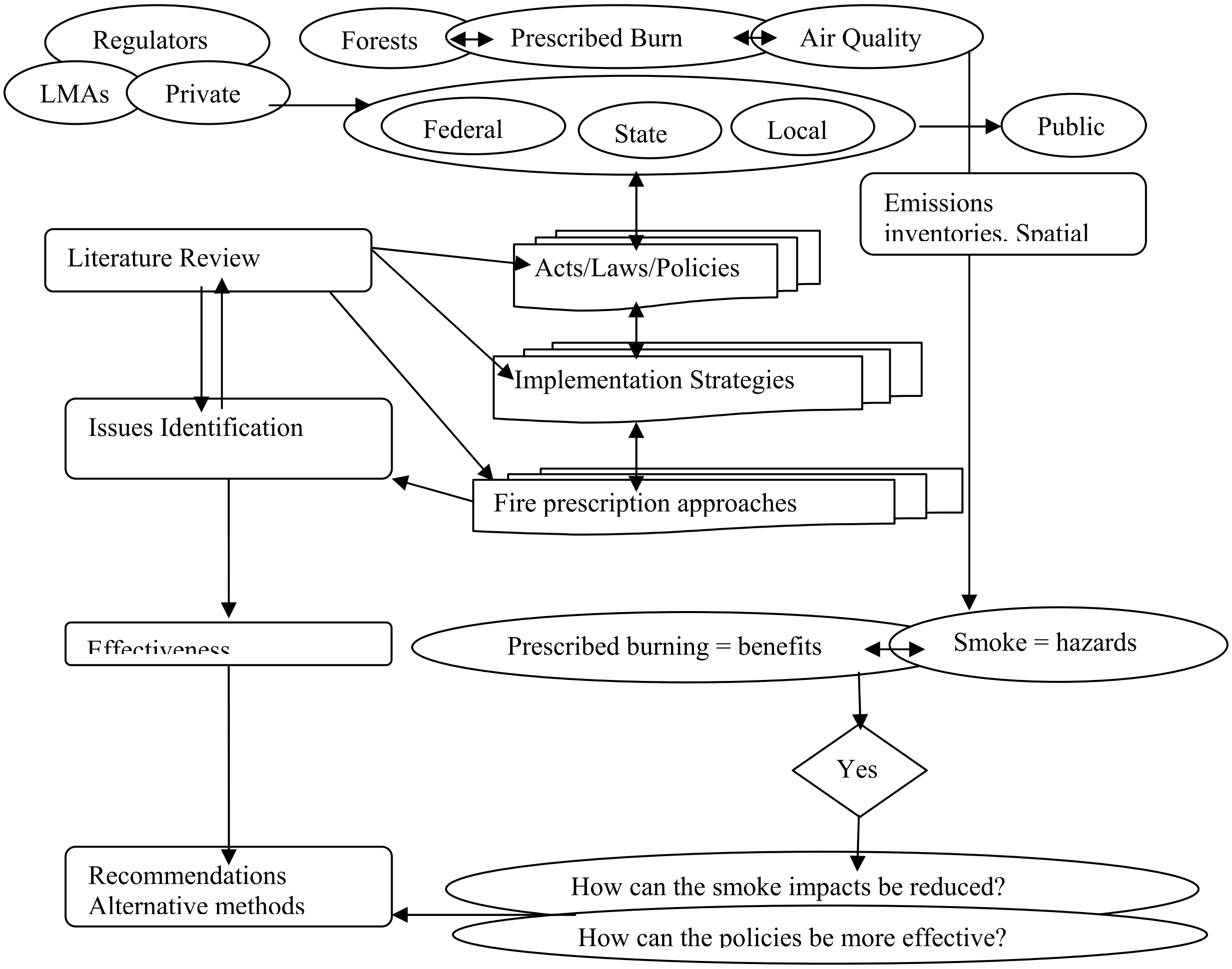


Figure 1. Schematics of the study methodology and assumptions with overview of different stakeholder levels and relationships

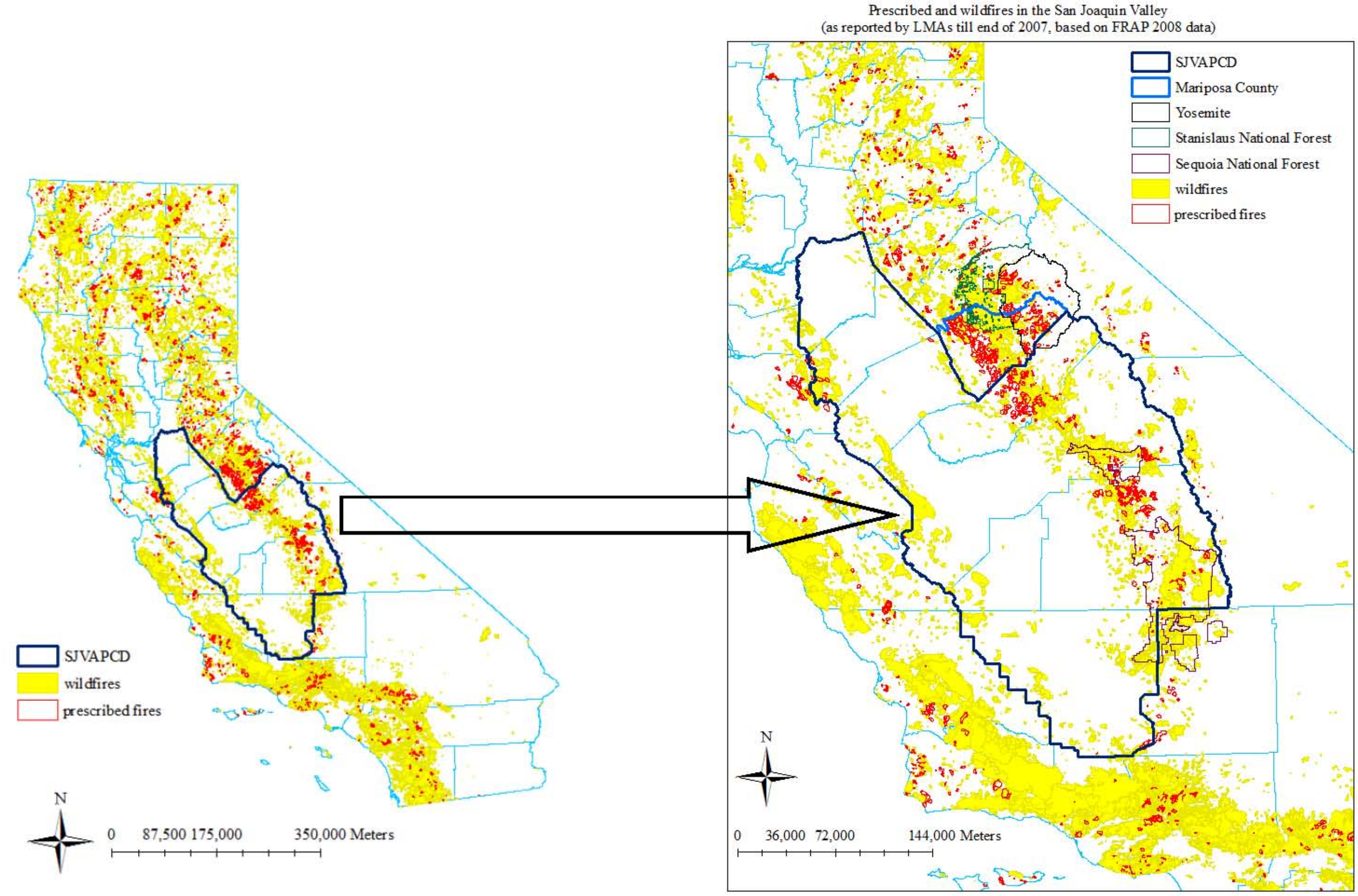


Figure 2. Spatial coverage of widlfires and PB

[Reported by LMAs to have occurred from years 1878 (for widlfires) and 1900 (for PB) to 2007 in California and the SJV (spatial analysis based on raw data from on FRAP 2008 geodatabase). This study focuses on the SJV area, which is circumscribed in blue.]

