

Stabilité du charbon végétal (biochar) dans le sol et impact sur la productivité et les cycles des nutriments des prairies alpines

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Laboratoire BIOEMCO

Stabilité du charbon végétal (biochar) dans le sol et impact sur la productivité et les cycles des nutriments des prairies alpines

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Thèse de doctorat de : Sciences du sol et de l'environnement

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À ma grande mère

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Introduction

Les changements climatiques observés récemment sont liés à un réchauffement de la planète. L'augmentation de la température moyenne globale est causée *très probablement* par une augmentation de la concentration des gaz à effet de serre dans l'atmosphère, dont les émissions sont liées principalement aux activités anthropiques. La mise en œuvre de modes de gestion des terrains agricoles et pâturages aptes à augmenter les stocks de carbone dans les sols a été évoquée parmi les stratégies possibles de mitigation des changements climatiques (IPCC Core Writing Team R.K. Pachauri and L.A. Meyer (eds.), 2014).

Le 21ème siècle est également caractérisé par une augmentation de la population mondiale, qui passera de 7.4 milliards en 2015 à 11.2 milliards en 2100 (United Nations. Department of Economic and Social Affairs. Population Division, 2015), ce qui nécessite de doubler les productions agricoles avant 2050 (Tilman et al., 2011). L'objectif parait très ambitieux pour de multiples raisons parmi lesquelles on peut citer l'impact des changements climatiques sur les productivités agricoles elles-mêmes (Ray et al., 2013; Rosenzweig et al., 2014).

Pour répondre à ces deux problématiques, depuis une décennie, l'enfouissement du charbon végétal (*biochar*) dans les sols est proposé comme une stratégie durable pour à la fois (1) mitiger les changements climatiques et (2) augmenter les productions agricoles (*win-win*) (Biederman and Harpole, 2012; D. A. Laird, 2008). En effet, le temps de résidence du biochar dans les sols est probablement de l'ordre de plusieurs centaines d'années (J. Wang et al., 2015). Ainsi, l'amendement modifie les caractéristiques physiques, chimiques et biologiques des sols à long terme. Toutefois, jusqu'à présent ces impacts et les mécanismes sous-jacents sont peu connus et mal compris.

Une évaluation de l'impact des biochars sur les écosystèmes nécessite des études à long terme. Cependant, les expériences scientifiques menées jusqu'à présent ont été conduites à court terme car ces expériences ont été mise en place quand l'intérêt sur ce thème s'est accru, il y a une dizaine d'année maximum.

Une alternative à ces expériences sont les sites historiques où le charbon est présent dans les sols depuis des centaines ou même des milliers d'années. Ces sites offrent la possibilité d'avoir une échelle temporelle d'observation plus longue. L'exemple le plus connu et le plus étudié est celui de la *Terra Preta de Indio* dans la forêt Amazonienne, où le charbon végétal serait présent depuis 500-

7000 ans et son impact sur la qualité des sols et leurs productivité est encore visible (Neves et al., 2003). Cependant en Amazonie le charbon était enfoui avec d'autres résidus organiques. En Europe, il existe des sites d'anciennes charbonnières caractérisés par une teneur élevée en charbon dans le sol. Ces lieux ont été jusqu'à présent peu utilisés pour comprendre l'effet de l'ajout du charbon sur les propriétés du sol à long terme.

L'objectif général de cette thèse a été donc de comprendre l'effet des charbons/biochars altérés dans les sols sur les cycles biogéochimiques et la croissance des plantes. Je me suis servie des sols de charbonnières des Alpes italiennes comme modèle, que j'ai comparé aux sols échantillonnés dans les prairies aux alentours (sol témoin) et aux sols témoins amendés avec du charbon/biochar similaire mais nouveau, que j'ai produit en laboratoire.

Les objectifs spécifiques de cette thèse ont été d'évaluer :

Objectif n°1 : le potentiel de stockage de C dans les sols induit par l'ajout de charbon à long terme :

Pour répondre au premier objectif les activités suivantes ont été effectuées :

a) des sites historiques de production de charbon (1858) ont été identifiés dans des prairies des Alpes italiennes
b) le stock de carbone présent dans le sol de charbonnière aujourd'hui a été mesuré
c) le stock de carbone présent dans le sol en 1858 a été estimé à l'aide de techniques différentes et complémentaires (sources bibliographiques historiques, reproduction des méthodes traditionnelles de production de charbon, données LiDAR, mesures et bilans isotopiques et élémentaires)
d) le temps de permanence (MRT) du charbon dans le sol a été calculé à partir de b) et c)

Objectif n°2: l'impact du charbon/biochar sur les flux des nutriments dans le sol :

Pour répondre au deuxième objectif les activités suivantes ont été effectuées :

a) exposition aux précipitations naturelles pendant une année de carottes de terrain de charbonnière et de sols témoins amendés avec du charbon/biochar récent
b) mesure de la teneur en nutriments des sols à travers des analyses élémentaires
c) mesure des taux d'accumulation/lixiviation des sols grâce à l'emploi de résines ioniques

d) évaluation du rôle des dépositions atmosphériques dans l'enrichissement des sols de charbonnière par rapport aux sols témoins

Objectif n°3 : l'impact du charbon/biochar sur la fertilité des sols et sur la valeur nutritive des plantes fourragères à court et long terme :

Pour répondre au troisième objectif les activités suivantes ont été effectuées :

a) cultivation de deux espèces fourragères de prairie alpine en serre dans des sols de charbonnière, des sols témoins et des sols témoins amendés avec du charbon/biochar récent
b) mesure de la teneur en nutriments des sols
c) mesure de la production de biomasse herbacée et du contenu de nutriments des plantes
d) évaluation du taux de germination des deux espèces fourragères dans les sols de charbonnières, sols témoins et sols témoins amendés avec charbon/biochar récent dans une expérience en boîte de Petri

L'ensemble des recherches menées est présenté en cinq chapitres. Le premier est une synthèse bibliographique, dans laquelle je définis le biochar, ses caractéristiques physico-chimiques, son potentiel à augmenter le stockage de C des sols, à en modifier les cycles biogéochimiques et son impact sur la production végétale des prairies alpines. Le deuxième chapitre présente le site d'étude. Les trois chapitres suivants sont des articles scientifiques qui répondent aux objectifs présentés plus haut. Le premier article, publié en 2014, décrit les charbonnières alpines d'un point de vue historique, chimique et physique et quantifie la capacité de stockage de carbone pendant 150 ans. Le deuxième article analyse l'effet des charbons anciens et récents sur les flux des nutriments dans les sols alpins. Le troisième article, publié en 2016, étudie l'impact des charbons anciens et récents sur la germination, la croissance et la valeur nutritive de deux plantes alpines. La thèse se termine avec les conclusions générales.

Chapitre 1 : Synthèse bibliographique

Biochar et charbon

Définition et caractéristiques physico-chimiques du biochar/charbon

Le biochar est le sous-produit de la pyrolyse, une décomposition thermochimique de la matière organique qui se réalise quand de la biomasse est exposée à des températures supérieures à 350°C en l'absence ou très basse concentration d'oxygène (O_2) (Lehmann and Joseph, 2009). Ces conditions sont similaires à celles de la production du charbon de bois lors d'un feu de forêt ou de champs (M.W. I. Schmidt and Noack, 2000) ou lors de la carbonisation dans les charbonnières traditionnelles.

Historiquement le charbon a été principalement une source énergétique domestique (cuisson, chauffage) ou industrielle (fonte de minerais, production d'acier) même si d'autres applications possibles étaient la médecine, les peintures rupestres et l'agronomie (R. Brown, 2009). Le biochar est le charbon produit spécifiquement pour être appliqué au sol pour en améliorer la productivité, les qualités physicochimiques et les stocks de carbone (Johannes Lehmann et al., 2006a).

La production de charbon et de biochar est associée à la production de substances huileuses et de gaz (*syngas*) qui peuvent être employés à des fins énergétiques. La proportion des trois sous-produits change selon les caractéristiques de la biomasse au départ (tel que la teneur en cellulose, hémicellulose et lignine (Shafizadeh, 1982) et les conditions de production, principalement la température (température maximale et taux d'augmentation de la température par unité de temps) et le temps d'exposition de la biomasse aux conditions de pyrolyse. La pyrolyse lente est mise en place si on veut maximiser la production de charbon/biochar, la pyrolyse rapide pour maximiser les huiles combustibles, la gazéification pour le gaz (Tab. I-1). Dans cette thèse, je me suis focalisée sur le charbon produit avec des méthodes traditionnelles de carbonisation, décrites en détail dans la section « Sol de charbonnières: caractéristiques, distribution géographique, utilité pour étudier l'impact des charbons à long-terme » ainsi que par pyrolyse lente avec un four à moufle et *Elsastove*, un four pyrolytique conçu par Blucomb s.r.l. pour la cuisson domestique dans les Pays en Voie de Développement (Fig. I-1).

Tableau I-1: Techniques de pyrolyse et gazéification et leurs produits typiques (Bridgwater, 2007)

Technique de production	Paramètres	Produits		
		Liquide (%)	Charbon (%)	Gaz (%)
Pyrolyse rapide	température modérée ~ 500°C temps brefs de résidence vapeur ~ 1 sec.	75	12	13
Pyrolyse à vitesse modérée	température modérée ~ 500°C temps moyens de résidence vapeur ~ 10 - 20 sec.	50	20	30
Pyrolyse lente	température modérée ~ 500°C temps très longs de résidence vapeur ~ 5 - 30 min.	30	35	35
Gazéification	température élevée > 750°C temps moyens de résidence vapeur ~ 10 - 20 sec.	5	10	85



Figure I-1 : Elsastove (Blucomb s.r.l.), four pyrolitique employé dans le cadre de cette thèse pour la production de biochar

Le biochar est caractérisé sur la base de ses caractéristiques physiques et chimiques même si elles sont très variables selon la matière organique d'origine et les conditions de production.

D'un point de vue chimique le biochar est une matrice composée principalement de carbone (C : 70-90% de sa masse) (Cohen-Ofri et al., 2007, 2006). Après le C les éléments plus abondants sont l'oxygène et l'hydrogène (H). Leur concentration est inférieure au C parce qu'ils sont volatilisés de manière plus importante pendant la déshydratation sous forme d'H_2O, et pendant la pyrolyse, sous forme de hydrocarbures, vapeurs de goudron, H_2, CO et CO_2 (Antal and Grønli, 2003).

Le rapport H/C du biochar est plus faible, que celui de la biomasse de départ (black carbon ≤0.2 Kuhlbusch and Crutzen (1996) ; charbon/biochar produit autour de 400°C ≤0.5 ; cellulose et lignine ~1.5 (Graetz and J.O. Skjemstad, 2003)) surtout pour les biochars produits à de hautes températures. La même tendance est observée pour le rapport O/C (Karen Hammes et al., 2006).

Le biochar contient aussi des éléments minéraux (cendres) en proportion variable selon la matière d'origine et les conditions de pyrolyse. En générale les biomasses ligneuses sont pauvres en cendres (<1% du poids) tandis que dans les biomasses herbacées ou graminées ainsi que dans la couverture des graines, les cendres peuvent représenter jusqu'à 24% du poids (Raveendran et al., 1995). Le contenu des cendres de la biomasse d'origine se reflète dans le contenu de cendres du biochar et, à cause de l'évaporation de C, H et O, elles représentent une portion du poids plus importante dans le biochar que dans la biomasse fraiche (biochar de litière de poulet : 45% de cendres, (Koutcheiko et al., 2007).

Enfin le biochar est aussi composé d'une partie des huiles qui sont produites lors de la pyrolyse et qui restent attachées à la surface (Schnitzer et al., 2007) en forme de composés N-heterocycliques, furanes substitués, phénols, benzène, groupes carbocycliques et aliphatiques.

Les produits de pyrolyse (charbon et biochar) présentent des structures cristallines amorphes et des couches de graphène non-ordonnées très stables (Paris et al., 2005). Le niveau d'organisation de ces matériaux augmente avec la température de production (>600°C) (Cohen-Ofri et al., 2007, 2006). Leur structure est dominée par des composés aromatiques récalcitrants. Si la température de production est entre 350 et 500°C les caractéristiques moléculaires de la biomasse d'origine restent partiellement visibles. Au-dessus de 500°C la conversion des groupes fonctionnelles de la plante tend à être plus complète en passant des groupes alkyl et O-alkyl C, associés avec cellulose et hémicellulose, à aryl C et formation de structures heterocycliques avec N (S.Krull et al., 2009).

La surface du biochar/charbon peut être hydrophile ou hydrophobe, acide ou basique, plus ou moins réactive et avec une capacité de sorption d'anions ou cations plus ou moins forte, des caractéristiques opposées qui peuvent coexister sur la surface du même morceau de biochar/charbon à cause de la présence de différents groupes fonctionnels attachés aux couches de graphène, ainsi que d'hétéroatomes (H, O, N, P et S) (Brennan, J. K., Bandosz, T. J., Thomson and Gubbins, 2001). Le type de groupes fonctionnels présents dépend de la biomasse de départ (par exemple le biochar de fumier a plus de groupes N et S par rapport à un biochar ligneux), qui peut s'altérer dans le

temps. En effet, suite à des réactions avec l'oxygène de l'air, les groupes contenant O sur la surface du biochar/charbon augmentent (Bourke et al., 2007).

Le biochar est une matière très poreuse. Les micropores (diamètre <2 nm) se forment lors de l'exposition de la biomasse à des températures de pyrolyse hautes (surtout autour de 750°C, (R. A. Brown et al., 2006) et sont responsables de la plus grande partie de la grande surface spécifique du biochar (surface intérieure maximale du biochar de bois de pin obtenue à 750°C : 400m^2/g). Les macropores (diamètre >50nm) dérivent directement de la structure vasculaire des plantes utilisées pour la production du biochar. Elles sont responsables de la plus grande partie du volume intérieur du biochar (3 cm^3/g de biochar pour les biomasses herbacées, 1.25 cm^3/g pour les biomasses ligneuses (Brewer et al., 2014).

Le biochar perd entre 3 et 91% du poids de la biomasse de départ pendant la pyrolyse ou gazéification (150-1000°C) (Baldock and Smernik, 2002; Czimczik et al., 2002) tandis que le volume extérieur se réduit beaucoup moins. Par conséquent, la densité du biochar est toujours plus faible que la densité de la matière organique de départ (Byrne and Nagle, 1997).

La capacité d'échange cationique (CEC) du biochar est en général plus basse que celle de la matière organique du sol (Cheng et al., 2008a, 2006) mais elle augmente avec la température de production (Lehmann, 2007). La capacité d'échange anionique (AEC) est plus élevée, surtout à des pH bas (Cheng et al., 2008a). Les propriétés d'échange ionique du biochar changent une fois qu'il est amendé au sol : la CEC augmente avec le temps à cause de l'augmentation des groupes fonctionnelles oxygénés sur la surface du biochar (carboxylique, phénolique, hydroxyle, carbonyle or quinone) tandis que la AEC tend à disparaitre (Cheng et al., 2008a, 2006; Lehmann et al., 2011).

Le pH du biochar peut varier de 4 à plus de 12 (Lehmann, 2007) : le pH est bas (acide) pour de basses températures de production, avec une biomasse de départ à basse teneur en cendres et d'une présence élevée de groupes fonctionnels O (Lopez-Ramon et al., 1999) (Lehmann, 2007). Après apport aux sols le pH du biochar peut diminuer (biomasse ligneuse) ou augmenter (biomasse herbacée) (Nguyen and Lehmann, 2009).

La variabilité des caractéristiques décrites plus haut rend le biochar une matière très complexe à étudier et c'est ce contexte qui a stimulé cette recherche.

Le potentiel du biochar/charbon à augmenter le stockage de C dans les sols

Le biochar est une matière très riche en carbone organisé dans des formes chimiques stables (voir section précédente). Une fois ajouté au sol il permet donc d'en augmenter le potentiel de stockage du carbone à des échelles de temps plus longues par rapport à d'autres amendements organiques. L'amendement avec le biochar pourrait permettre de stocker le CO_2 atmosphérique.

La stabilité du biochar récent est prouvée par analogie avec les résidus de feux de forêt trouvés dans les sols qui peuvent être âgés de plus de 10.000 ans (Lehmann et al., 2008; Preston and Schmidt, 2006) ou les résidus des feux de camp trouvés, par exemple, dans les sols amazoniens de "*Terra Preta*" âgés de 500-7000 ans (Neves et al., 2003) ou encore des expériences de terrains agricoles contenant du charbon, cultivés pour des longues périodes aux Etats Unis (Skjemstad et al., 2002) et en Allemagne (Schmidt et al., 2001).

Le potentiel maximal de séquestration du carbone au niveau global grâce à l'enfouissement du biochar dans les sols agricoles a été quantifié en 1,8 Gt CO_2-$C_{équivalent}$, ce qui correspond au 12% des émissions anthropiques de C (Woolf et al., 2010). Pour ce scenario une application de 50 Mg C ha^{-1} à une profondeur de 0,15 m a été considérée. Le potentiel de séquestration a été estimé en prenant en compte a) la séquestration directe du C due à l'enfouissement de la matière organique stable (Joseph et al., 2007); b) la réduction potentielle des émissions d'autres gaz à effet de serre (N_2O et de CH_4) de la part des sols suite à l'application du biochar (Yanai et al., 2007) et c) les émissions de CO_2 évitées en raison de la substitution des combustibles fossiles grâce à la production d'énergie lors de la pyrolyse et de la gazéification.

Cependant la stabilité du biochar a été mise en question. La méta-analyse de Singh et al., (2012) met en évidence que le biochar contient une composante labile et une autre plus récalcitrante avec des temps de résidence moyens de 3 et 870 ans respectivement en moyenne.

