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Amazon Basin forest pyrogenic carbon stocks: First estimate of deep storage

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ABSTRACT

Amazon Basin forest soils contain considerable soil organic carbon stocks; however, the contribution of soil pyrogenic carbon (PyC) to the total is unknown. PyC is derived from local fires (historical and modern) and external inputs via aeolian deposition. To establish an initial estimate of PyC stocks in non-*terra preta* forest with no known history of fire, to assess site and vertical variability, as well as to determine optimal sampling design, we sampled 37 one hectare forest plots in the Amazon Basin and analysed PyC via hydrogen pyrolysis of three individual samples per plot and of bulked samples to 200 cm depth. Using our data and published total organic carbon stocks, we present the first field-based estimate of total PyC stock for the Amazon Basin of 1.10 Pg over 0–30 cm soil depth, and 2.76 Pg over 0–100 cm soil depth. This is up to 20 times higher than previously assumed. Three individual samples per 1 ha are sufficient to capture the site variability of PyC in our plots. PyC showed significant, large-scale variability among plots. To capture 50% of the PyC in 200 cm soil profiles, soil must be sampled to a depth of at least 71 cm. PyC represents a significant (11%) portion of total organic carbon in soil profiles 0–200 cm depth. This finding highlights the potentially important role that historical fire has played in modifying soil C stocks. Our data suggest that PyC is an important carbon pool for long-term storage, involved in millennial scale biogeochemical cycling, particularly in the subsurface soil.

1. Introduction

Amazon forest soils represent a large soil carbon pool, containing approximately 36.1 Pg C in the upper 30 cm and 66.9 Pg C in the upper 1 m (Batjes and Dijkshoorn, 1999). A substantial part of this carbon pool may exist as pyrogenic carbon (PyC) resulting from biomass burning. Following biomass burning, a fraction of PyC can quickly be lost from the soil through erosion in steep slopes (Rumpel et al., 2006, 2009) and decomposition (Kuzyakov et al. 2009; Bird et al., 2015). The remaining PyC is highly resistant to degradation through its chemical structure and through environmental conditions unfavourable to decomposition such as low oxygen and protection of PyC in organo-mineral complexes (Knicker, 2011). Therefore, PyC may reside in soils from decades to millennia (Gouveia and Pessenda, 2000; Pessenda et al., 1996, 2001; Knicker, 2011). Given its stability, PyC in the form of biochar (pyrolysed biomass used as soil amendment) receives much interest as a C sink and soil conditioner globally (e.g. Mao et al., 2012; Turcios et al., 2016). Anthropogenic Amazon Dark Earths, also referred to as *Terra Preta de Índio*, show significantly increased fertility through PyC additions (Glaser 2007); however, it is unknown if PyC in natural forest soils in the Amazon Basin affects biomass and vegetation dynamics. Knowledge on PyC in global carbon stocks and cycling is also needed for monitoring and management of soil organic carbon under land-use change and climate change (e.g. Cerri et al., 2007). Evaluating the impact of PyC on natural forest soil dynamics, requires first quantifying PyC stocks in ecosystems globally.

The pools and fluxes of PyC in forest soils remain largely unknown and poorly quantified (Santín et al., 2015), although Rodionov et al. (2010) has estimated PyC stocks in grasslands around the world. For example, Forbes et al. (2006) estimated that anywhere between 1 and

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35% of soil organic carbon (SOC) in soil is PyC. Estimates of soil PyC stocks are scarce for many areas worldwide (Bird et al., 2015). For the humid tropical forest soils, Bird et al. (2015) assumed 1% PyC/SOC, but it remains to be tested whether this is an accurate estimate. In the Amazon Basin, the amounts and spatial distribution of PyC in forest soils can be linked to the historical occurrence of fire, due to drier climatic periods in the past or through human disturbance in the last 9000 years (Pessenda et al., 2004). Filling the knowledge gaps concerning PyC stocks and distribution in tropical forest soils will allow explicit incorporation of PyC dynamics into soil carbon models.

Forest soil carbon exhibits significant spatial heterogeneity. Adequate sampling is needed to capture this heterogeneity, which can reveal patterns of both fire and above-ground biomass variation. Soil organic carbon in the topsoil can vary significantly over a lateral scale of centimeters to meters, with coefficients of variation (CVs) larger than 20% (Amador et al., 2000; Schöning et al., 2006; Metcalfe et al., 2008). Lateral and horizontal PyC in soil content is probably even more variable than SOC, as PyC distribution is controlled by the spatial variation of modern and past fire, biomass and post-fire erosion processes (Preston and Schmidt, 2006). Adequate sampling to capture heterogeneity of SOC in terra firme Amazon forest soils may require between 2 and 102 samples within 0.6 to 1 ha plots, depending on sampling depth and other physical and biological soil parameters (Metcalfe et al., 2008).