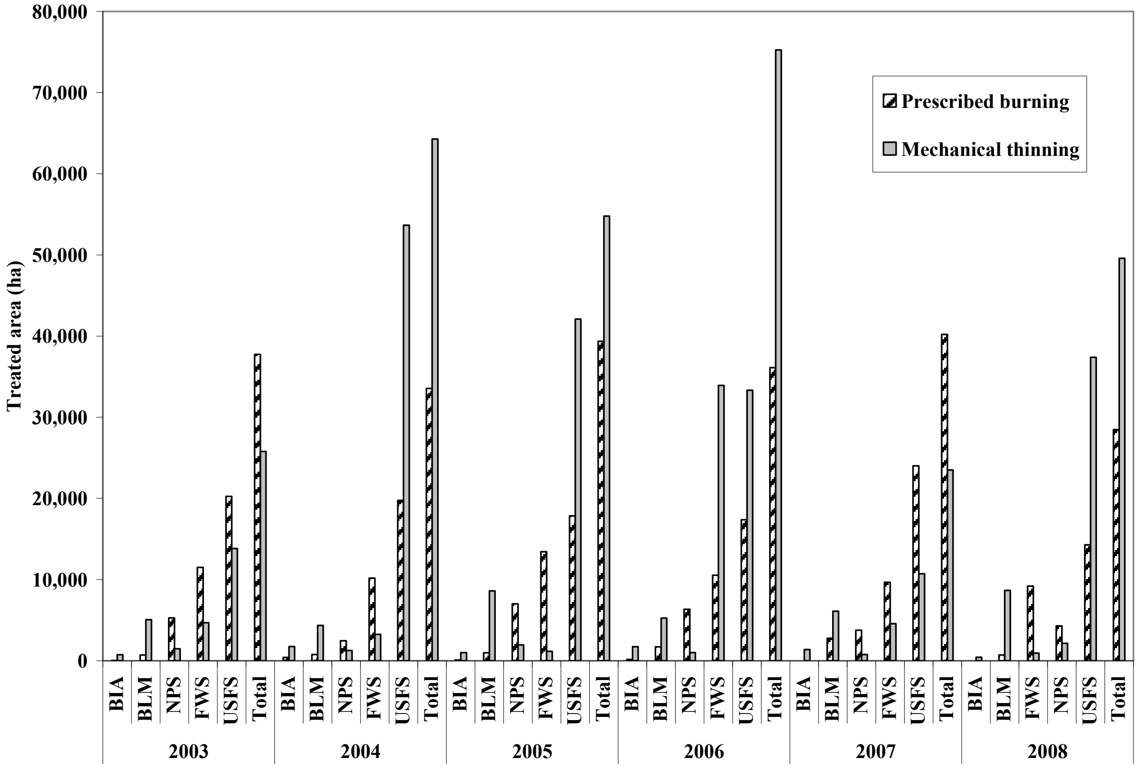


Figure 3. Prescribed fire and mechanical thinning by LMAs
in California from 2003 to 2008 (based on data derived from
www.forestandrangelands.gov, last accessed on March 12, 2009)

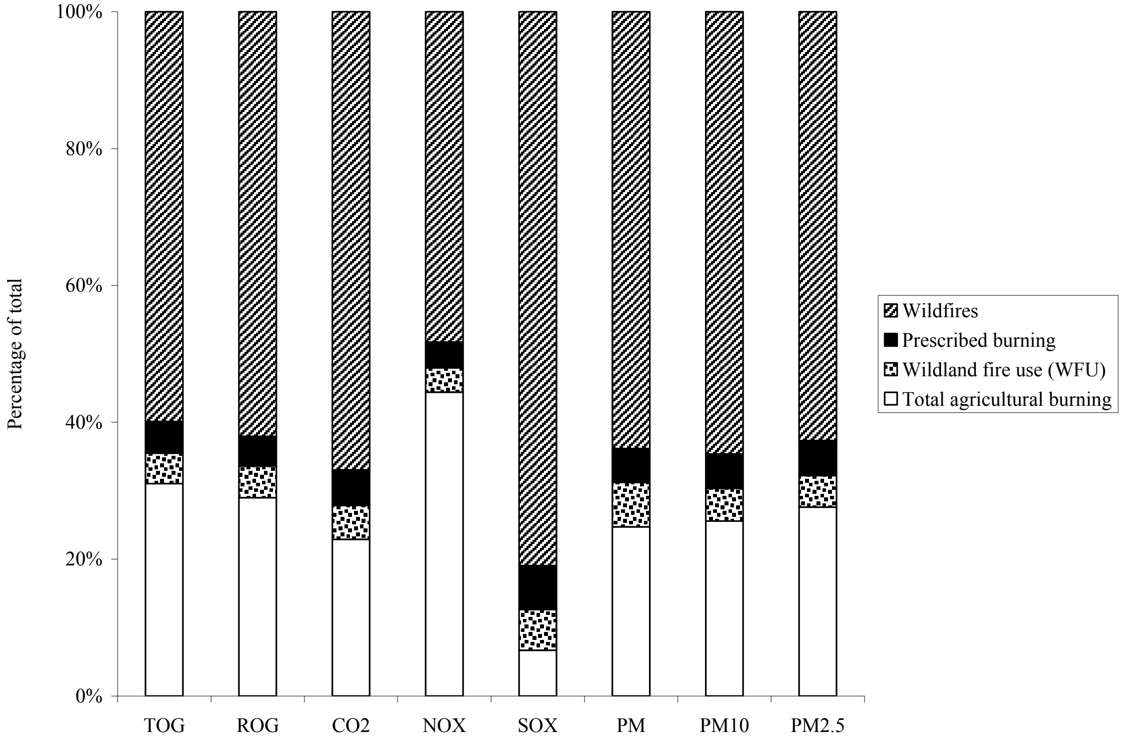


Figure 4. Comparison of estimated contribution of emissions from forest fires [Prescribed fires versus those from wildfires and agricultural burning for the year 2006 in the San Joaquin Valley Air District (based on annual average data from CARB Almanac Emission Projection Data, 2007)]