Les facteurs qui influencent la dégradation du charbon/biochar sont multiples et bien synthétisés dans la Fig. I-2 :

– Décomposition biologique : le biochar peut être métabolisé par les microorganismes (bactéries et surtout les champignons) et cela représente le mécanisme le plus important en terme de décomposition du biochar dans les sols (Baldock and Smernik, 2002; Cheng et al., 2006). La métabolisation du charbon/biochar est favorisée par la présence d'autres composés organiques labiles dans le sol ou dans le biochar lui-même qui sont facilement

disponibles pour les microorganismes et qui peuvent stimuler la dégradation du biochar par le 'priming effect' (Cheng et al., 2006).

– processus abiotiques : une fois apporté au sol, la surface du biochar est modifiée par hydrolyse et oxydation, et la plus grande partie de ces changements a une cause abiotique dans les premiers mois d'incubation (Cheng et al., 2006). L'oxydation abiotique ne cause pas la perte directe de quantités importantes de carbone mais peut faciliter la suivante métabolisation par les microorganismes (Lehmann et al., 2009) ;

– Transport : Le biochar peut être transporté en profondeur dans les sols par l'action de l'eau (percolation) (Czimczik et al., 2005; Preston and Schmidt, 2006) ou érodé de la surface du sol surtout dans les premiers temps après l'application (Rumpel et al., 2006). Suite à l'érosion le charbon/biochar s'accumule dans des dépressions ou dans des sédiments fluviaux ou océaniques où, en l'absence d'oxygène, le biochar reste stable pour des temps géologiques (Masiello and Druffel, 1998). Ces phénomènes de transport peuvent être responsables de la plus grande partie de la perte de biochar observée dans les études qui ont calculé des temps de résidence moyens dans le sol très courts (de l'ordre de la décennie) (Nguyen et al., 2008).

– Fragmentation : la taille des fragments de charbon/biochar amendés au sol se réduit dans le temps (Nguyen et al., 2008). Cela permet une augmentation de la surface directement accessible aux microorganismes et de celle exposée aux réactions abiotiques, facteurs importants pour la dégradation du biochar car l'oxydation commence en surface (Cheng et al., 2006) et atteint difficilement la partie intérieure du fragment même après des millénaires (Lehmann et al., 2005; Liang et al., 2006). De plus, des petits morceaux de charbon/ biochar sont plus susceptibles d'être transportés par rapports à des fragments de grande taille. Les cycles de congélation-décongélation *freeze–thaw* dans les régions froides ainsi que les pratiques agricoles (*labour)* peuvent contribuer au fractionnement du biochar, ainsi que les processus abiotiques (Naisse et al., 2015).

En plus d'être partiellement décomposé, le biochar est aussi stabilisé dans les sols, ce qui augmente son temps de résidence moyen. Cela se réalise par :

– l'intéraction avec les composantes minérales du sol surtout sur la surface du biochar où s'établissent des associations avec Al, Si, Fe (Nguyen et al., 2008). L'adsorption de métaux est un mécanisme qui réduit la biodisponibilité du biochar et donc augmente sa stabilité dans les sols (Lehmann et al., 2009).

– l'inclusion dans des agrégats du sol (Liang, 2008) est un phénomène qui protège le biochar des décomposeurs et qui se réalise par exemple à travers l'action des vers de terre (Topoliantz et al., 2006). La présence du biochar dans les sols peut favoriser elle-même la création d'agrégats par la prolifération de mycorhize (Warnock et al., 2007).

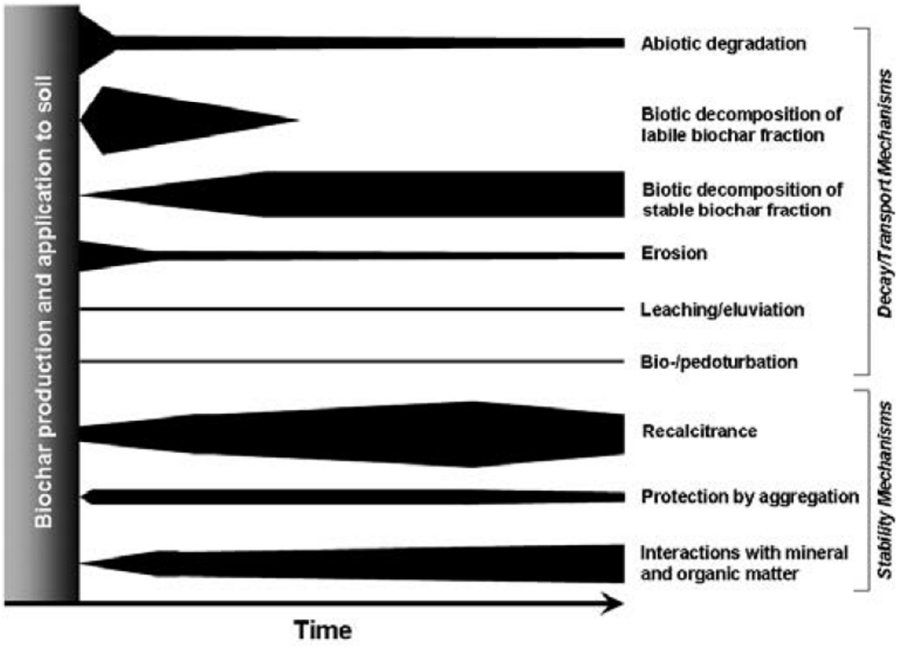


Figure I-2 : Facteurs qui influencent la stabilité et la décomposition ou transport du biochar dans les sols dans le temps. L'épaisseur des barres représente l'importance de chaque facteur dans le temps.

Source : Lehmann et al., (2009)

Tous ces facteurs vont avoir un impact plus ou moins important sur la dégradation et la stabilisation du biochar selon la biomasse de départ et la technique de production du charbon/ biochar, le type de sol et le pédoclimat au lieu de son épandage. De plus, d'un point de vue méthodologique, des techniques différentes de mesure et de calcul des temps de résidence peuvent donner des résultats contrastés (Lehmann et al., 2009). Le potentiel de stockage du C par les biochar à long terme n'a jamais été vérifié en condition de terrain. Dans cette thèse, je me suis proposé de quantifier ce potentiel en utilisent des sols d'ancien charbonnières.

Impact du biochar/charbon sur les propriétés du sol

Grâce à sa nature poreuse le biochar/charbon est capable d'améliorer l'aération et la capacité de rétention de l'eau des sols (Chan et al., 2007). La teneur en cendres alcalines (hydroxydes et oxydes de Ca, Mg, K and Na) des biochar/charbon peut, après ajout aux sols acides, altérer le pH (Chan and Xu, 2009) et augmenter la teneur en nutriments. L'effet des biochars/charbons sur ces paramètres physicochimiques peut être important, surtout s'il est issu d'une biomasse riche en nutriments tel que la litière de volaille (Atkinson et al., 2010; Glaser et al., 2002). La présence des biochars/charbons peut aussi augmenter la Capacité d'Echange Cationique (CEC) du sol (Lehmann et al., 2003; Yuan and Xu, 2012). À cause de la création des groupements fonctionnels à la surface du biochar/charbon pendant les processus d'oxydation la CEC continue à augmenter dans le temps (Cheng et al., 2008a, 2006). En effet, une importante teneur en nutriments et le changement du pH ont été observés non seulement dans les sols récemment amendés avec des biochars/charbons (Yuan et al., 2011) mais aussi dans les sols où le biochar/charbon a été présent depuis des millénaires, comme la *Terra Preta* en Amazonie (Lehmann et al., 2003).

En revanche, la richesse en sites adsorbants à la surface du biochar peut porter aussi des conséquences négatives tel que l'accumulation de métaux lourds et pesticides (J. R. Jenkins et al., 2016) tandis que l'apport de nutriments peut se traduire par une lixiviation accrue de P et de K comme démontré par Buecker et al., (2016). Mais ce phénomène en général est moins important dans les sols dans lesquels le charbon est présent depuis des siècles (Lehmann et al., 2003). Toutefois, l'impact que le même biochar a sur la lixiviation des nutriments à différentes échelles de temps n'a jamais été objet d'étude.

L'apport de biochar/charbon augmente aussi les stocks d'azote des sols. Même si cet élément est présent sous forme de composés organiques hétérocycliques (Chan and Xu, 2009), difficilement utilisable pour les microorganismes du sol, il a été montré qu'il peut être absorbé par les plantes (De la Rosa and Knicker, 2011). Au contraire des autres macroéléments, l'ajout des biochars est en général associé avec une réduction de la lixiviation de nitrates et ammonium. Cela a été observé dans des expériences en pot (Buecker et al., 2016; Ding et al., 2010; Laird et al., 2010) sur le terrain (Ventura et al., 2012), à plusieurs échelles temporelles (Lehmann et al., 2003) et a été expliqué par plusieurs mécanismes. Les nitrates (NO_3^-) sont moins lixiviés grâce à une réduction de l'activité de nitrification (Yang et al., 2015) et à l'immobilisation de l'azote dans la biomasse microbienne qui augmente grâce à la présence d'une grande quantité de carbone (Clough et al.,

2013; Clough and Condron, 2010). L'ammonium est moins lixivié parce qu'il est adsorbé sur la surface du biochar/charbon (Yang et al., 2015).

Le biochar influence profondément aussi les caractéristiques physiques d'un sol tel que : l'épaisseur, la texture, la granulométrie, la porosité, la densité et le niveau de tassement, facteurs qui influencent la disponibilité en eau et en air pour les plantes, l'ouvrabilité du sol, le niveau d'agrégation, la perméabilité, la capacité de rétention des cations, la provision d'habitat pour les microbes ainsi que sa réponse aux fluctuations des températures (Downie et al., 2009). L'impact du biochar sur ces caractéristiques et généralement positif, mais dépend des caractéristiques du biochar comme aussi celles du sol amélioré (Brady and Weil, 2008). Enfin le biochar réduit l'albédo de la surface des sols (L Genesio et al., 2012). Grâce à ces améliorations différents auteurs ont observé une augmentation de la production de biomasse ou des rendements (Biederman and Harpole, 2012; Jeffery et al., 2011) dans les sols améliorés à plusieurs échelles de temps. Toutefois, les flux des éléments dans le système sol-plante n'a jamais été évalués pour un même biochar apporté au sol à différents échelles du temps.

L'effet positif que le biochar a sur les cycles biogéochimiques, sur la présence de pathogènes dans les sols ainsi que sur la croissance des plantes peut être expliqué aussi par les changements induits dans les communautés microbiennes du sol. En effet dans la plus grande partie d'études menées sur ce sujet on a observé une augmentation de la biomasse microbienne ainsi qu'un changement significatif de la composition des communautés et de l'activité enzymatique. Cependant ces phénomènes sont encore peu compris compte tenu de leur complexité. Les effets du biochar sur la faune du sol sont encore moins étudiés sauf quelques rares recherches sur les vers de terres (Lehmann et al., 2011).

À cause de la longévité du biochar/charbon dans les sols, les modifications induites par son ajout aux sols doivent être évalués à court ainsi qu'à long terme. Cette thèse propose donc d'évaluer ces effets dans les sols alpins sous prairie à différentes échelles de temps en comparant les sols amendés avec un nouveau biochar/charbon et des sols similaires contenant le même type de charbon depuis 150 ans.

Impact du biochar/charbon sur la croissance des plantes

La littérature qui a essayé de répondre à la question « Quel est l'impact que le biochar a sur la croissance des plantes ? » est très vaste et complexe à synthétiser à cause de la grande variété de biochar/charbons employés (biomasse de départ et conditions de production), quantité de biochar/charbon amendé, type de sol et climat où le biochar/charbon est épandu, type d'expérience scientifique (au laboratoire, sur le terrain) ainsi que l'espèce de plante semé/planté. Deux synthèses de littérature (méta-analyses) ont été publiées récemment pour résumer cette complexité de résultats. Biederman et Harpole (2012) à partir de 114 articles scientifiques concluent qu'en moyenne le biochar stimule la productivité de biomasse aérienne et les récoltes agricoles même s'ils n'y a pas de relation évidente entre la quantité de biochar/charbon amendé au sol et la réponse des plantes en terme de productivité.

La méta-analyse de Jeffery et al. (2011) montre que la productivité de biomasse aérienne et les récoltes agricoles augmentent en moyenne de +10% mais la gamme des résultats varie entre −28% et +39%. Les meilleures performances ont été obtenues dans le cas de biochars produits à partir de litière de volaille, amendé en quantité de 100 t/ha, dans des sols acides et avec une texture grossière. Cela suggère que le biochar non seulement agit sur la croissance des plantes en augmentant la disponibilité de nutriments mais aussi à cause de son effet de chaulage *(liming)* et par son effet sur la capacité de rétention de l'eau qui est majeure dans les sols amendés par rapport aux sols non amendés.

L'effet positif que le biochar/charbon a sur les récoltes dépend aussi d'autres facteurs tels qu'une augmentation de l'activité microbienne dans le sol (Lehmann et al., 2011) et de la température des surfaces des sols à cause d'un changement de l'albedo (L Genesio et al., 2012), l'hormesis (Graber et al., 2010) et plus souvent une combinaison de plusieurs facteurs (Lehmann et al., 2011).

Il est important de noter que la méta-analyse de (Jeffery et al., 2011) inclut des études menés sur des sols de charbonnière en Afrique (Chidumayo, 1994a) ainsi que les sols d'Amazonie ou le charbon a été amendé depuis des millénaires (Lehmann et al., 2003), tandis que dans la revue de (Biederman and Harpole, 2012) exclue ces recherches, mais les conclusions générales sur l'impact du biochar/charbon sur la productivité des plantes sont similaires.

Cependant, l'effet des biochars/charbons sur la croissance des plantes peut changer suivant le vieillissement de ces matériaux dans les sols, qui modifie leurs propriétés physico-chimiques. Ces

changements n'ont jamais fait l'objet d'étude et je me suis proposée dans cette thèse d'évaluer les effets des biochar/charbons récents et anciens sur la croissance des plantes des prairies alpines.

Sol de charbonnières: caractéristiques, distribution géographique, utilité pour étudier l'impact des charbons à long-terme

La production annuelle de charbon de bois dans le monde était de 47 millions de tonnes en 2009 et continue d'augmenter (Steierer, 2011). Elle est concentrée principalement en Afrique (63% de la production), et emploi 15% de la totalité des ressources de bois utilisées comme source énergétique. Le charbon est en général produit avec des charbonnières traditionnelles, une technique basée sur la pyrolyse lente, c'est-à-dire le réchauffement du bois à une température maximale de 500°C en l'absence d'oxygène. Dans une charbonnière, le bois est organisé en une pile avec une entré très limité d'air. Pendant la pyrolyse il est transformé en gaz, en liquides et en charbon. Pour être de bonne qualité commerciale, la teneur en carbone du charbon devrait être autour de 75%. Le rendement des charbonnières traditionnelles est très bas, entre 8 et 12% du bois initial, avec un impact important en termes de déforestation et pollution de l'air. Aujourd'hui, on propose des technologies améliorées pour augmenter le rendement (entre 5-50%) en jouant sur plusieurs facteurs tels que le taux d'humidité du bois, la taille de la pile, les méthodes de contrôle du procédé. Mais de manière générale la technologie la plus utilisé est restée la même depuis des millénaires. En alternative aux piles de bois, le charbon est produit aussi dans des fosses. Le choix entre ces deux techniques peut être basé sur la qualité des sols : les piles sont faites dans le cas de sol rocheux et peu profonds où quand la nappe phréatique est proche de la surface tandis que les fosses sont à préférer quand les sols sont bien drainés, profonds et limeux. De plus les piles peuvent être refaites à l'infinie alors que les fosses peuvent être utilisé un nombre limité de fois (FAO, 1987).

Dans les deux cas, les sols sur lesquels le charbon est produit restent enrichis en charbon. Ces sols sont très nombreux et répandus partout sur la planète. Leur analogie avec les sols amendés avec le biochar les rend aujourd'hui très intéressants pour mieux comprendre l'impact de cet amendement sur les sols et les productions agricoles. C'est pourquoi des études y ont été effectuées aux latitudes tropicales et plus récemment aux latitudes tempérées.

Les sols de charbonnière sont en moyenne plus riches en macronutriments et carbone par rapport aux sols témoins, ils ont une plus forte CEC et un rapport C/N plus élevé, ils sont plus poreux et avec une densité apparente réduite, ils ont un pH et une température à la surface plus élevés. L'ensemble de ces facteurs se traduit en une augmentation des productions agricoles et de la

biodiversité par rapport aux sols limitrophes pas amendés avec du charbon (Carrari et al., 2016; Hernandez-Soriano et al., 2015; Naisse, 2014; Oguntunde et al., 2008, 2004).

Le contexte des prairies alpines: caractéristiques et enjeux

Les prairies alpines sont un écosystème à très haute biodiversité (Väre et al., 2003) et forte accumulation de carbone (Ciais et al., 2010; Gamper et al., 2007), qui fournit plusieurs services écosystémiques (Fontana et al., 2013), ainsi que les matières premières à la base de la production d'aliments à haute valeur ajoutée (Bovolenta et al., 2011). L'application de techniques de gestion anciennes et spécifiques garantit le soutien de la productivité de cet écosystème semi-naturel depuis des millénaires (Poschlod and Wallisdevries, 2002) et elles varient selon l'espèce et la densité du bétail, le temps de pâturage, la fréquence du fauchage, de l'apport d'engrais et de semailles (Maurer, 2005 ; Tozer et al., 2013) et l'emploi éventuel de l'irrigation (Riedener et al., 2013).