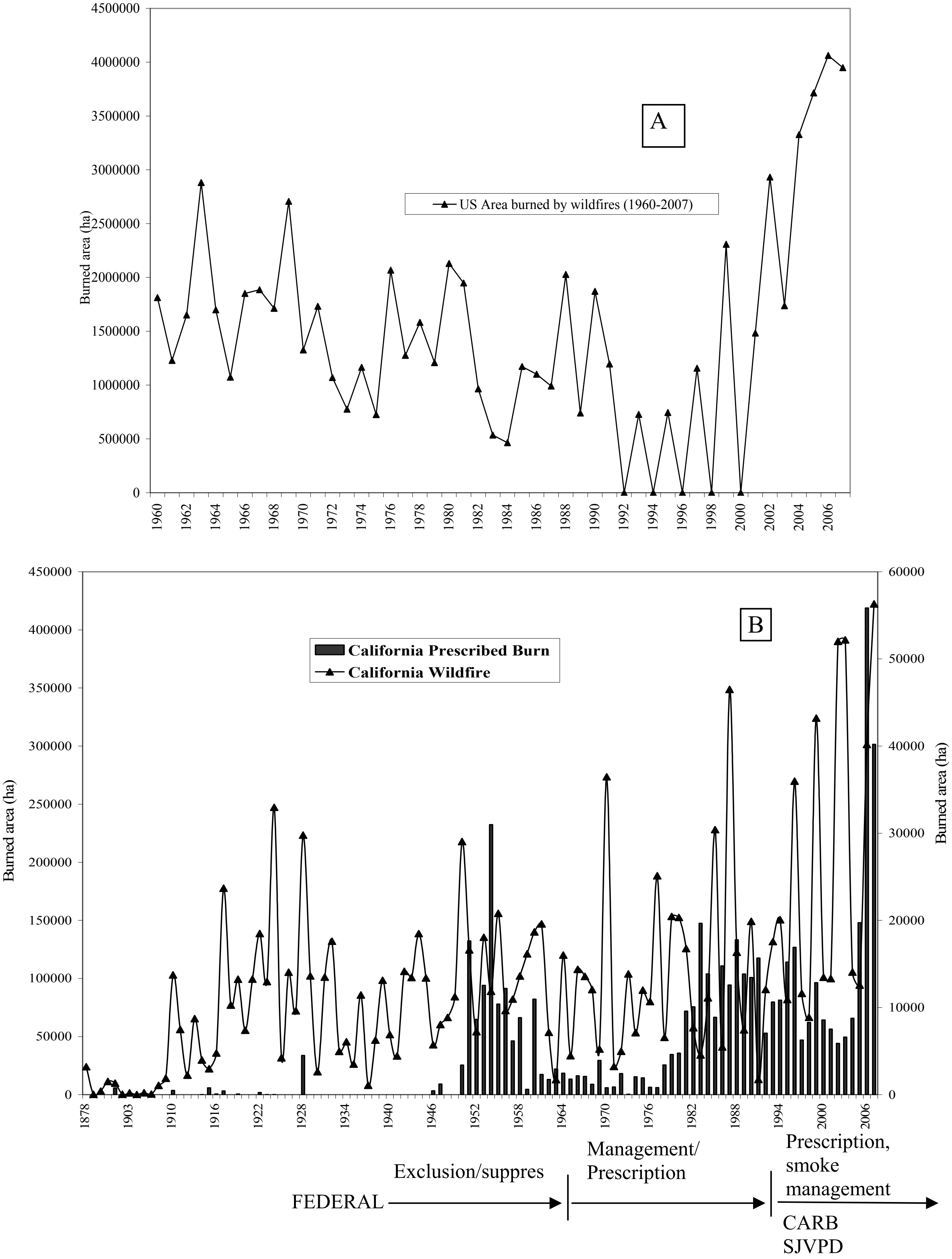


Figure 5: A. Coverage of wildfires across the United States from year 1960 to 2007 (Based on data from NIFC 2007). B. Wildfires from 1880 and prescribed fires coverage in California from 1940 to 2007 (based on data derived from FRAP 2008), showing years of policy changes.

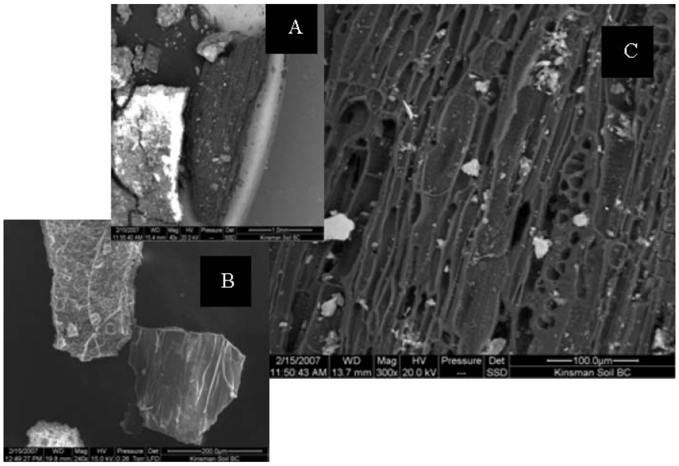


Figure 6: Scanning Electron Microscopy (SEM) images of biochar from prescribed burns [at magnifications of 40X (A), 240X (B) and 300X (C); biochar (black carbon) naturally produced by prescribed burns in Yosemite National Park (Shrestha 2010, in prep.) Such biochar can be produced in a commercial scale from forest debris collected before fires.]

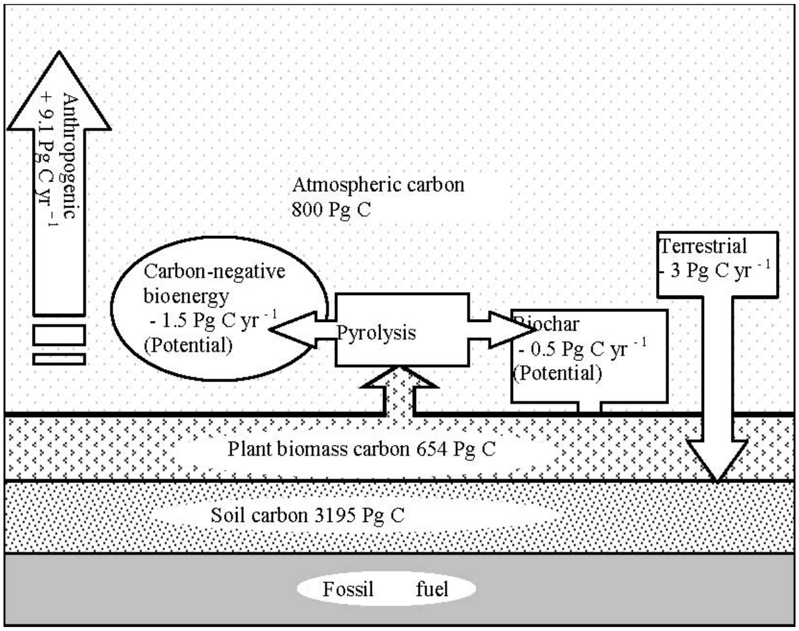


Figure 7: Representation of potential carbon offsets from biochar production through pyrolysis

[Assuming 2.1% of the annual net primary production would be globally available for biochar production with 40% carbonization efficiency), compared to other terrestrial fluxes of carbon (for the period 2000-2005). Terrestrial input includes uptake by plants and soil microbes. Major anthropogenic outputs include fossil fuel emissions and land use change. 1 Pg C equals 3.67 Pg CO_2. (Based on information from the International Biochar Initiative 2009, Lehmann and Josephs 2009, Lal 2008, and Sabine et al. 2004.)]

APPENDICES

APPENDIX A: Notes on Radiocarbon Analysis

1) $\delta^{13}C$ values are the assumed values according to Stuiver and Polach (Radiocarbon, v. 19, p.355, 1977) when given without decimal places. Values measured for the material itself are given with a single decimal place.

2) The quoted age is in radiocarbon years using the Libby half life of 5568 years and following the conventions of Stuiver and Polach (ibid.).

3) Radiocarbon concentration is given as fraction Modern, $\Delta^{14}C$, and conventional radiocarbon age.

4) Sample preparation backgrounds have been subtracted, based on measurements of samples of ^{14}C-free coal. Backgrounds were scaled relative to sample size.

5) Note, for the hexane we did NOT subtract a background.

APPENDIX B: Note on Merced terraces black carbon study

We collected surface soil (0-2 cm) and biomass from Merced Terraces (Merced Virginia Smith Terrace) a protected area located adjacent to the University of California Merced. This grassland has no known incidents of prescribed burns or wildfires in recent times and its pedogenic age is estimated at almost 3 million years. They contain the oldest soil in the conterminous United States. The grassland is protected as a reserve. As controls, soils from underneath rocks were sampled in this site. They are referred to as control (unexposed) soils in this text. Soil sampled from underneath the open grass is referred to as exposed (control or ‘rock-covered’) soil. These rocks are spread across the grassland and appeared to be firmly lodged in their locations by ancient riverine flows.

The sample pre-treatment and analyses methodologies (^{13}C NMR spectroscopy, carbon quantification and radiocarbon analyses) were similar to those described in Chapter III and IV. A summary of the results and a brief discussion based on them is presented below.

Carbon and BC concentration

The Merced grassland soil surface carbon concentration was lower than that for Yosemite soils, with 122 g C Kg^{-1} soil compared to 78 g C Kg^{-1} soil for control soil under the rocks. The C:N ratio was the same, 11, for both, with the nitrogen concentration as 7 and 11 g N Kg^{-1} soil respectively. The control (unexposed) soil had lower SOC than the exposed soil. The unexposed (control) soil had lower BC and total C concentration than soil exposed to air. (Table 1).

The soil organic carbon in exposed soil could have been higher than control soil because the control soil was presumably covered with a rock for a long time, preventing the replenishment of SOC from biomass growth on the soil. The exposed soil had twice the BC concentration than unexposed control soil. Part or all of this extra BC could be attributed to non-local deposition of fossil fuel or biomass combustion since the grassland itself is not treated with prescribed burning. Furthermore, no known incidences of local wild grassfires in recent years were reported for this area.

Radiocarbon dead carbon and age of BC

The exposed Merced soil showed more negative $\Delta^{14}C$ (or lower ^{14}C concentration) than the unexposed (rock-covered) control. Merced composite soil samples showed a higher percentage of ^{14}C dead BC in the exposed soil than in the rock covered control soil. Unlike the composite samples, the Merced control soils under the rocks showed an average radiocarbon dead BC concentration of 42% compared to 29% average for the exposed soils (Figures 1 and 2). While the vertisol SRM and the n-hexane soot SRM showed respective $\delta^{13}C$ values of approximately -29.4 and -22.5 ‰, the soil samples' representative $\delta^{13}C$ were approximately -27.3 ‰ for the Merced exposed (no-burn) soil. Merced grass litter showed a $\delta^{13}C$ value of - 27.8 ‰.

In the exposed soil, we observed more than 10% difference in radiocarbon dead BC from the control (non-exposed) soil which itself showed 8% radiocarbon dead BC out of total BC. This amount could reflect the amount of recently deposited fossil fuel BC in that area.

Table 1: Total carbon and black carbon concentration in Merced Terrace Soils, with organic functional groups percentage derived from ^{13}C NMR spectroscopy

Site	Treatment or type	Total carbon	Total percentage carbon in this form (fraction ×100%)						
			paraffinic	aliphatic	aromatic	O-subst aromatics	carboxyl and carbonyl	Total BC = aromatic fraction × total carbon	aromaticity
		g/kg soil	0-50 ppm	50-110 ppm	110-140 ppm	140-160 ppm	165-215 ppm	g/kg soil	
MER	control	5.68	45.53	43.78	1.98	1.59	7.11	1.12	0.02
	no-burn	10.69	40.97	47.92	1.98	1.38	7.75	2.12	0.02

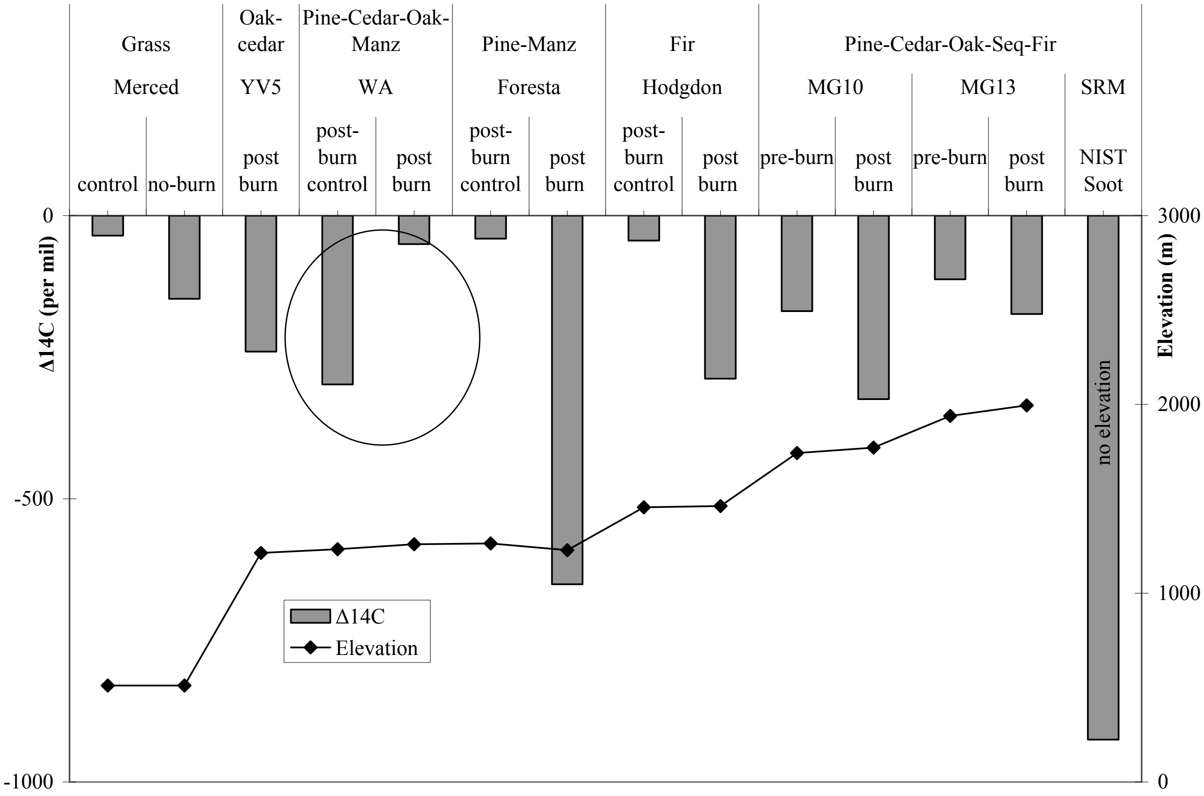


Figure 1: $\Delta^{14}C$ of soil BC in Merced compared to Yosemite National Park sites, treatments and dominant vegetation for composited soil BC samples (Samples treated with CTO-375 method and AMS).