Les prairies alpines sont aujourd'hui menacées par leur abandon d'une part et par l'intensification de leur exploitation avec des méthodes inadéquates d'autre part. L'abandon a causé une forte réduction de la superficie occupée par cet écosystème en Europe (Tasser et al., 2007), accompagné d'une expansion de forêts secondaires (Tasser and Tappeiner, 2002). L'intensification mal gérée a provoqué l'augmentation des risques d'érosion, éboulements et avalanches (Tasser et al., 2003). Les deux phénomènes ont contribué à l'extension d'espèces non fourragères (Krahulec et al., 2001), à la perte de biodiversité (Dullinger et al., 2003), à la réduction de l'attractivité pour les touristes (Hunziker, 1995) ainsi qu'à la perte de stocks de carbone des sols (Poeplau and A. Don, 2013). D'après ma revue de la littérature concernant les effets positifs de l'enfouissement du biochar/charbon dans les sols, je propose de tester cette option pour améliorer les propriétés et la productivité des prairies alpines.

Chapitre 2 : Matériels et méthodes

Site d'étude

Les charbonnières étudiées sont situées en Val di Pejo, une vallée alpine dans la région italienne du Trentin Haut-Adige (46°20'16.18'' N, 10°36'07.02'' E), entre 2120 et 2170 m d'altitude, avec une température moyenne annuelle de 3.5°C et 903 mm de précipitations (Di Piazza and Eccel, 2012). La zone d'étude fait partie du Parc national du Stelvio, un parc naturel établi en 1935 sur le massif montagneux de l'Ortles-Cevedale, avec une étendue de 130.700 hectares, qui est limitrophe de 5 autres parc naturels. Les forêts de la Val di Pejo sont constituées principalement d'Epicéa (*Picea abies* L.) et de Mélèze d'Europe (*Larix decidua* Mill.), espèce dominante aux altitudes de notre site d'étude où les arbres deviennent rares et, en se rapprochant de la limite de la forêt, les prairies occupent de plus en plus de superficie.

À partir du XVI^{ème} siècle les forêts de la Val di Pejo ont été destinées à la production du charbon de bois selon une technique très similaire à celle que l'on peut observer encore aujourd'hui un peu partout dans le monde. Des portions amples de forêt étaient complètement déboisées, le bois coupé en morceaux et transporté jusqu'à la charbonnière la plus proche, située à une altitude inférieure par rapport au lieu de collecte. Le bois était empilé en cercle, en plaçant au milieu les rondins les plus gros et en laissant une cheminée au centre de la pile pour dégager les gaz produits pendant le processus de pyrolyse. Le tas de bois était enfin recouvert de terre et branches d'arbres pour garantir les conditions d'anoxie nécessaires à la pyrolyse (Rizzi, 2010) (Fig.II-1). La carbonisation prenait entre 4 et 10 jours selon la dimension de la pile et, après deux jours de refroidissement, le charbon était transporté à une usine de sidérurgie située au fond de la vallée (Fig. II-2). En 1858 l'usine fut détruite par un incendie, raison pour laquelle la production de charbon de la Val di Pejo fut arrêtée et les charbonnières abandonnées (Favilli et al., 2010; Sonna, n.d.).

Aujourd'hui, après 158 ans, les charbonnières apparaissent comme des zones aplaties, de forme elliptique, avec une superficie moyenne d'environ 100 m^2 (Fig. II-3). La forme elliptique suggère que plus d'une pile de bois était préparé à la fois, parce que la forme la plus efficace pour la carbonisation du bois est une pyramide de base circulaire (Schenkel et al., 1998). Le charbon, qui a été en surface à la fin des cycles de production est aujourd'hui mélangé au sol préexistant en conséquence des processus de bioturbation (Eckmeier et al., 2007) et des cycles de congélation/décongélation, qui se sont répété tout le long des 158 ans (Carcaillet, 2001). Cette

couche de sol anthropique, riche en charbon, avec une épaisseur de 19.3 cm en moyenne, est couverte d'une fine couche organique (2 cm) et par une végétation typique des prairies alpines, principalement *Nardus stricta* L., plusieurs espèces de *Festuca*, et quelques buissons. La même végétation couvre les sols témoins, mais qui sont couverts aussi de Mélèze d'Europe, absents pour les sols de charbonnières. Les zones considérées comme témoins sont caractérisées par l'absence de charbon, par une texture sableuse-limoneuse, un pH acide, par des zones podzolisées, profondes de 35 à 70 cm et par une pente d'environ 25%.

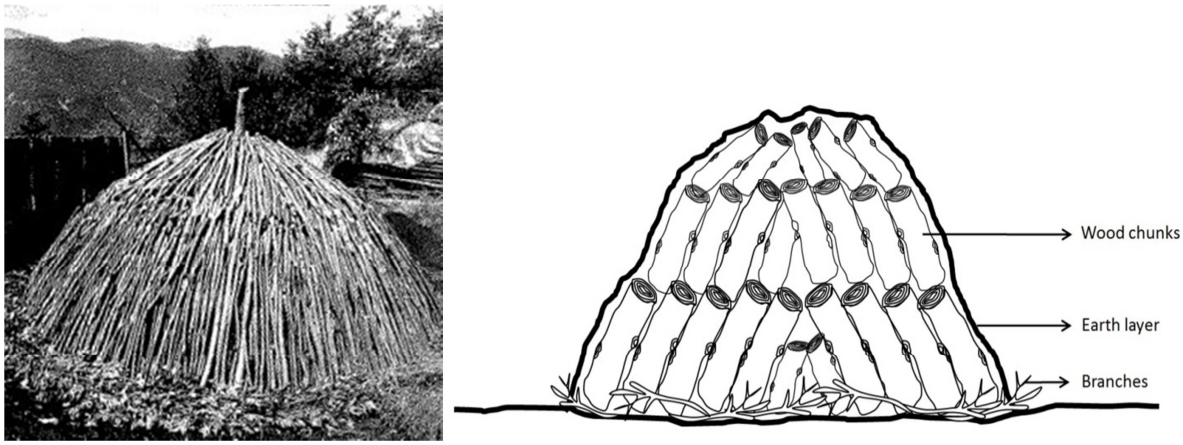


Figure II-1 : Photo et schéma d'une charbonnière typique du Trentino-Alto Adige

Source : Mantovani, 2006

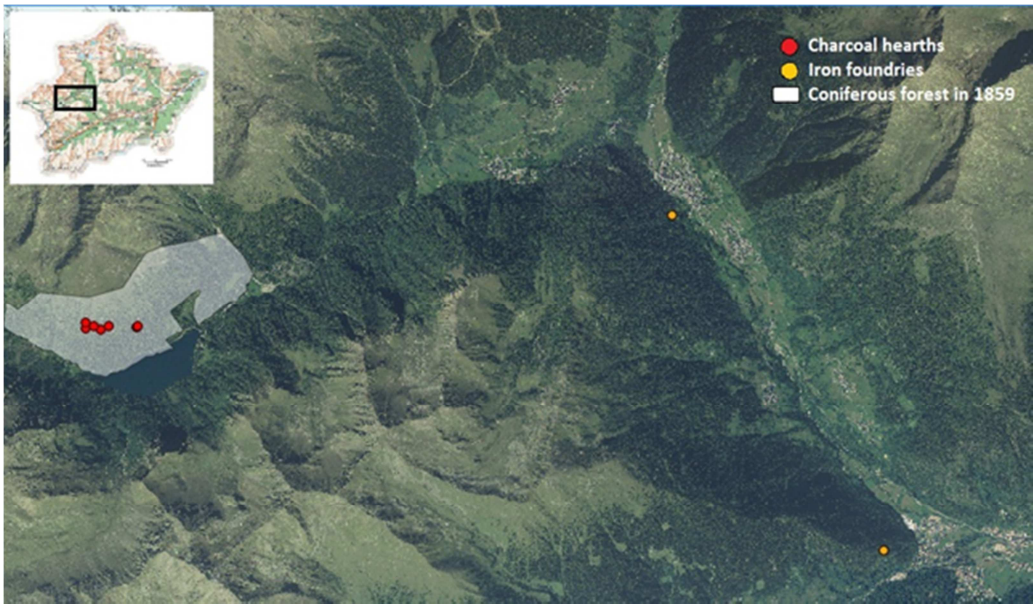


Figure II-2 : Plan de la Val di Pejo avec localisation des charbonnières (points rouges) et usines sidérurgiques (points jaunes) et couverture forestière de conifères en 1859

Source : "Terraitaly™ it NR – ortofoto digitale a colori ©Compagnia Generale Ripreseaeree S.p.A. - Parma."



Figure II-3 : Deux des charbonnières abandonnées il y a 158 ans et utilisées comme sites d’étude

L’étude se focalise sur trois des nombreuses charbonnières identifiées dans la Val di Pejo, sélectionnées parce qu’elles sont homogènes en terme d’exposition (SE) et parce que depuis leur abandon elles n’ont pas subi de modifications profondes d’origine anthropique ou naturelle (tels que des éboulements) visibles dans d’autres sites.

Chapitre 3 : Stocks de Carbone et fertilité des sols après 150 ans d'incubation du charbon

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“A quantitative description of biochar decomposition can, in these cases, only be obtained if additional information about the amount of biochar at deposition is available. But since the period for which information is sought in most cases exceeds the availability of archived samples or historical records, very few opportunities may ever exist to conduct a straightforward mass balance” (Lehmann et al., 2009)

Abstract

The addition of pyrogenic carbon (C) in the soil is considered a potential strategy to achieve direct C sequestration and potential reduction of non-CO_2 greenhouse gas emissions. In this paper, we investigated the long term effects of charcoal addition on C sequestration and soil physico-chemical properties by studying a series of abandoned charcoal hearths in the Eastern Alps of Italy established in the XIX century. This natural setting can be seen as an analogue of a deliberate experiment with replications. Carbon sequestration was assessed indirectly by comparing the amount of pyrogenic C present in the hearths (23.3±4.7 kg C m^{-2}) with the estimated amount of charcoal that was left on the soil after the carbonization (29.3±5.1 kg C m^{-2}). After taking into account uncertainty associated with parameters' estimation, we were able to conclude that 80±21% of the C originally added to the soil via charcoal can still be found there and that charcoal has an overall Mean Residence Time of 650±139 years, thus supporting the view that charcoal incorporation is an effective way to sequester atmospheric CO_2. We also observed an overall change in the physical properties (hydrophobicity and bulk density) of charcoal hearth soils and an accumulation of nutrients compared to the adjacent soil without charcoal. We caution, however, that our site-specific results should not be generalized without further study.

Introduction

Thermo-chemical conversion of organic material under limited oxygen supply, within a certain range of temperatures (200– 1200°C), transforms biomass into bio-oil and syngas, which may be used as an energy source, and produces a carbonaceous coproduct (i.e. biomass-derived Pyrogenic-C or charcoal or biochar (Lehmann et al., 2006) which has been proposed as a tool to mitigate climate change and improve soil fertility (Laird, 2008). A recent study (Woolf et al., 2010) quantified the theoretical carbon (C) sequestration potential of biochar following its incorporation in agricultural soils at a maximum rate of 50 Mg C ha^{-1} to a depth of 0.15 m as 1.8 Gt CO_2-$C_{equivalent}$ per year. This estimate corresponds to 12% of current global anthropogenic C emissions and includes: a) direct C sequestration, associated with the burial of recalcitrant organic C forms (Joseph et al., 2007); (b) potential reduction of N_2O and CH_4 emissions from soils associated with biochar application (Yanai et al., 2007); and (c) CO_2 emissions avoided due to fossil fuel substitution by the energy released by biomass during pyrolysis and gasification. Moreover, several studies have shown that the addition of biochar to both poor and fertile agricultural soils may have beneficial effects on plant yields, thus amplifying its environmental benefit. These effects are associated with improvements in soil physical (Peng et al., 2011) and chemical properties (Oguntunde et al., 2004), microbiological activity (Lehmann et al., 2011), temperature increase due to changes in surface albedo (L Genesio et al., 2012), hormesis (i.e. favorable biological responses to low exposures; Graber et al., 2010), as well as combinations of several of these different drivers (Lehmann et al., 2011).

However, while short-term studies have confirmed the potential of biochar to increase C storage and to improve soil physicochemical properties in the short-term, the long-term effects of incorporating large amounts of pyrogenic C into the soil remain rather elusive. The actual ability of biochar to act as a C sink into the soil remains controversial due to uncertainties related to its long term stability (Gurwick et al., 2013). Thousand-year old charcoal residues identified in archeological sites and areas interested by wildfires have been considered a demonstration of its long term stability in soils (Favilli et al., 2010; Schmidt et al., 2002) even though some studies have outlined the fact that the amount of Pyrogenic Carbon measured in soils is much lower than what would have been expected according to other paleontological and archeological artifacts (Kaal et al., 2008) or the frequency and intensity of fires (Masiello, 2004). Rapid transformations of charcoal in soils by abiotic and biotic oxidation can occur (Zimmermann et al., 2012) and its stability varies according to the initial feedstock, the charring conditions, and the environmental characteristics of

the burial site (Knicker, 2011). Very ancient charcoal deposits, such as Terra Preta de Indio in Amazonia (Smith, 1980) and Bronze Age human settlements of Terramare in the Po Valley in northern Italy (Cremaschi et al., 2006), are still rich in C and are still fertile substrates (Bruno Glaser et al., 2001; Mercuri et al., 2006).

The present study aimed to explore the centennial time scale stability of pyrogenic C incorporated as charcoal in soil. To do this, we used Alpine areas where charcoal, produced in traditional charcoal piles, was added to the soil more than one century ago and was not mixed with other organic sources. Moreover, we were able to assess the effect on physio-chemical soil properties after char addition to soil.

Materials and Methods

Ethics Statement

Collection of soil samples was authorized by the Stelvio National Park and Trentino Forest Service.

Site Description and Soil Sampling

The study site is located in Val di Pejo (Trentino, Northern Italy; 46°20'16.18" N, 10°36'07.02" E) at an elevation ranging from 2120 to 2170 m a.s.l. The mean annual temperature at the site is 3.5°C and the mean annual precipitation is 903 mm (Di Piazza and Eccel, 2012). The lowest precipitations are registered in January, while the highest are distributed between April and November.

Starting from the 16th century the area was subject to intensive wood resource exploitation for larch charcoal production which was subsequently used in the local iron industry. Production ceased in 1858 when a severe fire event destroyed the major iron foundry in the valley (Favilli et al., 2010; Sonna, n.d.). Charcoal production was based on large forest clear-cuts, wood chopping and downhill transportation to artificial flat terraces (charcoal hearths) with an elliptical shape. Some of these hearths are still identifiable today as terraces where wood piles were prepared and subsequently covered by soil and tree branches (Rizzi, 2010). The relatively large size and elliptical shape of the hearths suggest that more than one pile of wood was carbonized at a particular time as it was already well known that only circular piles could ensure a uniform and high quality charcoal production (Schenkel et al., 1998). Wood carbonization required between four and ten days

according to the dimension of the wood pile. After a two-day cooling down period, the charcoal was finally transported to the foundry.

Three hearths and three adjacent control areas with southerly aspects and unaffected by significant geo-morphological dynamics (erosion or sedimentation) or recent anthropogenic disturbances were selected. These are flat (2% slope) and have an average surface area (s) of 94 m^2. Soils within the control areas are shallow to moderately deep (35–70 cm), sandy-loam brown acid soils and with restricted areas of podzols (Lithic Dystrudept and Entic Haplorthod according to USDA, 2010 (Smith and Atkinson, 1975)) with an approximate 25% slope. Soils in the charcoal hearths show a truncated profile, with a shallow surface organic horizon approximately 2 cm deep covering a thicker (19.3±2.8 cm) black anthropogenic layer. This horizon contains a large amount of charcoal fragments and fine particles left after carbonization which have been subsequently incorporated and well mixed with the pre-existing soil in response to bioturbation (Eckmeier et al., 2007) and freeze-thaw processes (Carcaillet, 2001) (Figure 1). Both control soils and charcoal hearths are, nowadays, covered by the same herbaceous vegetation dominated by *Nardus stricta* L. while the surrounding forest is dominated by *Larix decidua* L. and *Picea abies* L.

The exact date of charcoal production was assessed using a dendro-anthracological approach. This method relies on cross-dating tree ring widths in charcoal fragments with known tree chronologies and has been used previously by (Backmeroff, 2013), who showed that the oldest and youngest tree rings identified in charcoal fragments at our study area were dated 1530 and 1858 respectively. This last date corresponds to the year in which a wildfire event down in the valley caused the destruction of industrial plants thus determining the interruption of the local iron industry and charcoal production in the area (Favilli et al., 2010).

Soil Sampling and Chemical Analysis

The anthropogenic layer within the charcoal hearths was sampled using a manual soil corer at five different sampling points in each hearth. Similarly, the soil at approximately the same depth was sampled at five points in each control area. Soil samples were dried for 72 hours at 35°C and sieved to 2 mm. In the case of the charcoal hearths, the fraction of soil >2 mm was further separated into two subsamples, one including charcoal fragments and one including plant debris, roots and stones. All further analysis was completed on the five sampling points separately.



Figure III-1: Soil profile at the control site (Panel a) and the charcoal hearth (Panel b). The letters indicate different pedologic horizons. In the charcoal hearth the dark anthropogenic layer (Acoal; 0–10 cm) can be easily identified.

Soil pH was measured in a soil/water solution (1:2.5 ratio). Soil C and N contents were determined by dry combustion using a CHN elemental analyzer (Perkin Elmer 2400 series II CHNS/O elemental analyzer). Total Ca, K, Mg, Na, P, and available Ca, K, Mg, P concentrations were determined for subsamples oven-dried at 105°C for 24 h according to the EPA method 3052 (USEPA, 1996) and the filtered solutions were analyzed using an ICP-OES spectrophotometer (Varian Inc., Vista MPX). A further set of subsamples was used to assess NO_3^--N according to the method proposed by Vendrell and Zupancic (1990) and NH_4^+-N according to the method proposed by Willis et al., (1993). Hydrophobicity was measured following the method of Letey (1969). Such term defines the affinity for soils to water controlling infiltration or wetting. It can be caused by coating of long-chained hydrophobic organic molecules on individual soil particles in response to the decay of organic matter but also to the diversity of soil micro-organisms. Increased hydrophobicity is normally observed after wildfires that leaves charcoal fragments at the soil surface.