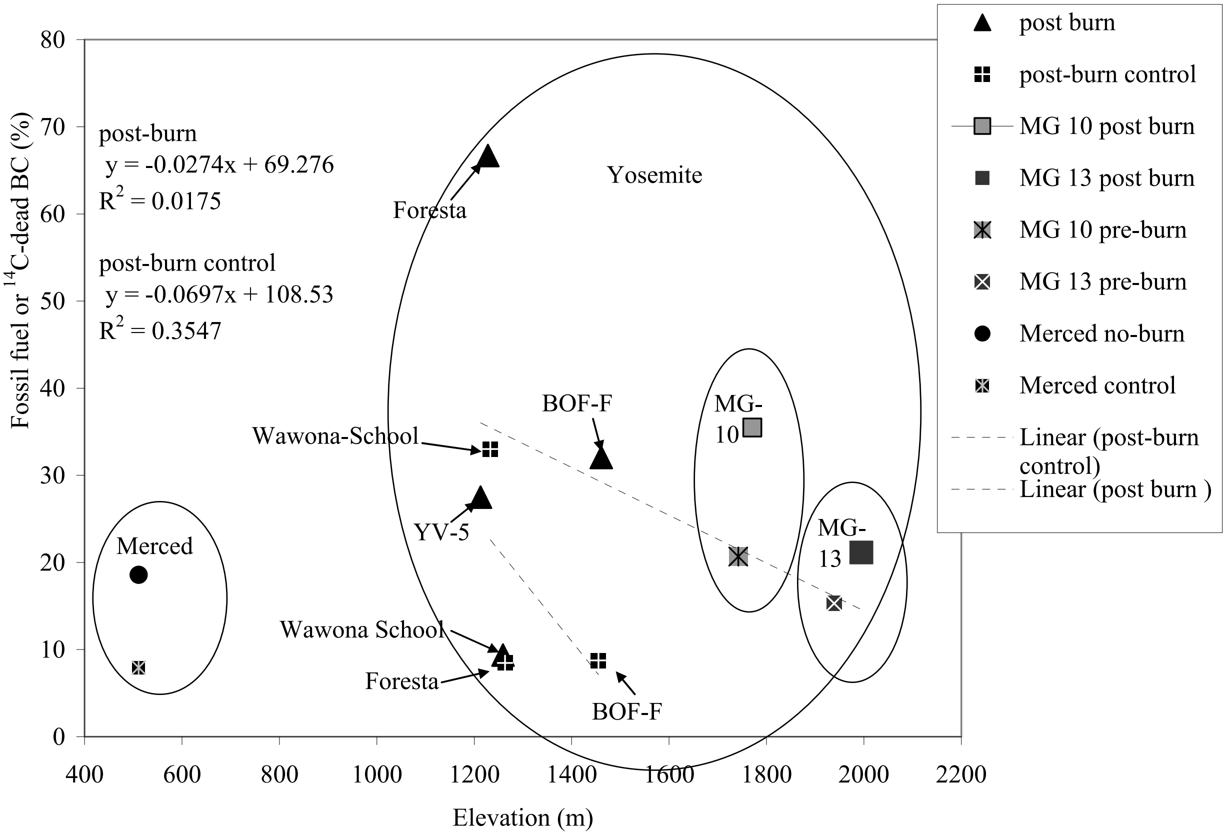


Figure 2: Percentage of radiocarbon dead black carbon Merced soils compared to Yosemite Soils. (Composite samples)

APPENDIX C: ^{13}CNMR spectra of some samples from Yosemite National Park

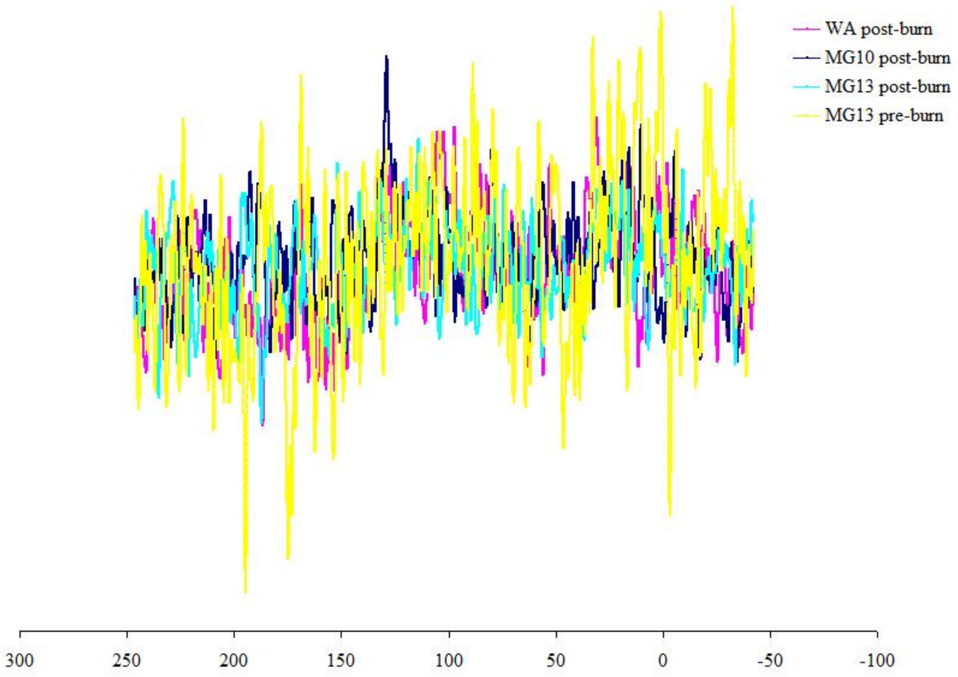
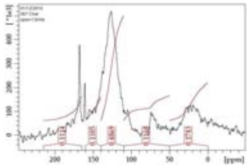
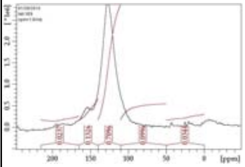
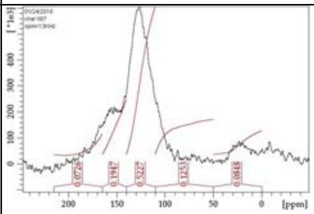
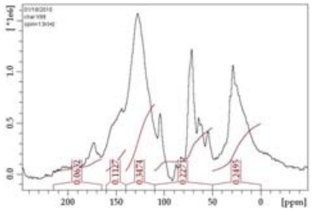
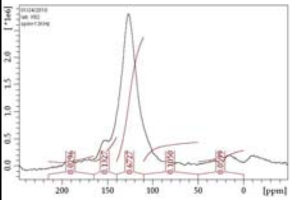
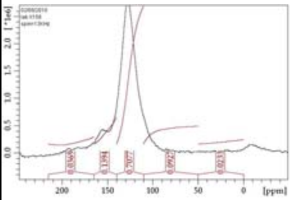
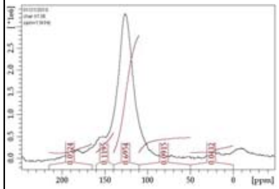
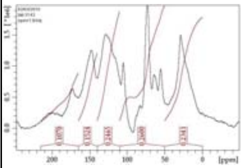
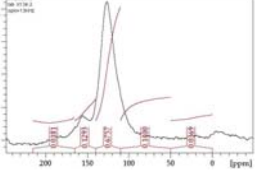
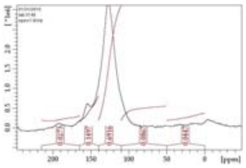
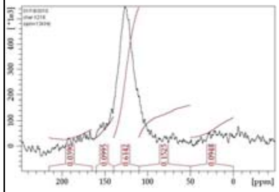
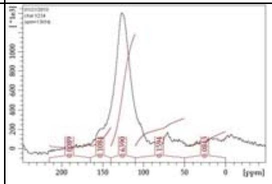
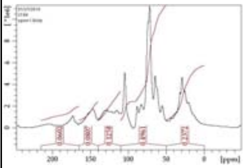
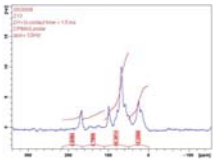
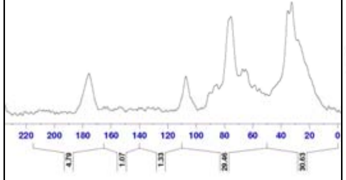
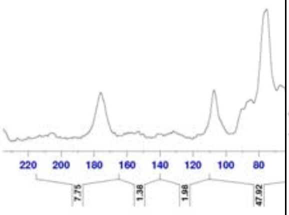
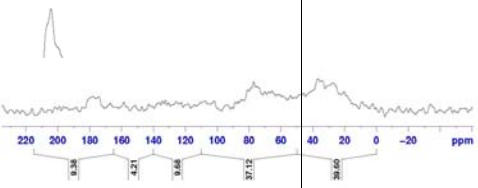


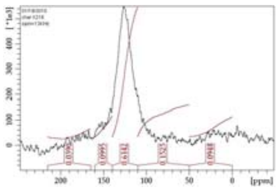
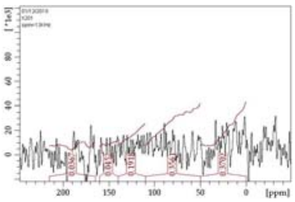
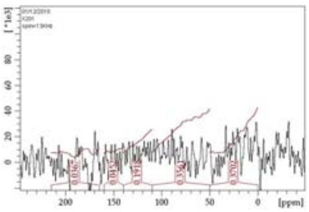
Figure 1: 13 C NMR spectra of 4 soil samples treated chemo-thermally for radiocarbon analysis using the CTO375 method. All samples from 0-5 cm depth below the char or litter surface.