C and N content, and total and available Ca, K, Mg, Na, P concentrations of >2 mm charcoal individual fragments were determined using the same methodology described above. Micrographs of those charcoal fragments were made using a Scanning Electron Microscope, XL 20 FEI SEM, with CRYOGATAN ALTO 2100 technology on samples dried under vacuum, following standard procedures (Pusceddu et al., 2013).

To enable a comparison between old and fresh charcoal, fragments of larch wood were carbonized in a muffle furnace at 400°, 500°, 600°, 860°C. The time needed to complete the carbonization corresponds to the time needed for the sample to stabilize its weight loss. C and N contents were determined on samples using the methodology described above.

Pyrogenic C Determination

The relative contribution of charcoal-C (C_{CHAR} : C_{TOT}) to total soil carbon (C_{TOT}) was estimated using a mass balance method (Del Galdo et al., 2003) based on the $\delta^{13}C$ values of charcoal fragments excavated from the anthropogenic soil layer ($\delta\ ^{13}C_{CHAR}$), the mean $\delta^{13}C$ of the entire layer ($\delta^{13}C_{TOT}$) and the $\delta^{13}C$ of the SOM contained in the adjacent control soils ($\delta^{13}C_{SOM}$) (Table III-1):

$$\frac{C_{CHAR}}{C_{TOT}} = \frac{\delta^{13}C_{TOT} - \delta^{13}C_{SOM}}{\delta^{13}C_{CHAR} - \delta^{13}C_{SOM}} \qquad (1)$$

Stable C isotope ratio ($\delta^{13}C$) measurements were made on the fine fraction (<2 mm) of representative subsamples of control and hearth soils using an Isotope Ratio Mass Spectrometer (© Thermo Fischer Scientific, Delta V Plus) following total combustion in an elemental analyser (© EA Flash 1112 ThermoFinnigan).

The $\delta^{13}C$ signature of respired CO_2 from incubated charcoal hearth and control soils was measured using the Picarro G2131-*i* $\delta^{13}C$ High-precision Isotopic CO2 Cavity Ring Down Spectrometer (CRDS) and Keeling plot method (Keeling, 1960) . Representative subsamples (~250 cm^3; n = 3) were incubated in Erlenmeyer flasks at 40°C for 15 minutes. Air was continuously circulated from the flask to a pump and then back into the flask at a rate of 0.8–1.0 l min^{-1}. The CRDS was connected to the pump inlet tube and the air sub-sampled at 0.015 l min^{-1} for measurements of CO_2 concentration and $\delta^{13}C$. Sampling frequency was 0.5 Hz. To determine the $\delta^{13}C$ signature of the respired CO_2, the Keeling method was applied (Keeling, 1960). The intercept of the linear regression with the y-axis represents the isotopic signature of the source of the flux. Regression coefficients were calculated on averaged data at each 50 ppm interval of CO_2 concentration, starting from 450 to 800 ppm to establish a steady mixing within the flask. Finally, mean and standard deviation values of $\delta^{13}C$ were computed for both charcoal hearth and control soils (n= 3). We assumed that any difference in the $\delta^{13}C$ of SOM in control and charcoal hearths would also be reflected by a difference in the $\delta^{13}C$ of the respired CO_2.

Table III-1: Parameters, coefficients and variables used to distinguish and quantify the different carbon pools in charcoal soil layer (means ± standard error, n = 3).

Parameter/ coefficient/ variable	**Definition**	**Unit**	**Value±s.e.**	**Source(s)**
C_{TOT}	Carbon content of anthropogenic soil layer in hearths	kg C m^{-2}	26.2±5.3	Measured and calculated
C_{CHAR}	Pyrogenic Carbon content of anthropogenic soil layer in hearths	kg C m^{-2}	23.3±4.7	Calculated with mass balance
C_{SOM}	Soil Organic Matter content of anthropogenic soil layer in hearths	kg C m^{-2}	2.9±0.6	Calculated with mass balance
$\delta^{13}C_{TOT}$	Isotopic signature of the bulk anthropogenic soil layer in hearths	‰	-24.72±0.25	Measured with IRMS
$\delta^{13}C_{CHAR}$	Isotopic signature of charcoal fragments extracted from the anthropogenic soil layer in hearths	‰	-24.53±0.02	Measured with IRMS
$\delta^{13}C_{SOM}$	Isotopic signature of Soil Organic Matter of control soils	‰	-26.28±0.53	Measured with IRMS
$\delta^{13}C\text{-}CO_{2HEARTHS}$	Isotopic signature of respired CO_2 from incubated hearths soils	‰	-25.22±1.96	Measured with CRDS and Keeling plot
$\delta^{13}C\text{-}CO_{2CONTROL}$	Isotopic signature of respired CO_2 from incubated control soils	‰	-24.81±0.53	Measured with CRDS and Keeling plot

Net C Sequestration

Ancillary information that is required to estimate the net C sequestration in hearths' soils was gathered from different sources:

– the amount of wood that was harvested and used for the carbonization process (*Ws*) was estimated on the basis of forest stand volume at three sub-alpine larch forests of varying ages. One forest was located on the slopes above the hearths of Val di Pejo, one in the nearby Val di Rabbi and one in Val Comasine. All forests had the same altitude (2000 m) and the latter two sites are known to be old-growth forests where 600 year old larch trees can still be found. Stand volume (m^3 ha^{-1}) was estimated using Light Detection And Ranging (LiDAR) measurements processed according to (Tonolli et al., 2011) and converted into biomass using an average wood basal density of 860 kg m^{-3}. For each forest, maximum wood stock was calculated using a fixed number of pixels;

– forest surface area that supplied each hearth during charcoal production (*h*), was determined by geo-referencing the charcoal hearths and drawing a 26 ha polygon on a digital orthophoto (Terraitaly™; © Compagnia Generale Ripreseaeree S.p.A. – Parma). *h* was calculated according to the following two criteria: i) the wood collection area should be located above each charcoal hearth up to the tree line; ii) the lateral boundaries of the area corresponded to the mean distance between two charcoal hearths (~100 m). Finally, the total area was divided by the total number of hearths identified in the area (n=7).

– carbonization efficiency, i.e. the ratio between produced charcoal and used wood (*q*), was assumed to be equal to 20% according to (Mantovani, 2006);

– the fraction of charcoal that was left on the soil surface at the end of each carbonization cycle after char was removed by charcoal makers (*w*), was experimentally estimated using a modern analogue. A charcoal hearth that is currently in use was identified at short distance from the Val di Pejo, where expert charcoal makers repeat traditional charcoal production mainly for didactical purposes. They also recorded, year by year, the exact amount of wood used and of charcoal produced. The amount of pyrogenic C left on hearth soil was quantified using the loss-on-ignition (LOI) method (Ball, 1964) using four replicates randomly selected within the hearth area. *w* was determined as the ratio between the sum of C contained in the charcoal that was made over the last ten years and the corresponding amount of C that was found in the soil. The uncertainty was estimated as the standard error of the mean;

– C content of freshly produced larch wood charcoal (r_0) was also assessed experimentally. Known amounts of larch wood taken from wood disc collected in the proximity of Val di Pejo charcoal hearths were pyrolized at different temperatures in a muffle furnace. The C concentration was measured on each charcoal sample using a CHN elemental analyzer. Measured C content data were fitted to production temperature using a second order polynomial relationship and C content at a reference temperature of 450°C was assumed to be an analog of the charcoal originally produced (FAO, 1987).

Uncertainty and Sensitivity Analysis

All data in the text and in the tables are reported as mean ± standard error (n= 3) if not differently indicated.

Gaussian error propagation technique (GEP) was used in error analysis to analytically determine the error or uncertainty produced by multiple and interacting measurements or variables. For this, the uncertainty associated to each measurement was calculated as standard error (se) of the

mean (se = standard deviation/root square of the number of samples) and the classical error propagation theory and equations were used (Lehrter and Cebrian, 2010). Error sensitivity analysis was also made by constructing an error budget (Lo, 2005), thus enabling further understanding of the error structure, i.e. the relative contribution of the errors associated with each parameter to the overall error estimate. Such sensitivity indices provide in this way a measure of the percentage rate of change in an output variable produced per unit percentage change in its input variable, an information that may be used critically to identify where error reduction of estimates may lead to lower uncertainty.

Results and Discussion

Soil Bulk Density and Hydrophobicity

The anthropogenic layer of the charcoal hearth soils has a lower bulk density than control soils (0.60±0.08 vs. 0.87±0.12 Mg m^{-3}; $p<0.01$). Soil bulk density is an important indicator of physical soil quality, being linked to air capacity, resistance to root growth and capacity of storing and transmitting water (Reynolds et al., 2009). Such a decrease in bulk density is associated with a 97.3% ±1.6 decrease in hydrophobicity. This is in line with the water infiltration data from charcoal production sites in Ghana (Oguntunde et al., 2008), but in contrast with short term observations following biochar applications to soil (Lane et al., 2004; Scott and Van Wyk, 1990) that showed small but consistent increases in soil hydrophobicity which is largely controlled by the surface chemistry of fresh biochar particles (Kinney et al., 2012). We speculate that a prolonged residence time of charcoal caused substantial leaching or degradation of hydrophobic compounds (Briggs et al., 2005), a shift in soil texture (Glaser et al., 2002; Oguntunde et al., 2008), and a microbially-driven creation of functional groups (Lehmann et al., 2005). Decreased hydrophobicity is known to increase water availability for plants and is also important for nutrient cycling, as it favors water infiltration into the soil and reduces runoff, thus preventing lateral nutrients losses.

Nutrients and Carbon

Nutrient content (total and plant available fractions) is higher in the hearths than in the control soils (Table III-2; Table III-3). In particular, the total P-stock is 107% larger in hearths than in the control (95±6 vs. 46±3 g m^{-2}, $p = 0.003$), while the plant available P is 24% higher (1.2±0.04 g m^{-2} vs. 0.9±0.3 g m^{-2}). The higher P content is not surprising as charcoal contains at least 20% of P originally contained in the wood (Table III-2). If we assume that charcoal made in the middle of

the XIX century had a P content comparable to that of modern charcoal (3.0±0.05 g P kg^{-1}; Table 3), we may estimate that carbonization events led to the addition of 117±21 g P m^{-2} (Table III-2). In the absence of grass mowing, a virtually closed P-cycle can be hypothesized for these soils as P-leaching does not usually occur if the overall concentrations are low so that P can be considered ‘‘virtually immobile’’ (Flueck, 2009; Hesketh and Brookes, 2000). Nevertheless, large herbivores are known to be net P-exporters in alpine grasslands as they may preferentially graze in P-enriched areas and then release P as dung elsewhere (Schütz et al., 2006). This export largely depends on the grazing pressure, but it is unlikely to exceed the maximum value of 0.07 g P m^{-2} y^{-1} that was assessed experimentally in the Swiss Alps (Schütz et al., 2006). When scaled to the time that charcoal was added to the soil the amount of P exported would not have exceeded 11.5 g m^{-2}. Atmospheric deposition may have also contributed to the P balance as a result of long-range desert dust transport and as a consequence of atmospheric pollution, including biomass combustion (Bergametti et al., 1992). Although the latter is known to be variable in time and space, this input is not large in the Eastern Alps, with less than 0.01 g P m^{-2} y^{-1} (Mahowald et al., 2008). When measured today, the total amount of P contained in the anthropogenic layer of the hearth’s soil is only 19% less than what was initially added during the carbonization events (95±6 vs. 117±21 g m^{-2}; Table III-2). This highlights the fact that charcoal production was indeed a long-lasting source of P in an otherwise P-limited environment. P-fertilization persisted on a centennial time-scale and it is also interesting to observe that both organic and inorganic (extractable) fractions of P that were added to the soil are now mostly contained in the non-pyrogenic fraction of the SOM, as the P contained in old charcoal fragments is only 12% of that of modern laboratory-produced larch charcoal (Table III-3).

Table III-2: Total carbon and nutrient stocks in the control soils and charcoal hearths and the estimated amount added by carbonization calculated according to Eq. [2].

Element	**control soils**	**charcoal hearths**	**p-value**	**Input by carbonization**
C (kg m^{-2})	8.1±0.3	26.2±5.3	0.03	29±5
P (g m^{-2})	45.8±3.1	95±7	0.003	117±21
K (g m^{-2})	231±34	285±70	0.53	112±20
Ca (g m^{-2})	136±23	368±80	0.1	229±41
Mg (g m^{-2})	127±88	62±5	0.51	59±10
N (g m^{-2})	582±84	500±29	0.42	80±15
Mean ± standard error (n = 3). Results of the comparison between control and charcoal hearth (p-value) are also reported.				

Other nutrients, such as potassium (K) and calcium (Ca) are also more abundant in the charcoal hearth soils even though there are no significant differences with control soils due to the large spatial variability (Table III-2). Furthermore K and Ca are 155% and 61% higher than what was added to the soil with charcoal (Table III-2). This excess may be attributed to a higher retention of atmospheric K and Ca depositions which have been previously reported to be relevant in the Alpine region (Tait and Thaler, 2000) and can be related to the higher cation exchange capacity (CEC) of charcoal (Basso et al., 2013). A strong correlation between current atmospheric deposition rates and element excesses found in the hearth soil seems to confirm such hypotheses (Figure III-2).

Total N content is not significantly different between hearth and control soils ($p = 0.42$; Table III-2) and no significant difference was found in the concentrations of mineral N (NO_3^-: $p = 0.31$; NH_4^+: $p = 0.92$; Table III-3).

Total C content of the anthropogenic layer at the charcoal hearths is three times higher than that of the adjacent control soils ($p = 0.03$; Table III-1). The amount of C that is now contained in the anthropogenic soil layer (C_{TOT}, kg C m^{-2}) is the sum of pyrogenic (C_{CHAR}, kg C m^{-2}) and non-pyrogenic components (C_{SOM}, kg C m^{-2}) as carbonates are absent due to the low pH (4.2±0.3 and 4.6±0.3 in charcoal hearths and control areas, respectively). Charcoal fragments larger than 2 mm represent approximately 4.1±1.7% (by weight) of the entire mass of the anthropogenic layer within the deeper soil horizons where no charcoal debris can be identified (Figure III-1).

Any meaningful evaluation of net C sequestration achieved in charcoal hearths firstly requires a precise separation of C fractions contained in the charcoal (C_{CHAR}) and in the rest of the soil, followed by an accurate estimation of the C input at the time of the carbonization event.

Table III-3: Total and available nutrient concentrations (mg kg^{-1} dry matter ± standard error; n = 3) measured in control soils, charcoal hearths, old and new charcoal fragments and larch wood.

	Control soils		Charcoal hearths		Old charcoal fragments	Fresh charcoal fragments	Larch wood
Element	**Total concentration**	**Available**	**Total concentration**	**Available**	**Total concentration**	**Total concentration**	**Total concentration**
Ca^{2+}	993±135	278±35	3300±185	1006±158	3438±275	5920±70	5334±53
K^{+}	1603±116	147±30	2463±69	279±120	885±66	2899±39	1415±77
Mg^{2+}	2739±73	80±12	2378±384	245±4	1215±76	1533±32	1158±12
Na^{+}	297±50	34±1	86±8	33±26	216±1	207±4	190±4
P	321±7	7±2	921±206	12±4	346±81	3005±53	2716±46
$N\text{-}NO_3^{-}$	1.96±0.74	-	2.34±0.89	-	-	-	-
$N\text{-}NH_4^{+}$	3.93±1.00	-	3.73±1.80	-	-	-	-

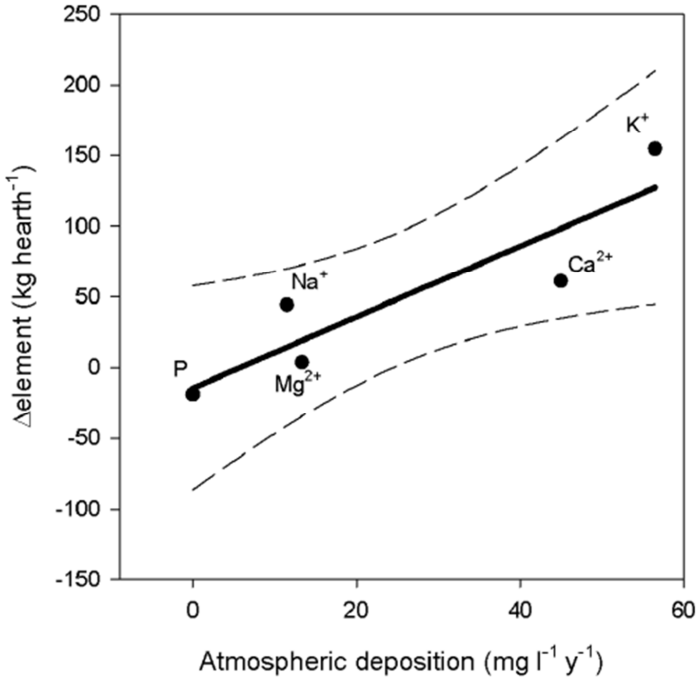


Figure III-2 : Correlation between average annual atmospheric deposition of P, K^+, Ca^{2+}, Mg^{2+}, Na^{2+} (mg l^{-1} y^{-1}) and the difference between the input of the same elements due to charcoal application in 1858 and the amount found today in hearth's soils (Δelement, kg $hearths^{-1}$) (y=2.50x–14.31, R^2 = 0.82, p = 0.035). Dashed lines represent 95% confidence interval.