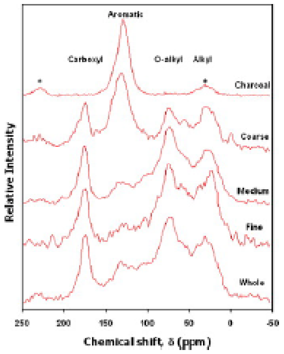
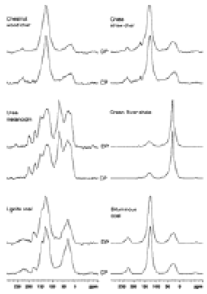
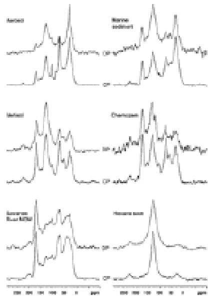
Table 1: ^{13}C NMR Spectra from individual samples

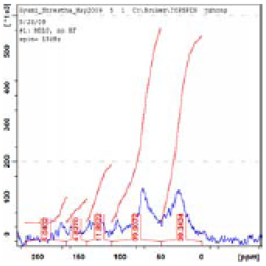
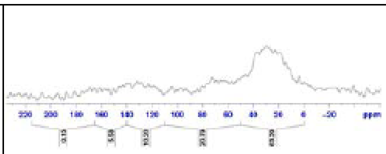
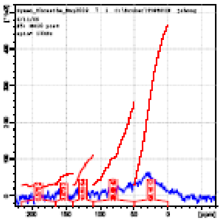
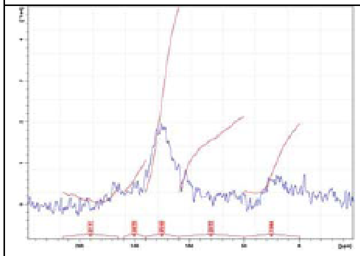
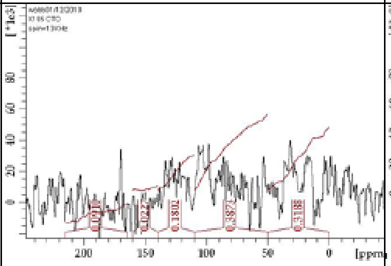
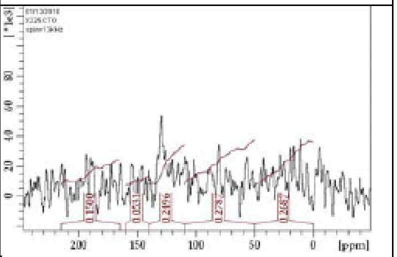
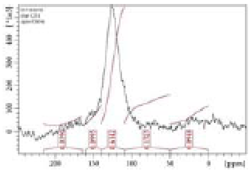
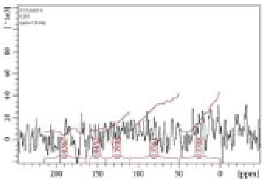
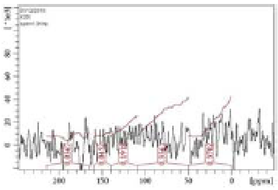
Sample Site	Post-burn field char	Lab char pre/post-burn control litter	
		222°C	450°C
X67 /X69 Hodgdon BOF-B		Litter 	
25X87 YV5			
X99/X92 Wawona			Litter  Pine needles 

Sample Site	Post-burn field char	Lab char pre/post-burn control litter	
		222°C	450°C
X138/ X143/ X 146 Foresta		litter 	Twigs  Wood 
X216 MG13			
X234/ X184/ MG10		Pine needles 	

Merced Control Z13	Merced control composite	Merced (open)	Vertisol (SRM)
	 	 	

 MG13 post-burn field char	 MG13 post-burn CTO	 MG13 post-burn CTO

 (Source: Hockaday Hatcher 2007	 Solid-state ^{13}C NMR direct polarisation and cross polarisation spectra (top and bottom respectively) of BC-rich chars (Hammes et al., 2006) and non-BC, potentially interfering materials (Hammes et al. 2008).	 Solid state ^{13}C NMR direct polarisation and cross polarisation spectra (top and bottom respectively) of environmental BC matrices and BC-rich hexane soot (Hammes et al. 2008) .

 MG10 pre-burn, no HF	 MG10 pre-burn	 MG10 post-burn
 soot	 CTO-375 (WA post-burn)	 CTO-375 (MG10 post-burn)
 MG13 post-burn field char	 MG13 post-burn CTO	 MG13 post-burn CTO

APPENDIX D: Assessment of historical and recent developments in prescribed burns' policies and implementation process of regulators and land management agencies at federal, state and local levels

(SUPPLEMENTARY INFORMATION for Chapter V
Prescribed burns in Central California: coverage, emissions, policy recommendations and alternatives)

<u>Regulators</u>

Environmental Protection Agency (Federal)

The Clean Air Act: Visual air quality in National Parks and wilderness areas receives special protection under the EPA issued Clean Air Act (CAA). The 1977 amendments to the Act established as a national goal to prevent and remedy any future and existing impairment resulting from manmade air pollution to visibility in Class I Federal areas. The EPA's authority is in enforcing the requirement of the CAA on Federal, State and Local LMAs while conducting prescribed burns.

The Grand Canyon Commission: The 1996 report (Western Governor's Association, 1996) created by this Congress mandated commission was one of the first federal level documents recommending that prescribed fires should be implemented by minimizing emissions and visibility impacts and educating the public.

The Interim Air Quality Policy on Wildland and Prescribed Fire: To mitigate the impacts of air pollutant emissions from wildland and prescribed fires on air quality in consideration of public health and welfare, the Environmental Protection Agency (EPA) in cooperation with federal land managers, States and Tribes issued the Interim Air

Quality Policy on Wildland and Prescribed Fire (AQPWPF) (EPA, 1998). Through this policy, the EPA urges the state and tribal air quality managers to collaborate with wildland owners to mitigate air quality impacts from increase in burns prescribed for resource management benefits through development of smoke management programs (SMPs). This document is the first federal regulatory document that specifically focuses on management of prescription fires in careful consideration of local air quality conditions.

The Regional Haze Rule: The Regional Haze Rule (40 CFR 51.308-309) was issued by the EPA in 1999 to improve visibility in 158 national parks and wilderness areas throughout the U.S. It requires states to develop and implement long-term State Implementation Plans (SIPs), to reduce visibility-impairing emissions. Coordination with the EPA, the National Park Service, U.S. Fish and Wildlife Service, the U.S. Forest Service, and other interested parties is required for SIPs. States should address all types of manmade emissions contributing to impairment in Class I areas, including prescribed fires. This rule recognizes that the purpose of most prescribed fires is restoration of healthy forest ecosystems.

Exceptional Events: On December 22, 2008, the EPA rule on ‘the treatment of data influenced by exceptional events’ became effective. These events determined by an administrator to be affecting air quality but unlikely to recur at a particular site. Emissions from PB may be considered exceptional events by states if proper SMPs were in place during their implementation and if there were no feasible alternatives for reduction of loading in particular areas. Non-exceptional events PB continue to be addressed by the 1998 Interim Air Quality Policy on Wildland and Prescribed Fires.

California Air Resource Board (CARB) (State)

In response to the 1998 EPA Interim Air Quality policy, California adopted title 17 (Smoke Management Guidelines for Agricultural and PB) as a regulation to deal with management of prescribed and agricultural burning (CARB, 2001). It incorporates guidelines for registration and permitting for agricultural and PB, forecasting of meteorological and smoke dispersion, burn authorization and enforcement (CARB, 2006). Title 17 Section 80145(o) requires the adoption of rules and regulations that include specified provisions to minimize smoke from all kinds of burning events and activities. With an emphasis to air quality and prescribed burns, this section requires that any sort of vegetation and agricultural burn shall not be burned unless minimal smoke can be produced by promoting adequate pre-burn drying and loose arrangement for combustion (CARB 2001, SJVAPCD 2002). Section 80260 of Title 17 provides guidelines for the San Joaquin Valley. Like its other sections, it provides a very comprehensive list of assessments required to be conducted before prescribed burns.

San Joaquin Valley Air Pollution Control District (SJVAPCD) (Local)

The SJVAPCD issued the Proposed Smoke Management Program in 2002, describing the rules, policies and procedures to comply with the California Code of Regulations Title 17. This program presents guidelines not only for forest PB but also for agricultural burns. The District Forecaster produces forecasts of $PM_{2.5}$, PM_{10} and ozone for PB decisions and uses the forecast as a tool to make prescribe burn decisions. In addition to the requirement to use meteorological criteria for prescribed burns, the district forecaster is required to analyze the burn day status based on conditions causing smoke dispersion problems in the San Joaquin Valley. There is a provision for the forecasters to follow their own judgment, after adhering to Title 17 criteria, in response to certainties of smoke transport and dispersion factors.

Rule 4106, also called the PB and Hazard Reduction Burning Rule, was created in 2001 after amending rule 4103 from which it took the PB and hazard reduction regulations. Both rules incorporate Title 17 requirements in Smoke Management Programs (SMPs). Rule 4106 provides specific criteria for the type and condition of biomass that can be burned. It permits, regulates and coordinates PB to minimize smoke impacts on the public.

Section 80145 requires LMAs to consider Alternative Fuel Treatment Methods (AFTMs) in the SMPs to minimize smoke impacts. These AFTMs include biomass chipping, crushing, disking, mowing, selective logging, chemical treatment, and livestock grazing.

Federal Land Management Agencies

United States Department of Agriculture/Department of the Interiors (USDA/ USDOI (include USFS, NPS, F&WL and BLM)

In the year 1910, the US Forest Service (USFS), under USDA/USDOI propagated a forest management policy of total fire exclusion in response to the massive Idaho and Montana forest fires. Fire suppression was allocated state funding by the Clarke-McNary Act in 1924. Prescribed fires then referred to as ‘light burns’, were advocated for at that time in California and some Southern states, particularly by the timber industry pre-harvest forest growth promotion. (Agee, 2006). In 1974, USFS fire policy changed from fire control to fire management. In 1978, they adopted a new policy of prescription burn, abandoning the 10 am policy (controlling fire in the first burning period or by 10 am the following morning) that had been in place since 1935. However, the USFS designated wilderness areas still rarely have PB although a policy for prescription was applied for them in the mid 1990s (Stephens and Sugihara, 2001). In 1995, the Federal Wildland Fire Management Policy and Program Review (USFS and DOI, 1995) was formulated as a result of one of the first interagency efforts to manage risks and costs associated with wildland fires. In 1998, money from the federal emergency firefighting fund was authorized for PB on federal land (Agee, 2006). In 1999, the General Accounting Office (GAO) of the US government reprimanded the past fire suppression practices, particularly the decades old USFS policy of putting out wildfires in national forests which led to disruption in the natural fire cycles (Zanpure-Sattler, 2003). The federal Wildland Fire Management Policy which led to the formulation of the National Fire Plan (NFP), was created by USFS as a result of GAOs recommendations. Through the NFP, Congress appropriated $2.9 billion for wildland fire management in the year 2001. The NFP established long-term hazardous fuel reduction programs incorporating prescribed fires, mechanical thinning, herbicides, grazing, or combinations of these and other treatments focused on wildland/urban interface areas.

The 2002 Healthy Forest Initiative and the 2003 Healthy Forest Restoration Act (HFRA) provide provisions and authority to expedite hazardous-fuel reduction and forest-restoration projects on USFS and BLM land at risk of wildland fire and/or of insect and disease epidemics. The HRFA encourages biomass removal from both private and public lands. It also provides stewardship contracting authority for Federal Land Managing Agencies (FLMAs) to enter into long-term (up to 10 years) contracts with private parties (small businesses, communities and nonprofit organizations) for biomass removal, permitting FLMAs to trade forest goods for services from these private parties.

Currently, the United States Forest Service (under USDA), the National Park Service (NPS), the Fish and Wildlife Service (under the Department of the Interior, DOI), the Bureau of Land Management (BLM) and the Bureau of Indian Affairs (under DOI) have control over fire management plans strategies and plans at their respective national, state and local levels. The 1995 Federal Wildland Fire Management Policy and Programs Review along with its 2001 update have guided present federal prescribed fire programs and documents like the 2006 Interagency Prescribed Fire Planning and Implementation Procedures Reference Guide. These programs follow the principle that wildfire suppression, wildland fire use and prescribed fires be implemented ‘equally, consistently and concurrently’ to avoid fire risks. They also follow the 2003 Wildland Fire Management Policy of primary consideration to public and fire fighter safety in planning and implementation of prescribed fires (NIFC, 2006). In the following sections, we discuss the PB policies adopted by NPS, the National Fire and Aviation Executive Board and the National Interagency Fuels Coordination.

National Park Service (NPS)

The NPS policy from 1916 to 1968 was to strictly suppress all park forest fires. After the release of the 1963 Leopold Report on controlled burns at the Everglades National Park, NPS policy changed in 1968 to one that recognized prescribed fires as a means to achieve resources and fuel management objectives. Whereas the Organic Act of 1916, which created the NPS, mandates conservation of NPS resources, the other NPS policies, namely the Director’s Orders-18 (DO-18) and Reference Manual-18 are national level directions under which individual parks prepare environment compliance based fire management plans. Prescribed fire plans are at the bottom of this hierarchy of NPS authorities and plans (NPS 1998 and 2008). After the 1996 Federal Wildland Fire Management Policy and Program Review, DO-18 was implemented. According to DO-18, all parks with vegetation that can sustain fire must have a fire management plan incorporating natural fires allowed to burn for predetermined resource management objectives and PB intentionally ignited by park managers (NPS, 1998 and 2008). The use of forests for specific resource management objectives without compromising firefighter and public safety are stated to be ensured in these NPS directives. This is one of the first LMA document including such measures.

The National Fire and Aviation Executive Board (NFAEB) and the National Interagency Fire Center (NIFC)

In 2006, the NFAEB and NIFB released the Interagency Prescribed Fire Planning and Implementation Procedures Reference Guide for use by the Bureau of Indian Affairs, the Bureau of Land Management, National Park Service, US Fish and Wildlife Service and the USDA Forest Service (NIFC, 2006). It partially replaced the 1998 Wildland and Prescribed Fire Management Policy Implementation Procedure and Reference Guide (USDA/USDI, 1998) which was the first document to establish consistent agreement on federal policy directions for prescribed fire planning and implementation among the different land management agencies.