Assessing the exact ratio between C_{CHAR} and C_{TOT} using sable C isotopes is problematic because:

– Equation 1 assumes a net difference in the isotopic signature of old charcoal and modern SOM. This is supported by the observation that wood formed before 1900 is on average ~1‰ less negative than that formed after 1950 (Saurer et al., 2008) due to the recent rapid rise in $\delta^{13}C$ -depleted atmospheric CO_2 concentrations as a result of fossil fuel burning (Friedli et al., 1986). In addition, it has been reported that branch or stem wood of C_3 plants is generally enriched by 1–3‰ compared to leaves (Badeck et al., 2005). Despite the fact that limited ^{13}C-depletion may occur during wood carbonization at temperatures above 300°C (Bird and Ascough, 2012), it could be expected that the charcoal fragments found in the hearth's soils are significantly enriched in the heavier C isotope compared to the more recent SOM pools that are mainly derived from the decomposition of litter formed more recently;

– Equation 1 assumes that $\delta^{13}C_{SOM}$ in the hearth's soils is equal to $\delta^{13}C_{SOM}$ in the control soils. Such equivalence cannot be assumed *a priori*, but CRDS-based $\delta^{13}C$ flux measurements demonstrated that the signature of respired CO_2 was not significantly different between control and charcoal hearth incubated soil ($p = 0.75$; Figure III-3 and Table III-1). Similarly, it may be assumed that the $\delta^{13}C$ of the less recalcitrant (non-pyrogenic) SOM fractions is the same in both hearth and control soils. Such an equivalence is further confirmed by the linearity observed by plotting the reciprocal of the C content of charcoal fragments, hearth and control soils versus their respective stable C isotopic ratios (slope =-11.3; intercept=-24.3; $r^2 = 0.98$; n= 9; $p<0.0001$). The fact that the data points fall within close proximity to a straight line indicates that the two C pools (pyrogenic and non-pyrogenic C) are distinguished in the hearth's soils;

– The $\delta^{13}C$ of the charcoal fragments ($\delta^{13}C_{CHAR}$ in Equation 1) could be affected by the presence of organic debris or microorganisms in charcoal pores. The analysis of charcoal fragments with a Scanning Electron Microscope showed that, despite being exposed in soil for over 150 years, no organic or inorganic debris were present in the inner portion of the fragments (E Pusceddu et al., 2013; Figure III-4). A recent study (Quilliam et al., 2012) showed that, in spite of the large empty space in charcoal pores, these were only sparsely populated by microorganisms three years after application to soil. This was attributed to the adsorption of inorganic and organic compounds which may cause blockage of the charcoal pores and thus prevent microorganisms penetrating the inner portion of fragments. Our data support this observation, showing that charcoal, also in the long term, does not provide a habitat for microbes and, accordingly, the $\delta^{13}C$ of the charcoal fragments is unaffected.

Based on the above assumptions and considerations, the fraction of pyrogenic C (C_{CHAR}) contained in the overall soil C (C_{TOT}) was finally estimated using Equation 1 to be equal to 89±9%, corresponding to an absolute amount of 23.3±4.7 kg of pyrogenic C m^{-2} (Table III-1).

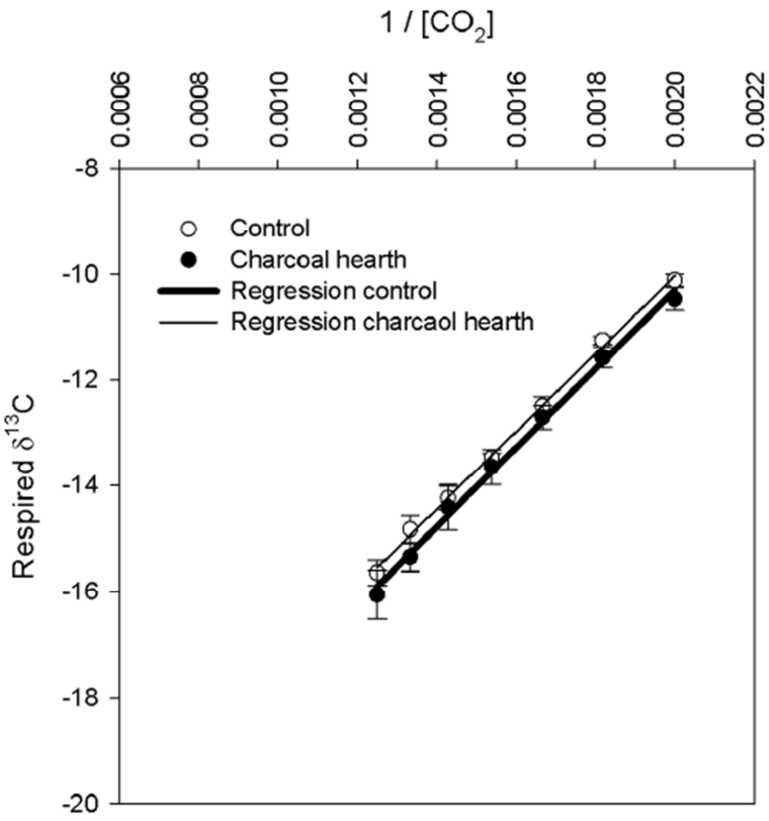


Figure III-31 : Keeling plots measured by CRDS showing the $\delta^{13}C$ of respired CO_2 fluxes versus the reciprocal of CO_2 concentration for control and charcoal hearth incubated soils ($\delta^{13}C_{CONTROL}$ = 7353*$[CO_2]^{-1}$-24. 8, R^2 = 0.99; $\delta^{13}C_{CHARCOAL\ HEARTH}$ = 7467*$[CO_2]^{-1}$-25.2, R^2 = 0.99). Horizontal and vertical bars indicate standard deviations (n = 3).

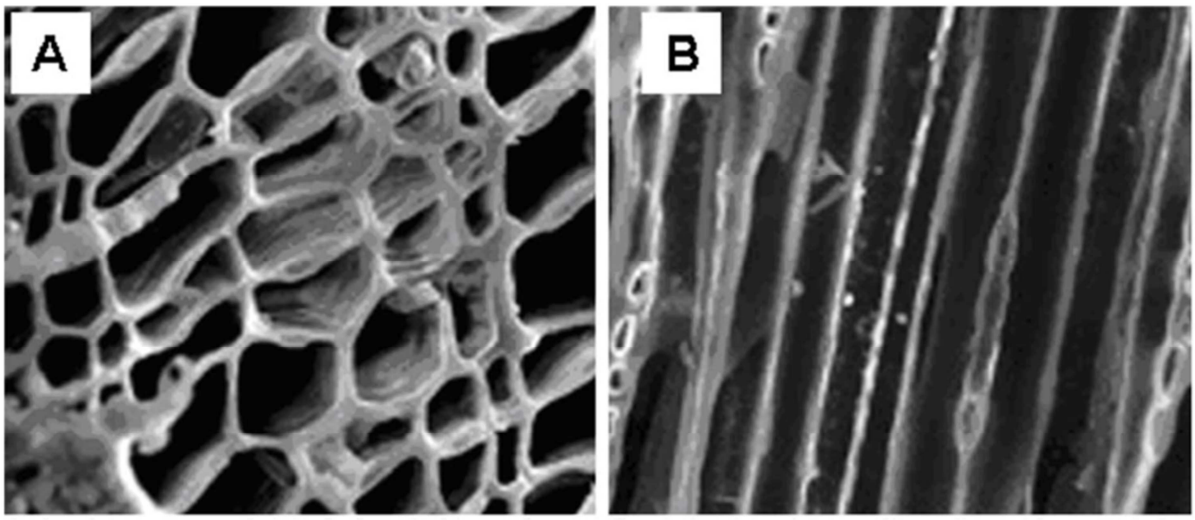


Figure III-4: SEM micrographs showing the inner morphology of charcoal fragments and the absence of any microbes or plant debris. a) is a radial section b) a longitudinal section.

Carbon Sequestration

Once the amount of pyrogenic C is known, a reliable estimation of the C sequestration achieved in the hearth soil over centennial timescale requires a proper estimation of the initial C input (C_{IN}, kg C m^{-2}). This can be obtained according to equation:

$$C_{IN} = \frac{W_s \times h \times q \times w \times r_0}{s} * 1000 \qquad (2)$$

Solving Equation 2 is problematic mainly because of the uncertainty associated with the determination of parameters *Ws*, *w* and r_0:

– the total amount of wood biomass (*Ws*) that was used for carbonization cannot be directly estimated but requires the use of a proxy. The assumption can be made that the forest standing biomass one and half centuries ago was comparable to what is currently found in our study area (288±41 t ha^{-1}; Table III-4). This assumption is partly confirmed by the fact that LIDAR-based standing volumes of two additional old-growth forest sites (>200 years) are comparable to the wood stock of the study area. The fact that tree volume is independent of stand age is not surprising and is confirmed by the usually reported plateau of forest wood stocks over centennial time scales (Mencuccini et al., 2005) in alpine larch forests (Poda, 1963);

– the fraction of charcoal left on the soil after carbonization can only be estimated indirectly as there a no reliable sources reporting such a value. We assumed that an experimental assessment using modern charcoal hearth is the most reliable proxy of ancient charcoal hearths. The value obtained in this way (*w* =0.02±0.002) was not far from judgment of two expert charcoal makers who unanimously said that no more than 2% charcoal fragments are normally left over the soil at the end of each carbonization cycle;

– the C content of new charcoal (r_0) is known to vary substantially with production temperature (r^2 = 0.94, p<0.0001; Figure III-5). Here again there are not historical data on temperature during charcoal production but FAO reports that the average temperature in traditional carbonization wood piles is around 450°C (FAO, 1987). Using this value, r_0 was estimated to be equal to 0.76±0.004.

Based on the above assumptions and considerations, C_{IN} could be calculated to be equal to 29.3±5.1 kg C m^{-2} (Table III-5) and the overall pyrogenic C lost was then quantified as:

$$\Delta C_{CHAR} = \frac{(C_{IN} - C_t)}{C_{IN}} \qquad (3)$$

where C_t is the actual pyrogenic C in the soil and t is time since the last char production at the charcoal hearth (153 years). Thus, the fraction of pyrogenic C lost since the time of carbonization was equal to 0.20±0.28 of C_{IN} (Table III-5). This value is given by the sum of the direct charcoal degradation by biotic and abiotic factors and the lateral transport due to surface runoff and erosion occurring during and after char production, before a new soil layer covered the anthropogenic layer (Jaffé et al., 2013). The presence of small amounts of minute charcoal fragments predominantly down-slope of the hearths seems to confirm the occurrence of such lateral flows.

Recent studies have used changes of the C-content of individual charcoal fragments buried in the soil as a proxy of the fraction of carbon lost from charcoal over long time scales (Cheng et al., 2008a). Such method is certainly questionable, as it cannot distinguish between actual C-losses due to oxidation and C-dilution effects associated to the deposition of inorganic salts and minerals on those fragments. Nevertheless, it is noteworthy, here, to highlight that the C content of individual charcoal fragments found in the charcoal hearth's soils (r_{155}= 0.60±0.03 gC g^{-1}) is consistently lower than the C content of modern larch charcoal made in the laboratory (r_0 = 0.76±0.04 gC g^{-1}). The fact that the relative difference between r_0 and r_{155} (0.21) almost exactly matches our estimate of the fraction of C lost on centennial time scale (Equations 2 and 3) is likely coincidental but suggests that more detailed investigations on the oxidation of ancient charcoal fragments (Naisse et al., 2013) and on mineral deposition on old charcoal fragments are needed.

The decay rate (k, $years^{-1}$) can be finally calculated as:

$$k = \frac{\ln\left(\frac{1}{1 - \Delta C_{CHAR}}\right)}{t} \qquad (4)$$

and is equal to 0.0015±0.0003. Such a value is less than half of the value estimated in a recent meta-analysis of charcoal decomposition (N. Singh et al., 2012) and corresponds to a Mean Residence Time (MRT) of 650±139 years (Table III-5).

Error sensitivity analysis performed on the results of Equation 2 and 3 illustrates the relative contribution of errors to the overall uncertainty of the result (Table III-6). The data show that the largest contribution to the overall uncertainty is in the error associated to the anthropogenic soil layer depth. Such large error suggests that variance among the three replicated hearths may not be simply random but reflects, instead, some systematic effects possibly associated to differences in the amount of wood that was carbonized in each hearth. This is indeed a critical aspect, possibly requiring a re-analysis of the simplifying assumption of an even distribution of carbonization intensity (amount of wood carbonized) among the replicated hearths. Such re-analysis would in fact enable a substantial reduction of the uncertainty, while not affecting the means. Other important sources of error are related to the estimation of the C-content of the anthropogenic layers (C_{TOT}) and in the estimated amount of wood that was used for the carbonization process (W_s). Error reduction would have been possible, in the first case, by increasing the number of replicates and more unlikely by increasing samplings in each replicate. Nevertheless, a relative large uncertainty would remain associated to the second case, as W_s was inferred on the basis of large simplification and that by no means new information could be retrieved to finally reduce its error.

Table III-4: Description of larch forests considered as analogues of the larch forest harvested for charcoal production in Val di Pejo (mean ± standard error).

Forest location name	**Forest location**	**Elevation (m a.s.l.)**	**Forest age**	**Number of plots**	**Wood stock (W, t ha^{-1})**
Val di Pejo	46°20’16.18’’ N, 10°36’07.02’’ E	2152	150	51	288±41
Val di Rabbi	46°26’39.45’’ N, 10°45’59.56’’ E	1864	500	20	213±27
Val Comasine	46°20’02.00’’ N, 10°39’58.78’’ E	2119	650	40	258±25

Table III-5: Parameters, coefficients and variables used to estimate charcoal stability in soil (mean ± standard error; n = 3).

Parameter/ coefficient/ variable	**Definition**	**Unit**	**Value±s.d.**	**Source(s)**
q	Carbonization efficiency	-	0.2	(Mantovani, 2006)
w	Fraction of charcoal left on the ground at the end of carbonization	-	0.02±0.017	Measured with LOI
r_0	Carbon content of larch wood charcoal produced at 450°C	g g^{-1}	0.76±0.04	Measured with CHN and extrapolation
r_{155}	Carbon content of charcoal fragments found in the hearths’ soil	g g^{-1}	0.60±0.032	Measured with CHN
h	Forest area for wood collection for charcoal production per hearth	ha hearth^{-1}	3.7	Measured on ortophotos
W_s	Larch wood stock of the forest in Val di Pejo	t ha^{-1}	288±41	Measured (LIDAR) and calculated to convert from m^3 ha^{-1} to t ha^{-1}
C_{IN}	Pyrogenic carbon left on the ground at the time of the carbonization	Kg C m^{-2}	29.3±5.1	Calculated using Eq. [2]
-	Fraction of pyrogenic carbon lost since the time of the carbonization calculated with Eq. [2]	-	0.20±0.28	Calculated
-	Fraction of pyrogenic carbon lost since the time of the carbonization calculated with r_0 and r_{155}	-	0.21±0.04	Calculated
k_{CHAR}	Annual pyrogenic carbon decay rate in hearths	years^{-1}	0.0015±0.0003	Calculated
MRT	Mean Residence Time of charcoal in the soil	years	650±139	Calculated
s	Surface area of charcoal hearths	m^2	94	Measured

Table III-6: Uncertainty and sensitivity analysis results for the estimation of equation 3 parameters.

Variable	**Variable uncertainty (standard error)**	**Relative contribution to the overall uncertainty in ΔC_{CHAR} in Eq. 3**
W_s	41	16%
w	0.0002	11%
r0	0.004	1%
Soil organic C content	0.03	18%
Soil bulk density	71	14%
Anthropogenic soil layer depth	0.04	26%
$\delta^{13}C_{TOT}$	0.14	11%
$\delta^{13}C_{CHAR}$	0.31	3%
$\delta^{13}C_{SOM}$	0.01	1%

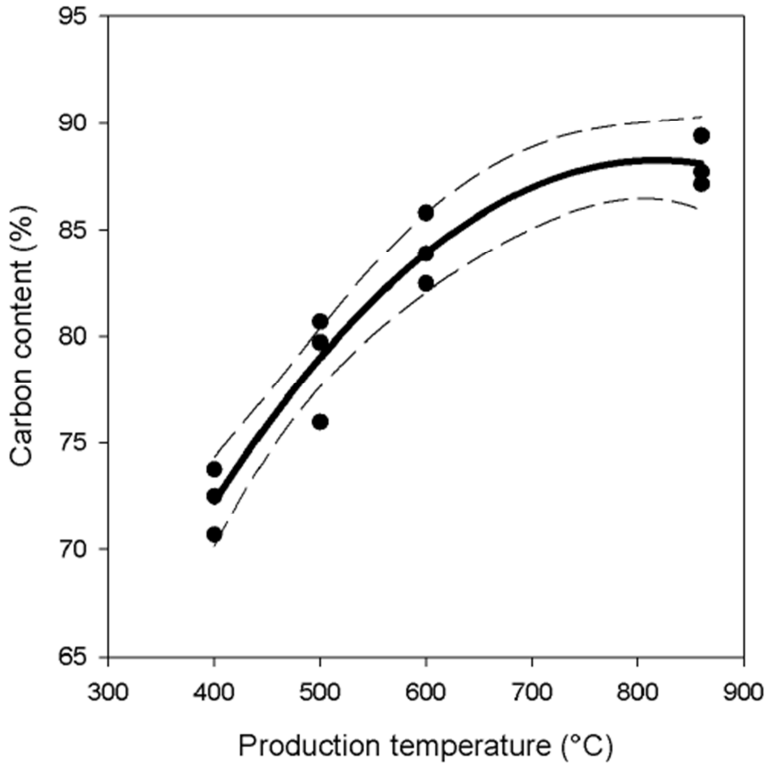


Figure III-5 2 : Carbon content of charcoal produced from larch wood at different temperatures. Wood samples were collected in close proximity to the hearths. Charcoal was produced in a muffle furnace at 400°, 500°, 600° and 860°C. Dashed lines represent 95% confidence interval. ($Y = 26.9+0.15\ X-9.2\ 10^{-5}\ X^2$; $r^2 = 0.94$; $p<0.0001$).