The 2006 the NFAEB and NIFB documents' elements 3 and 19 of this prescribed fire plan particularly mention the method of handling of complexity (risk) analysis of air quality and smoke hazards during and after prescribed burns. Under element 19, it is clearly stated that special consideration must be taken to address smoke when the PB is in a non-attainment area for a National Ambient Air Quality Standard (NAAQS) ensuring compliance with SIP/TIP provisions and conformity. Potential impacts on visibility in Class I areas should also be properly addressed and mitigated. All local, state, tribal and Federal pre-burn and post data reporting requirements must be met.

On January 7, 2009, the National Wildfire Coordinating Group (NWCG), which operates as part of the NIFC, released a memorandum summarizing most recent evaluations of forest fire rules. Both a 2001 review and a 2008 field test based review found that the 1995 Federal Wildland Fire Policy is 'sound'. The memorandum does not specify exactly what it implies by 'sound', though. They recommended an amendment to the 2003 implementation guideline of this policy, for more flexibility and reduced confusion. There is no direct mention of air quality and human health protection, although that could be included in the safety and protection goals that this NWCG recommendation aims at. This memorandum was followed by the "Guidance For Implementation of Federal Wildland Fire Management Policy" in February, 2009. It incorporates unplanned ignition as wildfire and planned ignition as prescribed fire by revising the Interagency Strategy for the implementation of Federal Wildland Fire Management Policy (NIFC 2003), which introduced policy requirements intended to avoid firefighter fatalities (NWCG 2009).

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APPENDIX E: Exchangeable cations concentration and pH

Due to its high surface area, charge density and negative surface charge, biochar BC has very high exchangeable cation sorption and retention capacity {Liang, 2006 #107}. Over time, carboxylic groups formed on the edges of the aromatic part of BC increases biochar's nutrient holding capacity {Glaser, 2001 #907}. These properties enable its use for topsoil productivity improvement as well for reducing leaching of pollutants such as dissolved phosphates and nitrates into the groundwater and other water bodies. The pyrolysis temperature has to be above 400 °C for these biochar benefits to be manifested via high pH, cation exchange capacity and surface area {Lehmann, 2007 #1756} (Chapter II). Below, we present a summary of pH and exchangeable cations concentrations analyses of the soils collected from our study sites in California.

For exchangeable cation concentrations, a gram of soil was mixed with 1.17 grams of NaCl and 1 L of deionized water to make a 0.02 M NaCl solution. 20 mL of the 0.02 M NaCl solution was mixed with each sample and shaken on a horizontal shaker for 30 minutes, then centrifuged for 15 minutes at 10000 RPM. An mL of the supernatant was placed in a sterile 15 mL centrifuge tube along with 9-11 mL 1% HNO_3 stock. Standard solutions were prepared and all the samples were analyzed using the Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES).

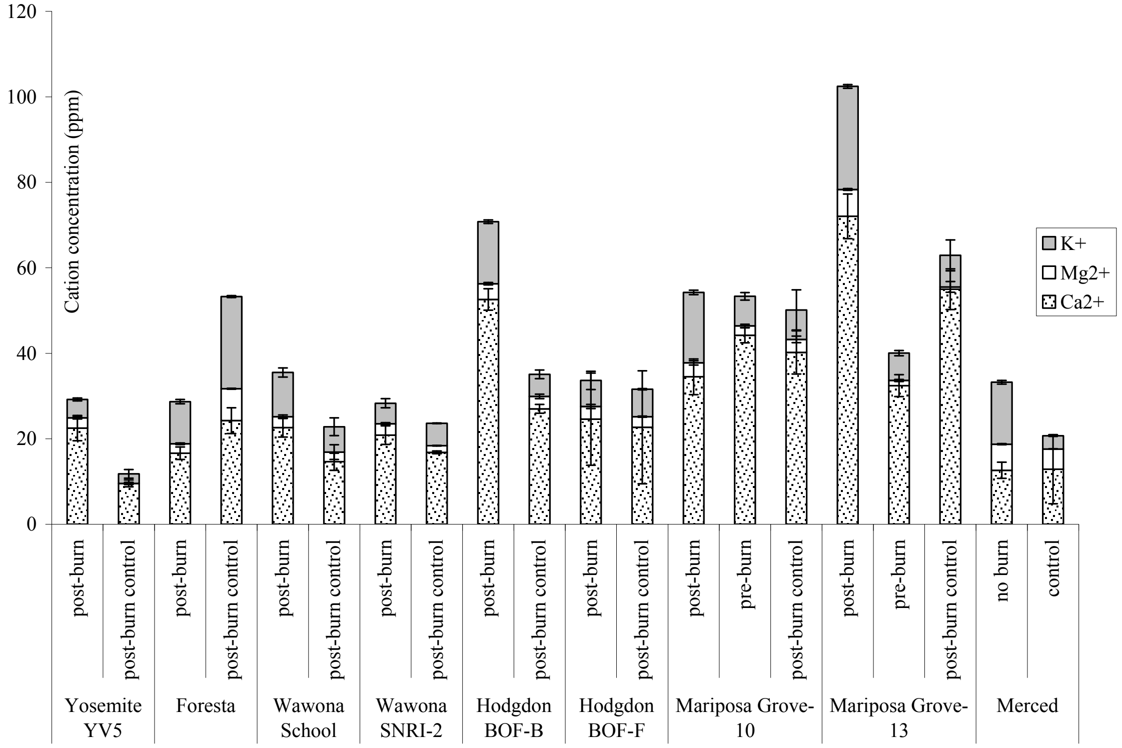

Figure 1: Soil cation concentration across treatments and sites at 0-5 cm depth below the surface litter and char layer.

For Yosemite, the Ca^{2+} exchangeable cation concentration was higher for post-burn soils in 4 out of 6 sites. The exchangeable K^{+} concentrations were higher than controls in 3 post-burn soils. Mg^{2+} was higher in control soils of 4 out of 6 sites (Figure 1). These results differ from Murphy et al. (2006) who found no significant effects of prescribed burning on these three exchangeable cations.

A 1:1 water: soil mixture was employed to study the pH of the soil samples. The average pH in the post-burn soils of Yosemite sites was 6.5 compared to 5.7 for control soils. All sites demonstrated lower soil pH for control soil than for post-burn soils (Table 1).

Table 1. Average pH of soil soils in the study sites.

site	post-burn	control	pre-burn
Yosemite YV5	6.6	5.4	.
Foresta	7.1	5.7	.
Hodgdon	6.6	5.8	.
Wawona School	6.1	5.7	.
MG10	.	.	7.1
MG13	.	.	6.4

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Appendix F: Geology and Soil Type of the study sites in Yosemite

Table 1: Geology and Soil info of the Yosemite study sites (based on information from http://virtual.yosemite.cc.ca.us and National Park Service GIS Portal)

Site	YV5	Foresta	Hodgdon	Wawona	MG10 & 13
Soil type	Mollic Xerofluvents, frequently flooded, mesic, 5 to 15 percent slopes	Humic Dystroxerepts-Tuolumne-Typic Xerorthents-Ultic Haploxeralfs complex	Humic Dystroxerepts-Typic Haploxerults complex, 5 to 35 percent slopes	Oxyaquic Dystroxerepts-Dystric Xerorthents-Vitrandic Xerorthents-Rubble lan	Dystric Xeropsamments-Typic Dystroxerepts-Badgerpass-Rock outcrop association
Geology	Alluvium	Tonalite of the Gateway, Fine Gold Intrusive Suite	Granodiorite of Ostrander lake, Intrusive suite of Buena Vista Crest	Tonalite of the Gateway, Fine Gold Intrusive Suite	Tonalite of the Gateway, Fine Gold Intrusive Suite