Conclusions

This study presents two key messages. First, it provides novel insights into the long-term decomposition of pyrogenic C in the soil, by demonstrating that charcoal addition to soil is indeed a way to obtain substantial C-sequestration. Despite some inevitable uncertainty, we have shown that 23.3±4.7 kg C m^{-2} of pyrogenic C are still present in the soil after an addition of 29.3±5.1 kg C m^{-2} that was made in the middle of the XIX century. Carbon sequestration was estimated as 80±21% of the original added C. Secondly our investigation provides substantial evidence that the availability of macro- and some micro-nutrients is higher in charcoal hearth soils over centennial timescales. This supports the common observation that the addition of various forms of pyrogenic C (biochar) increases soil fertility and plant yield, even in the long-term. The persistence of enhanced nutrient availability over centennial timescales is likely associated with mechanisms favoring their accumulation and improving soil water relations. Overall, this strongly supports the idea that the addition of biochar to soil is indeed a feasible, effective, and sustainable strategy to both sequester atmospheric C and to enhance crop yields.

However, we call for some caution on excessive generalization of our results: the hearths within the Val di Pejo are located in a mountainous area, at high elevations, and are exposed to peculiar climatic conditions, that are certainly different to the vast majority of areas where croplands are concentrated. Even if soil freeze-thaw cycles associated with large seasonal temperature fluctuations are likely to favor decomposition and C oxidation, it is not certain if and how the C decomposition rates that we observed are greater or smaller than in other climates. Additional caution is required since that the charcoal added to the studied hearths came from a single feedstock (larch wood) and was produced in traditional charcoal production systems. The fate and the effects of other feedstocks and of other production processes such as slow and fast pyrolysis, pyrogasification, and hydrothermal conversion may indeed create totally different biochar types, possibly behaving in different ways in the soil.

Charcoal hearths in Val di Pejo are certainly a unique resource for investigating the long term effect of pyrogenic C addition to the soil. The number of replications which are available, the long residence time of the charcoal in the soil, the accuracy of charcoal dating, the reliability of ancillary information on the sequence of events that were associated to charcoal production and its sudden cessation, contribute to the scientific value of these sites. A number of questions, not considered in the present study, could be addressed in the near future, such as, for instance, the

effect of long-term charcoal burial on (i) its physio-chemical properties; (ii) non-CO_2 greenhouse gas fluxes (CH_4 and N_2O); (iii) plant productivity; and (iv) shifts and changes in soil biodiversity.

In the next chapter we'll investigate the short and long-term impact of charcoal incubation on the chemical properties of soil, in particular we'll show the nutrient holding capacity of a soil amended with charcoal since 158 years and one freshly amended with the same kind of charcoal but freshly produced.

Chapitre 4 : Impact du charbon/biochar sur les flux des nutriments dans le sol

Irene Criscuoli[1,6], Leonardo Cerasino[6], Giorgio Alberti[2,3], Cristina Martinez[1,6], Silvia Baronti[4], Cornelia Rumpel[5], Franco Miglietta[1,4], Influence of char on soil nutrient holding capacity over a centennial time scale

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Introduction

Charcoal is the result of pyrolysis, the thermal decomposition that occurs when biomass is exposed to temperatures between 400 and 800 °C in the absence of oxygen (Lehmann and Joseph, 2008). In recent years the use of char as a soil amendment has been promoted as several studies have shown that char addition to both poor and fertile soils may have beneficial effects on yields, even if such positive effects are not always consistent (Biederman and Harpole, 2012; S. Jeffery et al., 2011). The mechanisms which control the interaction between char, soils and plants have only been partially elucidated. The main mechanisms that have been proposed thus far to justify such increased yield effects in croplands are the following:

i. changes in soil physical properties after biochar addition (Glaser et al., 2001; Kammann et al., 2011; Liang et al., 2006; Lim et al., 2016; J. Novak et al., 2016; Oguntunde et al., 2008; Peng et al., 2011);
ii. improvement of soil chemical properties (Angst and S. P. Sohi, 2012; Mukherjee and Zimmerman, 2013; Oguntunde et al., 2004; B. B. P. Singh et al., 2010);
iii. higher nutrient retention in highly weathered soils (Johannes Lehmann et al., 2003), particularly as a result of reduced ammonium (NH_4^+) and nitrate (NO_3^-) leaching (Taghizadeh-Toosi et al., 2011a, 2011b; Yao et al., 2011);
iv. habitat improvement for soil biota (Johannes Lehmann et al., 2011);
v. temperature enhancement due to changes in surface albedo (L Genesio et al., 2012);
vi. hormonal effects (Ellen R. Graber et al., 2010; K. a. Spokas et al., 2010);
vii. a combination of several different mechanisms.

With regards to the improvement of soil chemical properties, it has been shown that char application directly increases the soil content of potassium (K), calcium (Ca), magnesium (Mg) and phosphorus (P) in the form of alkaline ashes especially if it is produced from a nutrient rich biomass (Atkinson et al., 2010; Glaser et al., 2002). The same has been observed for traditional kilns in Zambia where charcoal fragments and ashes are left over the soil after charcoal production (Chidumayo, 1994b). Moreover, char application directly contributes to soil nitrogen (N), which, even if organized in heterocyclic structures, is partially available for the plants uptake (Chan and Xu, 2009; De la Rosa and Knicker, 2011)

The input of soil macronutrients can entail nutrient leaching of K, Ca, Mg and P (Angst et al., 2013; Buecker et al., 2016; Johannes Lehmann et al., 2003; Troy et al., 2014) immediately after

char addition, but this leaching is reduced followinglong term exposure of charcoal to soils (Johannes Lehmann et al., 2003). On the other hand, immediate effects of char addition to soil include reduced nitrate (NO_3^-) leaching, which has been observed in several pot experiments (Ying Ding et al., 2010; D. Laird et al., 2010) and field studies (Buecker et al., 2016; M Ventura et al., 2012). A reduction in NO_3^- leaching has also been reported in the ancient Amazonian Dark Earths, which contain high amounts of char (Lehmann et al., 2003). This decrease in leaching has been explained through a reduction of NH_4^+ biotransformation into NO_3^- due to a shift in soil biodiversity, and an increase in microbial N immobilization due to the input of labile carbon through biochar (Angst and Sohi, 2012; Clough et al., 2013; Clough and Condron, 2010). Similarly, the reduction in ammonium losses from the soil after biochar application has been explained with an increased sorption of NH_3 and NH_4^+ on the char surface (Yang et al., 2015).

Char application to soil might also retain nutrients from atmospheric depositions (Beck et al., 2011). Such a mechanism could be of particular interest in remote high-altitude areas of the Alps, where rain and snow may be the main source of solutes and nutrients for grassland and forest ecosystems (Greilinger et al., 2016; Rogora et al., 2016, 2006).

In northern Italy, Criscuoli et al. (2014) found that 156 year old charcoal hearth soils were richer in total (P, K and Ca) and available nutrients (P, K, Ca and Mg) compared to the surrounding soils. Moreover, the K and Ca content in the charcoal hearths is much higher today than it was at the time of char application (1858; Tab. IV-1). Criscuoli et al., (2014) hypothesized that such an increase in nutrient contents over time could be related to a direct input of ions through atmospheric depositions, which are relevant in the Alpine region (Mahowald et al., 2008; Tait and Thaler, 2000) and which could have been held in the soil because of the high cation exchange capacity (CEC), specific surface area and porosity related to the char contribution to soil (Cheng et al., 2008a; B. Liang et al., 2006). This could translate into an increase in plant biomass production (Criscuoli et al., 2016).

The main purpose of this study was to evaluate the effects of char addition to the soil on nutrient leaching and the retention of atmospheric depositions. In particular, we compared alpine grassland soils, where char was added 158 years ago (hearths) with adjacent charcoal-free soils amended with fresh char. We hypothesized that freshly amended soils leach macronutrients due to the higher input of ashes and hold NO_3^- and NH_4^+, while soils amended over a longer period of time would retain atmospheric depositions.

Tab. IV-1: Total nutrient stocks (g m^{-2}) in the control soils and charcoal hearths today, the nutrient input due to charcoal deposit in 1858 as calculated by Criscuoli et al. (2014) (mean ± s.e.; n=3) and pH. Asterisk indicates a significant difference between soil treatments ($p \leq 0.05$).

Element (g m^{-2})	**Control soil**	**Hearth soil**	**Δ% hearth soil vs. control soil**	**Input in 1858 through char**	**Δ% hearth soil vs. input in 1858**
P	46 ± 5*	95 ± 11*	107%	117 ± 36	-19%
K	231 ± 59	285 ± 122	24%	112 ± 35	155%
Ca	136 ± 41	368 ± 122	170%	229 ± 71	61%
Mg	126 ± 154	61 ± 9	-51%	59 ± 18	4%
N	582 ± 147	500 ± 49	-14%	80 ± 26	523%
pH	5.1	5.1		5.8	

Materials and methods

Site description

The study site is an Alpine larch grassland located in Val di Pejo, Trentino, Italy between 2120 and 2170 m a.s.l. The mean annual precipitation is 903 mm (Di Piazza and Eccel, 2012), with the highest rainfalls registered between April and November. The grassland is dominated by *Nardus stricta* L. and is surrounded by a forest of *Larix decidua* Mill. and, to a minor extent, *Picea abies* Karst.

As described by Backmeroff (2013) and Favilli et al. (2010), between the 16th century and 1858, the larch wood of the area was intensively exploited for charcoal production. Carbonization was made on flat terraces (hearths) (Rizzi, 2010), which are still identifiable today (Irene Criscuoli et al., 2014).

This study focuses on three of these hearths and the corresponding control (i.e. adjacent) soils, which are charcoal-free. The charcoal hearths show a truncated soil profile made of an organic horizon (~2 cm) and a thicker black anthropogenic layer (19.3±2.8 cm), rich in charcoal fragments and fine particles left after the carbonization and mixed in the soil via bioturbation (Eickmeier, et al., 2007) and freeze-thaw processes (C. Carcaillet, 2001). The surrounding control soils are sandy-loam brown acid soils with limited podzolisation (Smith and Atkinson, 1975) with a

slope around 25%. A more detailed description of the site, soil characteristics and historical charcoal production techniques can be found in Criscuoli et al. (2014).

Soil sampling and charcoal production

At each of the three charcoal hearths and control areas, two sampling points were selected. At each point within the charcoal hearth, a 10 cm diameter PVC tube was vertically inserted into the soil up to (20-25 cm) in order to collect an undisturbed soil profile. Each core was then stored at +4°C. The control soil was sampled to the same depth, air-dried, sieved at 2 mm and then mixed with fresh larch wood charcoal (diameter < 2mm) produced at 450°C in a pyrolytic stove (© Elsa Stove, Blucomb). Following the hearths' soil-charcoal ratio calculated in Criscuoli et al. (2014), six PVC tubes were thus filled with 292 g of dry control soil mixed with 185 g of fresh char.

Experimental set-up

PVC tubes were placed in an open field at the Fondazione Edmund Mach, San Michele all'Adige (Trento, Italy) from October 2013 to November 2014. 20 cm diameter funnels were placed on top of each PVC tube in order to increase the surface exposed to precipitation. 38 ml of an ion-exchange resin (Dowex Marathon MR-3 hydrogen and hydroxide form, Sigma-Aldrich) was placed at the bottom of each tube following the scheme described by Susfalk et al. (2002) and Ventura et al. (2012). The resin was made of cation (Marathon C) and anion exchanger (Marathon A) components, with a total exchange capacity of 3.2 meq ml^{-1}. In order to avoid any influence of fresh biomass inputs on the nutrient cycle over the experimental period, plants eventually growing on top of the soil cores were periodically removed and a 1mm x 1mm net prevented insects entering the tubes and reaching the soil surface.

Ion measurements in the soil and in charcoal

Subsamples of hearth and control soils at the beginning of the experiment were oven-dried at 105°C for 24 h. C and N content were determined with a CHN elemental analyzer (©Perkin Elmer 2400 series II CHNS/O elemental analyzer). The concentrations of total Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, P and available Ca^{2+}, K^{+}, Mg^{2+}, P were determined according to the EPA method 3052 (USEPA, 1996) and the filtered solutions were analyzed with an ICP-OES spectrophotometer (Varian Inc., Vista MPX). N-NO_3^{-} was quantified according to Vendrell & Zupancic (1990) and N- NH_4^{+} following the method proposed by Willis et al.(1993).

Elemental concentrations of charcoal fragments were determined using the same methodology described for soil.

The nutrient concentration of the soil amended with fresh charcoal was calculated on the basis of the nutrient content of the two components.

All ion concentrations were expressed in mg kg^{-1} (mean ± s.d., n=3) throughout the text.

Ion measurements in the resin

The resin at the bottom of each tube was removed and analyzed at the end of the experimental period to quantify the leached NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, NO_3^-, PO_4^{3-}, SO_4^{2-} as follows. A subsample of approximately 9 ml was transferred into a glass column with a porous septum (Vetrotecnica s.r.l., Padova, Italy) with the help of deionized water. The input and output water was analyzed in order to take into account possible accumulations or leaching of ions in the resin due to its use. Then, ions were extracted from the resin. Ventura et al. (2009) and Pakeman (2011) used KCl to extract ammonium and nitrates from the same resin type. The producer suggests to physically separate the two resin components and then to extract cations using HCl and NaOH from Marathon C and Marathon A, respectively (Dow, 2002, n.d.). However, due to the lack of an appropriate methodology for resin separation, we decided to use HCl to extract all ions.

The reliability of the measuring procedure was verified through multiple preliminary tests using an “artificial rain” produced in the laboratory mimicking the atmospheric depositions to which the tubes were exposed during the 13-month long experiment. Such tests showed that:

a) the fresh resin did not contain ions which could have influenced the results of the experiment (data not shown);
b) the resin was able to retain between 91 and 100% of the ion depositions during the experimental period (Tab. IV-2);
c) the extraction efficiency of HCl differs depending on the ions (Tab. IV-2). The results of the tube experiment were corrected accordingly;
d) the exchange capacity of the resin was not saturated: the ion depositions during the experimental period corresponded to 10.0% of the volume capacity for cations and 12.3% for anions.

The resin in each glass column was washed five times using 20 ml of HCl at a flow rate of 15 µl s^{-1}. To guarantee that all the HCl contained in the column removed, 10 ml of deionized water was finally passed through the resin, collected and analyzed. In order to keep track of possible contaminations and analysis errors, three extra columns were filled with 9 ml of fresh resin and treated using the same procedure as for all other samples in order to extract ions (blank samples). The exhausted solution of each column was filtered through 0.20 µm pore size cellulose acetate syringe filters (Sartorius Stedim) and samples containing HCl were diluted (1:100) before analysis (two replicates). NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-} and NO_3^- were analyzed by ion chromatography (Thermo Scientific - Dionex ICS 5000 system). Cations were quantified using a cationic column and methanesulphonic acid as eluent; anions were analyzed using an anionic column and potassium hydroxide (KOH) as eluent. PO_4^{3-} was analyzed through a colorimetric assay based on the molybdenum blue method (APHA AWWA WEF, 2012). Na^+ results were excluded because the error associated with the measurement was too large.

Tab. IV-2: Resin holding capacity (% of total ions loaded into the resin) and HCl ability to extract ions contained in the resin (% of ions held by the resin). Mean±s.d.

	SO_4^{2-}	**N-NO_3^-**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**N-NH_4^+**	**P-PO_4^{3-}**
resin holding capacity (%)	99.3 ± 0.2	99.8 ± 0.2	99.3 ± 0.5	90.9 ± 7.2	92.9 ± 0.3	100	99.6 ± 0.2	96.7 ± 0.4
HCl extraction efficiency (%)	63.7 ± 12.8	91.2 ± 17.2	46.1 ± 6.1	83.4 ± 8.1	94.4 ± 10.8	92.9 ± 8	99.3 ± 9.2	57.1 ± 8.2

Data analyses

The ions accumulated in the resin could have originated from atmospheric depositions not held in the soil core or from the leaching of ions already contained in the soil and charcoal. Thus, the overall change in soil ion concentration (Δ, mg kg^{-1}) during the 13 months of the experiment was expressed as:

$$(1)\ \Delta = \frac{(atmospheric\ depositions - resin\ ions)}{soil\ and\ charcoal\ weight} * 1000$$

Δ describes the holding (Δ>0) or leaching (Δ<0) capacity of the soil during the experimental period standardized according to the amount of soil and charcoal in the core.

Results in the text are always presented as an average of the three hearths and controls areas ± standard deviation (n=3). The differences between average data have been compared using the Mann-Whitney U test.

Results

Total soil nutrient contents in the cores are reported in Tab. IV-3. They were similar to the contents observed in Criscuoli et al., (2014). Concentrations in the hearth cores are higher than in the freshly amended soil for all nutrients (N, Ca^{2+}, K^{+}, Mg^{2+}), except for PO_4^{3-}.

The atmospheric nutrient depositions at the site during the experimental period are reported in Tab. IV-4. The highest depositions were recorded for Ca^{2+}, followed by NO_3^{-}, NH_4^{+}, SO_4^{2-}, K^{+}, Mg^{2+}, and PO_4^{3-}.

Tab. IV-3: Nutrient concentrations (mg kg^{-1}) in hearths soil cores and control soil cores amended with fresh charcoal at the beginning of the experiment. Mean ± s.d.

Soil type	**Element concentrations (mg kg^{-1})**				
	N	**$Ca2^{+}$**	**K^{+}**	**Mg^{2+}**	**PO_4^{3-}**
Hearths soil	5143 ± 1376	3309 ± 485	2474 ± 363	2435 ± 890	11 ± 5
Control soil + fresh char	3466 ± 858	2900 ± 143	2109 ± 123	2267 ± 78	21 ± 2

Tab. IV-4: Cumulative atmospheric depositions (mg $tube^{-1}$) between October 2013 and November 2014 (source: personal communication from FEM and PAT, Trento, Italy).

atmospheric depositions (mg $tube^{-1}$)						
$SO_4^{=}$	**NO_3^{-}**	**Ca^{++}**	**Mg^{++}**	**K^{+}**	**NH_4^{+}**	**PO_4^{3-}**
10.17	17.79	25.57	2.81	7.24	10.46	0.35

Soil nutrient losses and gains after one year of exposure to natural rainfall conditions are presented in Fig. IV-1. Both soils leached SO_4^{2-}, Ca^{2+} and Mg^{2+} (Fig. IV-1). For sulfates, control soils amended with fresh charcoal experienced much higher leaching rates (167 mg kg^{-1} of soil) compared to the hearths soils (17.06 mg kg^{-1}) (p=0.02). Similarly, control soil amended with fresh char leached 62.77 mg kg^{-1} of Ca^{2+}, while the hearths soils leached 17.62. However, such a difference was not statistically significant (p=0.13). On the other hand, Mg^{2+} was preferentially

leached from the hearths soils (-31.92 mg kg^{-1}) rather than from the control soils amended with fresh char (18.03 mg kg^{-1}) (p=0.06).

Both soils retained NH_4^+ and PO_4^{3-} (Fig. IV-1). For ammonium, control soils amended with fresh char showed a higher, even if not significant (p=0.27), nutrient holding capacity (12.36 mg kg^{-1}) compared to the hearths soils (8.38 mg kg^{-1}). Similarly, the control soil amended with fresh char was able to retain significantly more phosphates (0.45 mg kg^{-1}) than the hearths soils (0.14 mg kg^{-1}) (p=0.02).

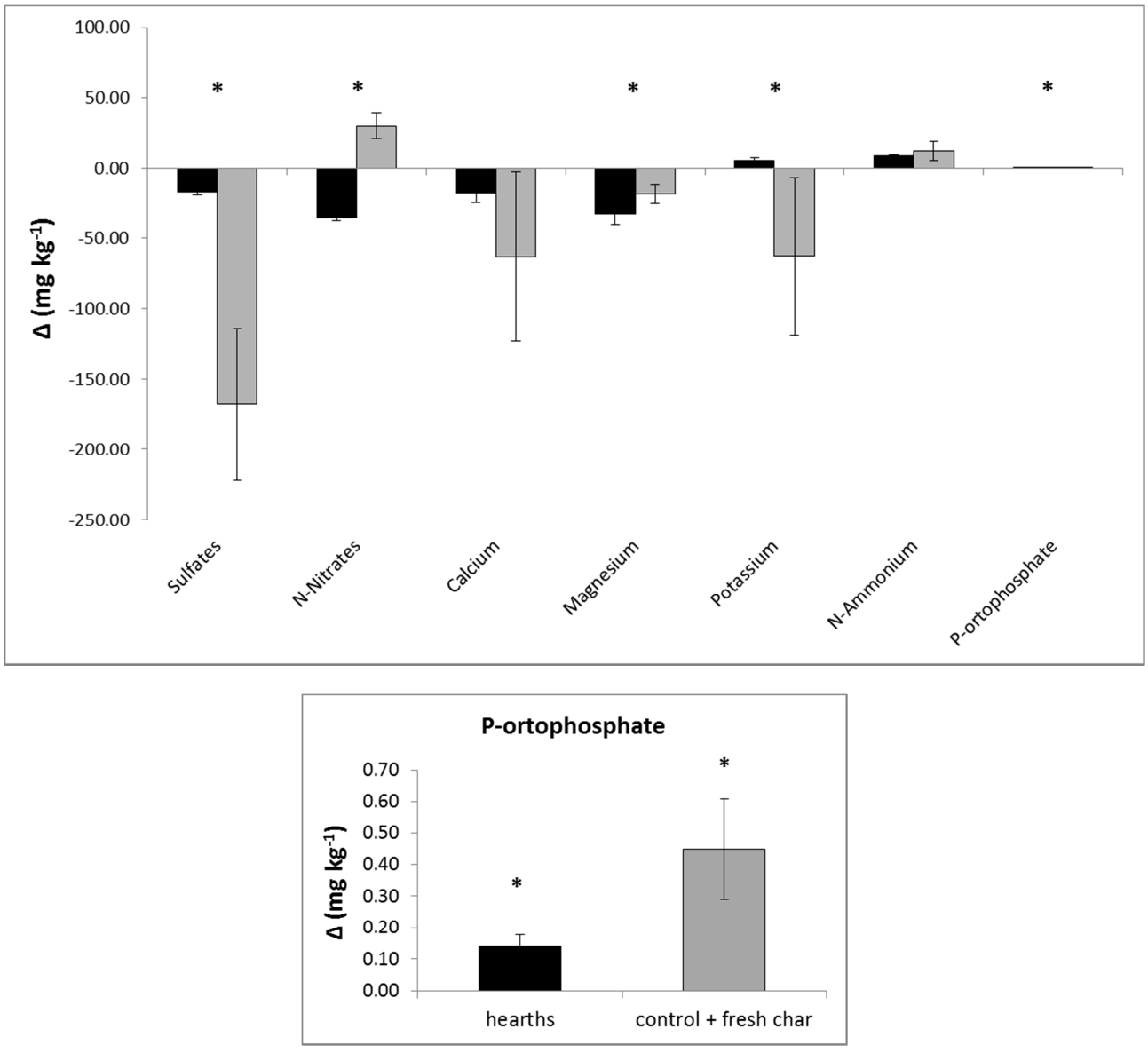


Figure IV-1 : Holding (Δ>0) or leaching (Δ<0) capacity in charcoal hearth soils (black) and control soil amended with freshly produced charcoal (grey) at the end of the experiment. Vertical bars indicate standard deviations. Asterisks indicate significant differences between treatments (p<0.10).

NO_3^- was leached from charcoal hearth soils (-35.25 mg kg^{-1}) while it was held by control soils amended with fresh char (30.27 mg kg^{-1}; p=0.02). The opposite trend was observed for K^+, which showed a positive (5.44 mg kg^{-1}) and a negative (-62.52 mg kg^{-1}) Δ for the charcoal hearth soils and the control soils amended with fresh char, respectively (p=0.02) (Fig. IV-1).

Discussion and conclusions

The results observed for potassium are in line with the available literature. In fact, when fresh charcoal is applied to soil, alkaline ashes (K hydroxide and oxide) are generally leached (Angst et al., 2013; Buecker et al., 2016; Johannes Lehmann et al., 2003; Troy et al., 2014) while other soil nutrients can be retained by fine charcoal particles which are very mobile in the soil (Kloss et al., 2014; Major et al., 2009). Conversely, aged charcoal, as in case of the *Terra preta dos Indios* in the Amazon, exhibited a reduction in K^+ leaching (Lehmann et al., 2003). In our experiment, the ancient charcoal hearth soils actually retained K^+ deposited over 13 months from the atmosphere. This may be explained by an increased CEC due to charcoal ageing, which leads to surface oxidation, forming carboxylic and phenolic functional groups (Cheng et al., 2008b, 2006). This has been demonstrated also for hardwood charcoal buried in a kiln soil for 150 years compared with a freshly produced char (Cheng et al., 2014). The ancient charcoal showed a 2-5 times increase in the sorption capacity of Cu^{2+} compared to the recently produced char. Such a result might also apply to other soil cations.

For the same mechanisms calcium was leached in both treatments, although at a lower rate in the charcoal hearth soil. As wood ashes are mainly composed of calcium (CaO) (Serafimova et al., 2011), the higher leaching observed in the freshly amended soils could be related to the higher concentration of such an element in the fresh char.

Similarly sulfate leaching was significantly higher in the control soil amended with fresh char. Char fragments have already been shown to leach sulfates, as part of the water extractable ions, in a short term lab experiment and pot experiment (Graber et al., 2010; Shinogi, 2004). SO_4^{2-} is the ion leached at the highest rate in the case of soil amended with fresh char even if its concentration in wood ashes is lower compared to calcium and potassium (Serafimova et al., 2011). The high leaching rate in this soil can be related to the low anion exchange capacity of fresh charcoal (Hollister et al., 2013). The leaching of sulfates is also associated with losses of cations as together they form soluble salts in acidic environments such as alpine grasslands (Tab. IV-1). The high loss of ashes in the early stages of char incubation (Lehmann et al., 2003) is probably the

reason behind the reduction of SO_4^{2-} leaching over time, as observed in the 156 years old hearth soil compared to the freshly amended soil.

Similarly to Ca^{2+} and K^+, magnesium was leached in both treatments. However, control soil amended with fresh char showed a lower leaching rate than charcoal hearth soil.

Phosphates were retained both in the freshly amended soil and in ancient charcoal hearths soil. The ability of the freshly amended soil to retain phosphate is in line with previous observations made using hardwood char (Hollister et al., 2013). Similarly, the behavior of the charcoal hearth soil is in line with Lehmann et al. (2003), who studied Amazon Dark Earths, rich in ancient charcoal. The observed reduction in the sorption capacity of hearth soils compared to the freshly amended soil over time may be due to a reduction in the positive charges on the charcoal surface as a result of oxidation (Cheng et al., 2008b). Phosphates can be taken up by plants and soil microorganisms in P-limited alpine grasslands. In fact, charcoal has been shown to promote the development of microorganisms (Thies and Rillig, 2009) and to increase P availability in soils via increased mycorrhizal colonization and changes in soil P speciation (Graber et al., 2015).

Nitrates are retained in the freshly amended soil, but leached in the charcoal hearths. The holding capacity of recently amended soils has been observed in the literature both in pot experiments (Ying Ding et al., 2010; D. Laird et al., 2010) and in field studies (Buecker et al., 2016; M Ventura et al., 2012) and has been related to a reduction in NH_4^+ biotransformation into NO_3^- because of a shift in soil microbes and an increase in microbial N immobilization because of higher C/N ratios following charcoal amendment (Angst and Sohi, 2012; Clough et al., 2013; Clough and Condron, 2010). Contrary to our results, previous studies in ancient soils such as the Amazonian Dark Earths also showed a certain holding capacity for NO_3^- (Lehmann et al., 2003). Charcoal can be excluded as a direct source of soluble nitrogen forms, as charcoal N is bound in forms not easily soluble in water (Bruno Glaser et al., 2002; Ellen R. Graber et al., 2010; B. Singh et al., 2010). Therefore, the leaching of anions observed in our charcoal hearth soils could be linked to a reduction of the anion exchange capacity of charcoal over time. An increase in nitrate leaching was also observed by Bruun et al. (2012).

Ammonium was retained in both charcoal hearth soils and control soils amended with fresh charcoal. This has been observed previously in the literature as NH_3 and NH_4^+ are absorbed on the char surface and because the losses of NH_3 are boosted compared to non-amended soils (Yang et al., 2015).

From our results, we can conclude that the contribution of atmospheric deposition on increasing nutrient concentrations in soils amended with char is quite limited. In particular, the overall increase in P and K concentrations over time since char application (Tab. IV-3) can be only partially explained by an increase in the retention of atmospheric depositions. In fact, since soluble P depositions via precipitation in the central Alps (7 mg m^{-2} on average) is 30 times lower than the annual requirement for plant growth (assuming a 10:1 tissue ratio of N:P) (Körner, 2011), another source of P and K has to be identified to justify the increase in plant yields observed for these soils (Criscuoli et al., 2016). Such a source could be represented by cattle excreta as charcoal hearths are flat terraces rich of highly valuable forage, an ideal place to graze, sleep and release feces in an environment otherwise characterized by steep slopes (Probo et al., 2014). The concentration of P through animal defecations can increase by more than 50 kg P ha^{-1} $year^{-1}$ (Jewell et al., 2007) together with an increase of K (Carran and Theobald, 2000).

The measured leaching of Ca^{2+} suggests that the increase in calcium content observed in the hearths compared to control soil and the input of 1858 (Tab. IV-1) cannot be explained by the retention of atmospheric depositions. Another source of Ca^{2+} could be alpine plants, especially dicotyledonous, which accumulate high concentrations of calcium. Their litter and the associated calcium may accumulate in the soil because of slow mineralization processes occurring at an altitude of 2000 m (Grzegorczyk et al., 2013).

On the contrary, N atmospheric depositions may play a central role in N cycling as N fixation in alpine grasslands is low and plant N uptake largely relies on recycling and inputs of soluble N through precipitation (i.e. meltwater; Körner, 2011). We showed that NH_4^+ is retained by both soils containing ancient charcoal and soils recently amended with fresh char. In contrast, NO_3^- is held by freshly amended soils, but not old hearth soils. Another possible source of N in the Alpine grasslands amended with char could be related tothe reduction in NH_3 losses from urine patches which is then available for plant growth (HAENI et al., 2012; TAGHIZADEH-TOOSI et al., 2012). The accumulation of total N observed in the hearths soil over time could be linked to the accumulation of organic matter in the soil, as organic nitrogen that can be partially available for plant up-take in the form of amino-acids (Cao et al., 2016).

Our study indicates that char addition to alpine soils influences their nutrient budget, especially following aging.

In the following chapter the actual fertility of ancient hearths soils will be compared with the fertility of non-amended and freshly amended grassland soils. The productivity of two alpine fodder species as well as their germination rate and nutritional values have been verified through a pot and a petri-dishes experiments.

Chapitre 5 : Productivité des prairies alpines et qualité du fourrage après 150 ans d'incubation du charbon

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Il résulte des observations faites, que le charbon végétal, mêlé au moment du labour avec les semences […] améliore les prairies naturelles et les vieux pâturages
(D'Arcet et al., 1832)

Abstract

Background and aims

Soil incorporation of charcoal (biochar) has been suggested as practice to sequester carbon, improve soil properties and crop yields but most studies have been done in the short term. Old anthropogenic charcoal rich soils in the Alps enable to explore the long-term impact of charcoal addition to alpine grassland on seed germination, fertility and fodder nutritive value.

Methods

A germination test and a growth experiment in pots with *Festuca nigrescens* Lam. and *Trifolium pratense* L. were performed using three different substrates: control soil (i.e. sandy-loam brown acid soils with some podsolization), charcoal hearth soil (i.e. charcoal enriched anthropogenic soils derived from the carbonization of larch wood on flat terraces) and control soil mixed with a fraction of fresh larch wood charcoal to reach the soil charcoal ratio of 0.6.

Results

Both aged and fresh charcoal improved germination and markedly increased plant growth of the two plant species. The addition of fresh charcoal had an initial detrimental effect that disappeared in the second and third growth cycles. Plant Nitrogen:Phosphorus ratio revealed that growth was N-limited in the anthropogenic soils and P-limited in the control and freshly amended soils demonstrating that biochar aging is critical to obtain a significant growth stimulation. Plant nutrient contents revealed an improved fodder quality in both the charcoal amended soils.

Conclusions

Despite the occurrence of limited toxic effects on seedlings, larch wood charcoal appears to have positive effects on fertility and fodder quality of alpine grasslands in the long term.

Conclusion générale

Le charbon végétal ou biochar est un amendement proposé pour l'amélioration des qualités physico-chimiques des sols, augmenter le stockage de carbone ainsi que les productions agricoles. Grâce à sa stabilité chimique le charbon/biochar pourrait rester dans les sols pour longtemps. Par conséquent il est nécessaire d'évaluer son impact à long terme. La production de charbon par des techniques traditionnelles laisse des résidus qui s'enfouissent dans le sol au cours du temps. Les anciennes charbonnières sont des très bons modèles pour étudier l'impact de l'ajout de charbon/biochar à long terme. J'ai étudié une série de charbonnières des Alpes italiennes datées de 1858 pour comprendre l'effet d'une incubation du charbon pour 150 ans sur les stocks de carbone et la fertilité des sols, la productivité de plantes fourragères et les flux de nutriments des prairies alpines.

Potentiel de stockage de C induit par l'ajout de charbon dans les sols des prairies alpines

La stabilité du charbon/biochar dans le sol est un des arguments les plus forts justifiant son utilisation comme amendement afin de lutter contre l'augmentation de la concentration du CO_2 atmosphérique. Pourtant la stabilité du charbon/biochar dépend de la biomasse de départ, des conditions de production, des caractéristiques du sol et du climat ainsi que des processus d'érosion et de lessivage. Les nombreuses études menées jusqu'à présent montrent une grande variabilité de résultats. Le charbon/biochar possède une composante plus labile qui a en moyenne un temps de résidence dans le sol de 3 ans et une composante plus stable qui reste dans les sols en moyenne 870 ans (Singh et al., 2012). Cependant, il existe des sites historiques et des sédiments qui montrent que le charbon peut rester dans les sols pour plusieurs millénaires (Glaser et al., 2002; Masiello and Druffel, 1998). La plus grande partie des recherches menées sur cet argument calcule le temps de résidence moyen sur la base d'expériences de laboratoire qui difficilement peuvent représenter la complexité d'une incubation à long terme dans le sol. Les expériences faites au champ ont une courte durée et donc n'arrivent pas à évaluer réellement la stabilité du charbon/biochar sur une longue période.

Lehmann et al., (2009) note que:

"A quantitative description of biochar decomposition can only be obtained if additional information about the amount of biochar at deposition is available. But since the period for which information is sought in most cases exceeds the availability of archived samples or historical records, very few opportunities may ever exist to conduct a straightforward mass balance".

Le but du troisième chapitre de cette thèse a été de répondre à cet objectif très ambitieux : évaluer la quantité de charbon restant dans les sols après 150 années par bilan de masse. Nous avons étudié les sols des charbonnières de la Val di Pejo au Nord de l'Italie où le charbon a été déposé en 1858. Il a fallu avant tout estimer les entrées, c'est-à-dire la quantité de charbon qui a été laissée sur le sol il y a 150 ans. Cela a été fait grâce à l'emploi de sources bibliographiques et plans cadastraux historiques, à la reproduction d'une charbonnière traditionnelle, à l'emploi de données LiDAR, mesures et bilans isotopiques et élémentaires. Selon nos calculs le 80±21% du carbone apporté en 1858 est encore présent dans les sols de charbonnières et le temps de résidence moyen du charbon est de 650±139 ans. Ces résultats ne sont pas très différent de ceux obtenus dans une recherche qui évalue la stabilité du charbon enfoui depuis 100 ans dans les sols de steppe suite à un feu de forêt (Hammes et al., 2008). Nous concluons donc que, sur les sites d'anciennes charbonnières en conditions alpines, le charbon a un temps moyen de résidence de plusieurs centaines d'années. Toutefois, l'environnement alpin est particulier et d'autres études du même style seraient nécessaires afin d'évaluer le potentiel de stockage de C induit par le biochar/charbon dans d'autres situations pédoclimatiques. Cependant les résultats obtenus dans cette thèse sont tellement nets qu'une extension à d'autres contextes agricoles est possible, même si avec prudence.

Impact du charbon/biochar sur les caractéristiques physico-chimiques des sols à court et à long terme

L'amendement de charbon/biochar change les caractéristiques physiques et chimiques du sol et cela a été démontré dans des études au champ, où le biochar a été ajouté pour une courte période et aussi dans les sols où les résidus de la production de charbon, feu de camp et feu de forêt sont présents depuis des centaines d'année (Lehmann et al., 2003; Oguntunde et al., 2008, 2004; Yuan et al., 2011). Les résultats des recherches reportés dans le troisième chapitre de cette thèse confirment l'amélioration des qualités physiques du sol (diminution de

l'hydrophobicité et de la densité apparente) et chimiques (teneur et disponibilité des nutriments) à long terme des sols de charbonnières par rapport aux sols des prairies alpines non-amendés (Criscuoli et al., 2014).

De plus les sols de charbonnière présentent aujourd'hui une concentration en nutriments supérieure aux apports de nutriments directement liés à l'ajout de charbon en 1858 (Criscuoli et al., 2014). Cela suggère la présence d'autres sources que le charbon même. Selon les résultats présentés dans chapitre n° 4 de ce travail de recherche la capacité de rétention des dépositions atmosphériques de la part du charbon joue un rôle central dans la fertilité des sols pour le phosphore et l'ammonium, deux formes minérales directement disponibles pour les plantes. Les nitrates sont retenus par les sols amendés seulement à court terme mais après 158 ans d'exposition du charbon dans le sol, les NO_3^- sont lixiviés, contrairement aux résultats d'autres recherches (Johannes Lehmann et al., 2003).

Les dépositions atmosphériques ne représentent non plus une source de K^+, Ca^{++}, $SO_4^=$, Mg^{++}. L'augmentation de la teneur en azote totale, Ca^{++} et Mg^{++} dans le temps serait donc plutôt liée à l'accumulation de matière organique qui se réalise dans les sols alpins, hypothèse qui est à tester dans notre contexte. L'accumulation de K^+ et $P\text{-}PO_4^{3-}$ serait liée aux selles du bétail qui broute de manière préférentielle sur les charbonnières, des zones plates riches en fourrage de bonne qualité (Probo et al., 2014, Jewell et al., 2007, Carran and Theobald, 2000).

Impact du charbon/biochar sur la croissance des plantes à court et à long terme

L'ajout de charbon/biochar au sol augmente aussi les productions agricoles même si les résultats dans les nombreuses expériences présentes dans la littérature sont très variables (Biederman and Harpole, 2012; S. Jeffery et al., 2011). Plusieurs études ont montré une augmentation de la productivité et de la biodiversité sur les sols de charbonnière par rapport aux sols non-amendés (Carrari et al., 2016; Hernandez-Soriano et al., 2015; Oguntunde et al., 2008, 2004). Les résultats du cinquième chapitre de cette thèse confirment la stimulation de la productivité de deux espèces fourragères dans le contexte des prairies alpines à une échelle temporelle de 150 ans environ. Au contraire l'application de charbon/biochar récent a un impact initial négatif, même si transitoire. De plus la croissance de *Festuca nigrescens* Lam. et *Trifolium pratense* L. subsp. *Nivale* (Koch) s'est avérée être limitée par l'azote dans les sols

de charbonnières et par le phosphore dans les sols de prairies non-amendés ou amendés avec un charbon récent (I. Criscuoli et al., 2016).

Schimmelpfennig et al., (2015) et Van de Voorde et al., (2014) ont démontré que l'ajout du charbon/biochar aux sols de prairie de plaine améliore la valeur nutritive des plantes. Notre étude confirme cette tendance aussi dans un contexte alpin à long terme. Néanmoins, nous concluons, qu'une meilleure valeur nutritive peut être atteinte après vieillissement des charbons dans les sols.

Il reste à établir, si cette augmentation de la fertilité s'est produite de manière linéaire, et quels ont été les processus impliqués.

La gestion des prairies alpines

Les résultats obtenus dans cette thèse ont été interprétés principalement dans un contexte de gestion et restauration de l'écosystème où les charbonnières sont situées : les prairies alpines, un environnement qui abrite une très grande biodiversité (Väre et al., 2003) et fournit plusieurs services écosystémiques (Fontana et al., 2013). Depuis des décennies la superficie couverte par les prairies diminue au sein des Alpes (Tasser et al., 2007) pendant que les prairies les plus facilement accessibles et productives subissent une exploitation plus intensive (Monteiro et al., 2011). Ces deux phénomènes ont des nombreux effets collatéraux qui nécessitent l'emploi de nouvelles méthodes de gestion.

Des anciennes évidences scientifiques nous suggèrent que l'emploi du charbon dans la gestion des prairies alpines est une option à prendre en considération. En effet déjà en 1832 d'Arcet et al. ont mis en place des expériences dans des prairies desquelles ils tiraient les conclusions suivantes:

> *''Il résulte des observations faites, que le charbon végétal, mêlé au moment du labour avec les semences, [ainsi que] le charbon animal qui provient des manufactures et des raffineries […] que les prairies naturelles et les vieux pâturages sont améliorés par ce moyen''.*

Cependant l'enfouissement du charbon/biochar dans les sols alpins peut être une opération particulièrement complexe à cause des caractéristiques géomorphologiques des

Alpes. En effet la couche de sol est généralement fine, pas loin de la roche mère et présente un profil irrégulier (Stanchi et al., 2012). Le labour augmente les risques d'érosions dans un sol qui est déjà fortement sujet à ce problème à cause des fortes pentes, l'épaisseur du sol même, le climat ainsi que la basse capacité de rénovation des sols alpins (Stanchi et al., 2012; Tasser et al., 2003). De plus la plus grande partie des prairies est localisée dans des zones très difficiles à atteindre avec les machines nécessaires pour l'application du charbon.

Toutefois, le biochar/charbon est un amendement bénéfique pour les sols alpins. Actuellement l'application du biochar/charbon est envisageable seulement dans des contextes de restauration de praires sérieusement endommagées comme dans les cas de l'ouverture de pistes de ski ainsi que la construction de routes. Des recherches en ingénierie sont nécessaires afin de surmonter les restrictions techniques empêchant son emploi dans les pairies alpines à une plus grande échelle.

Perspectives

Les résultats obtenus dans ce travail de recherche nécessitent d'ultérieurs approfondissements tels qu'évaluer:

- la productivité des charbonnières et de leur biodiversité directement sur le terrain ;
- l'accumulation de la teneur en azote totale, Ca^{++} et Mg^{++} dans la litière des sols de charbonnières par rapport aux sols de prairies non amendés ;
- l'évolution des flux des nutriments des sols amendés avec charbon/biochar dans le temps à travers le développement d'un model sur la base des résultats obtenus après un an et 158 ans d'incubation présentés dans le quatrième chapitre de cette thèse ;
- les solutions techniques qui permettraient de surmonter les restrictions empêchant l'emploi du charbon/biochar dans les pairies alpines à grande échelle.

De plus les charbonnières étudiées dans cette recherche sont un lieu privilégié pour comprendre l'impact à long terme d'un amendement en charbon/biochar. Des thèmes encore peu approfondis et qui pourraient trouver dans ce contexte un intéressant site d'étude sont :

- l'impact du charbon sur la population microbienne et la faune du sol ;
- le rôle des hormones dans l'interaction plante-charbon ;
- les émissions des gaz à effet de serre autres que le CO_2 de la part du sol (CH_4 and N_2O) ;

Enfin des charbonnières datées de 1400 ont été identifiées sur le même groupe montagneux. L'étude de ces sites par des méthodes similaire à celles présentées dans cette thèse permettrait d'évaluer l'impact que le charbon a sur une échelle de temps encore plus longue. En particulier une nouvelle évaluation de la stabilité du charbon dans ces sols serait très utile compte tenu de la complexité du travail présenté dans le premier article.

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Annexes

Publications

Criscuoli I., S. Baronti, G. Alberti, E.Pusceddu, M. Giordan, F. Camin, L. Ziller, C. Martinez, C. Rumpel, F. Miglietta "Anthropogenic charcoal-rich soils of the XIX century reveal that biochar leads to enhanced fertility and fodder quality of mountain pastures", 2016, *Plant and Soil*

Criscuoli I, Alberti G, Baronti S, Favilli F, Martinez C, et al. (2014) "Carbon Sequestration and Fertility after Centennial Time Scale Incorporation of Charcoal into Soil", *PLoS ONE* 9(3): e91114. doi:10.1371/journal.pone.0091114

Katja Wiedner, Daniel Fischer, Sabine Walther, **Irene Criscuoli**, Filippo Favilli, Oliver Nelle, and Bruno Josef Glaser "Acceleration of biochar surface oxidation during composting?", *Journal of agricultural and food chemistry*, Publication Date (Web): March 24, 2015 (Article), DOI: 10.1021/acs.jafc.5b00846

Pusceddu E., **Criscuoli I.**, Miglietta F., "Morphological investigation and physical characterization of ancient fragments of pyrogeniccarbon", 4th Young Researcher Meeting, Trieste 2013 *Journal of Physics*: Conference Series 470 (2013) 012003, IOP Publishing, doi:10.1088/1742-6596/470/1/012003

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Communications

Criscuoli I., Alberti G.**,** Baronti S., Favilli F., Martinez C., Calzolari C., Pusceddu E., Rumpel C., Viola R., Miglietta F., "Carbon sequestration and fertility after centennial time scale incorporation of charcoal into soil**",** 4th November 2014, *1st Mountfor PhD Day*, Bolzano, Italy. **Oral presentation**

Criscuoli I., Alberti G.**,** Baronti S., Favilli F., Martinez C., Calzolari C., Pusceddu E., Rumpel C., Viola R., Miglietta F., "Carbon sequestration and fertility after centennial time scale incorporation of charcoal into soil" 27th April – 2nd May 2014, *EGU 2014*, Wien, Austria. **Oral presentation**

Naisse C., Alexis M., Wiedner K., Glaser B., Pozzi A., Carcaillet C., **Criscuoli I**., Miglietta F., Rumpel C., "Biochar and hydrochar reactivity assessed by chemical, physical and biological methods", 27th April – 2nd May 2014 *EGU 2014*, Wien, Austria. **Poster**

Pusceddu E., **Criscuoli I.,** Genesio L., Vaccari F.P., Miglietta F., "Changes in morphological and physical characteristics of biochar after long-aging in soil", *2nd Mediterranean Biochar Symposium,* Palermo, Italy. **Oral presentation**

Baronti S., Alberti G., **Criscuoli I.,** Maas R., Stark A., Miglietta F., "Hydrothermal Biochar production: Effect on plant growth and Carbon degradation", *2nd Mediterranean Biochar Symposium*, Palermo, Italy. **Poster**

Miglietta F., **Criscuoli I.,** Favilli F., Calzolari C., Alberti G., Martinez G., Baronti S., "One hundred and fifty years later", *1st Mediterranean Biochar Symposium,* Como, Italy. **Oral presentation**

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Criscuoli, I., "Biochar: Carbon sink and soil amendment", *1st Annual meeting of French Organic Geochemists,* Orléans, France **Oral presentation**

Criscuoli I., Miglietta F., Si-Ammour A., Bertazza G., Di Lonardo S., "How biochar contributes to increase in agricultural yields? A study about the link between biochar and ethylene", *Eurosoil 2012,* Bari, Italia **Oral presentation**

K. Wiedner, M.L. Baumgartl, F. Favilli, **I. Criscuoli**, S. Walther, D. Fischer, F. Miglietta, B. Glaser, "Surface oxidation of modern and fossil biochars", *Eurosoil 2012,* Bari, Italia, **Poster**

Criscuoli, I., "Microgasifiers and biochar for climate change mitigation in Developing Countries". *Trentino Clima 2011*, Trento, Italy **Oral presentation**

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Résumé:

Le charbon de bois, également appelé biochar, est utilisé comme amendement pour améliorer les propriétés physico-chimiques du sol, augmenter le stockage du carbone et les productions agricoles. Du fait de sa stabilité chimique, le temps de résidence du biochar dans les sols est supposé être long, c'est pourquoi son impact doit être évalué sur le long terme. Les anciens sites de production de charbon de bois donnent l'opportunité de faire des recherches directement sur le terrain.
Dans le cadre de cette thèse on a échantillonné, dans une prairie des Alpes italiennes, une série de charbonnières abandonnées en 1858 ainsi que les sols adjacents, ne contenant pas de charbon de bois. Sur les sols on a déterminé l'effet que la présence de charbon récent et ancien a sur la capacité de stockage du carbone, les cycles de nutriments et la croissance des plantes alpines.
Les résultats montrent que 80±21% du carbone provenant de la production du charbon est toujours présent dans le sol et a un temps de résidence moyen de 650±139 ans. Le contenu des nutriments et leur biodisponibilité sont plus élevés dans les charbonnières par rapport à la prairie alentour et, sont plus élevés aujourd'hui qu'en 1858.
L'ajout de charbon apporte des nutriments au sol, mais à court terme les ions Ca^{2+}, K^{+}, SO_4^{2-} et Mg^{2+} sont lixiviés sous forme de cendres. Le charbon s'avère capable de retenir les dépositions atmosphériques de phosphates, ammonium, nitrates et, sur le long terme, de potassium. Le charbon de bois permet aussi de retenir d'autres sources de nutriments dans le sol tel que les fèces de bétail (PO_4^{3-}, K, NH_3), et la litière végétale (Ca^{2+}, N total).
L'augmentation du contenu en nutriments ainsi que la diminution de l'hydrophobie et la densité apparente du sol se traduisent en une augmentation de la productivité et de la valeur nutritionnelle de deux espèces alpines fourragères (*Festuca nugrescens* Lam. et *Trifolium pratense* L.). La croissance des plantes est inhibée sur le court terme après l'application de charbon, mais cet effet négatif transitoire disparait dès le deuxième cycle de croissance. De plus la croissance des plantes est limitée par l'azote sur les sols de charbonnière et par le phosphore dans les sols de prairies non-amendés ou amendés récemment.
De ces résultats nous pouvons conclure que l'amendement de charbon de bois/biochar peut être considéré comme une stratégie à long terme pour stocker le carbone dans les sols, augmenter la production de biomasse et la qualité du fourrage des prairies Alpines. Toutefois les opérations d'enfouissement du charbon de bois/biochar peuvent être très complexes à cause des caractéristiques géomorphologiques des Alpes. Des recherches en ingénierie sont nécessaires afin de surmonter ces restrictions techniques.

Mots-clés : charbon de bois, biochar, stockage du carbone dans le sol, lixiviation de nutriments, productivité des prairies alpines, qualité du fourrage

Abstract:

Charcoal (biochar) impact on soil carbon stocks, productivity and nutrient cycles of alpine grasslands

Charcoal, also named biochar, is proposed as a soil amendment to improve physio-chemical soil properties, increase soil carbon (C) stocks and agricultural yields. Because of its chemical stability, biochar residence time in soils is supposed to be long. Therefore its impact has to be evaluated in the long term. Ancient charcoal hearths soils provide an opportunity to investigate these topics under field conditions. A series of charcoal hearths and adjacent charcoal-free soils under grassland in the Italian Alps abandoned in 1858 was sampled. The C storage potential of these soils due to the presence of ancient charcoal was determined. Moreover, the effect of charcoal aging on nutrient dynamics and plant growth in these soils was investigated.

The results showed that 80±21% of the C originating from ancient charcoal is still present in the soil today and has a Mean Residence Time of 650±139 years. The content of total and available nutrients is higher in the hearths soils compared to the surrounding grasslands and it is higher today compared to 1858.

The input of charcoal directly adds nutrients to soils but Ca^{2+}, K^{+}, SO_4^{2-} and Mg^{2+} are leached in the short term after application, as they are lost in the form of ashes. Charcoal is able to retain atmospheric depositions of phosphates, ammonium, nitrates and in the long term potassium. Other sources of nutrients retained in the soil thanks to charcoal are those originating from cattle feces (PO_4^{3-}, K, NH_3) and plant litter (Ca^{2+}, total N).

The increase in soil nutrient content and decreases in hydrophobicity and bulk density translated into higher plant growth of two alpine fodder species (*Festuca nigrescens* Lam. and *Trifolium pratense* L.) as well as higher nutritional values in the hearths soils compared to surrounding grasslands. Plant growth was inhibited in the short term after charcoal application but this transitory negative effect disappeared already in a second growth cycle. Moreover plant growth was N-limited in the charcoal hearths soils and P-limited in the surrounding grasslands not amended or recently amended with charcoal/biochar.

From these results we can conclude that charcoal/biochar can be considered as a long term strategy to store carbon in soils, improve biomass productivity and fodder quality in alpine grasslands. However charcoal/biochar incorporation into soil can be very complex because of the geomorphology of the Alps. Engineering research is needed to overcome these technical limitations.

Keywords: charcoal, biochar, alpine grasslands, soil carbon stocks, nutrients leaching, biomass production, fodder quality