Past research suggests that bulking 25 samples from 5 transects into one bulk sample sufficiently captures the site distribution over several kilometers of SOC in woodlands, savanna, and deserts (Bird et al., 2004). Similarly, the site and vertical distribution of charcoal may be adequately described by taking between 2 and 10 samples per ca. 3 ha (McMichael et al., 2012). Establishing a robust and adequate sampling design for PyC determination would facilitate the integration of PyC in standard soil sampling and surveys, thereby improving estimates for PyC stocks globally. Furthermore, while soil sampling is usually restricted to the upper soil layers, a large body of evidence now suggests that deeper C and nutrient pools contribute significantly to ecosystem biogeochemical cycling (e.g. Harrison et al., 2011, Wigley et al., 2013, James et al., 2014). Charcoal abundance in the Amazon region has previously been observed to decrease with increasing depth in the soil (Desjardins et al., 1996; Cordeiro et al., 2014; Turcios et al., 2016), or to reach a maximum at 30–60 cm depth interval (Piperno and Becker, 1996; Santos et al., 2000; Hammond et al., 2007). Charcoal in *terra preta* soils and adjacent Ferralsols have been examined to a depth of 100 cm (Glaser et al. 2001). However, the amount of PyC and its vertical distribution in natural forest soils of the Amazon Basin to depths of 200 cm remains unknown.

The main objective of this study was to provide a first estimate of the total stock of PyC in forest soils in the Amazon Basin. Additionally, we sought to assess the variability and vertical distribution of PyC as well as develop an appropriate local-scale PyC sampling protocol to refine future estimates. Thus we specifically addressed the following research questions: 1) What is the average PyC stock in Amazon forest soils? 2) What is the heterogeneity of PyC concentrations in three individual samples per 1 ha, and are bulked samples of 5 individual samples enough to adequately represent this heterogeneity? 3) What is the vertical distribution of PyC to 200 cm, and what sampling depth is required to account for $>$ 50% of the PyC in the soil?

2. Methods

2.1. Plot selection and soil sampling

Thirty-seven 1 ha plots (excluding *Terra preta* soils) were sampled from the RAINFOR Amazon Forest Inventory Network (Fig. 1). These plots were randomly selected to provide geographic coverage of the basin, and to allow extrapolation for a first assessment of total PyC stocks in the Amazon Basin forest soils. Plots represented lowland terra firme tropical forest with no known history of recent fire or recent anthropogenic disturbance. Within each plot, one soil pit and five within-plot individual auger samples (undisturbed soil sampler, Eijkelkamp, Agrisearch Equipment BV, Giesbeek, the Netherlands) were taken from the following depths of mineral soil: 0–5, 5–10, 10–20, 20–30, 30–50, 50–100, 100–150, 150–200 cm. Within-plot individual samples were taken throughout the whole 1 ha plots. Sampling protocols for RAINFOR soils are described in detail by Quesada et al. (2010). Soils were classified according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2006).

2.2. Hydrogen pyrolysis quantification of pyrogenic carbon

PyC was determined as stable polycyclic aromatic carbon analysed via hydrogen pyrolysis (HyPy) presented as an abundance (g kg^{-1}) and as a ratio to TOC. TOC was determined by elemental analysis using a Costech ECS-4010 elemental analyser fitted with a zero blank autosampler. The PyC fraction of TOC was determined by elemental analysis following hydrogen pyrolysis, which quantifies the Stable Polycyclic Aromatic Carbon component of total PyC in a sample as defined by (Wurster et al., 2012). The HyPy analysis technique used in this study follows the procedure described by Meredith et al. (2012). Briefly, solid ~10–50 mg samples were loaded with a Mo catalyst, pressurized to 150 bar of hydrogen gas in the HyPy reactor and heated at 300 °C min^{-1} to 250 °C, then 8 °C min^{-1} until a final hold temperature of 550 °C which was maintained for 2 min. The carbon content of the sample before and after HyPy was used to calculate PyC content as a fraction of TOC. We used the following soil bulking scheme to assess variability by depth and lateral variability within plots. Depth variability: in a subset of 11 of the 37 sampled plots, chosen to represent as much as possible Amazon Basin forest soils, samples were analysed for all depths to 200 cm. In three plots, samples were analysed to 150 cm, and for the remaining 23 plots samples were analysed to 30 cm depth. Lateral variability: in 16 of the 37 sampled plots, three out of five individual samples were analysed for depths 0–5, 5–10, 10–20, 20–30 cm, in one plot three individual samples were also analysed for 30–50, 50–100 and 100–150 cm, while in three plots, three individual samples were also analysed from 150 to 200 cm. Not all five individual sample repetitions in each plot could be analysed due to limited resources. For all other plots, samples bulked from five individual samples were analysed, to capture variability of the samples, while limiting analyses.

2.3. Data analysis

PyC stocks for the Amazon Basin forest soils were estimated using mean PyC/TOC ratios, and the TOC stocks calculated by Batjes and Dijkshoorn (1999) for the Amazon Basin. Batjes and Dijkshoorn (1999) use the geographical region Amazon Basin with an area of 7618×10^3 km^2, of which approximately 6×10^6 km^2 is covered by forest. PyC/TOC ratios were weighted for TOC in 0–30 cm and 0–100 cm depths in this study to match TOC stocks' depths of Batjes and Dijkshoorn (1999). PyC stocks per soil type were calculated using weighted PyC/TOC ratios per soil type and TOC stocks per soil type of Batjes and Dijkshoorn (1999) as well as their area cover of each soil type in the Amazon Basin. Summary statistics were calculated for both TOC and PyC, with the standard error calculated for individual samples. TOC and PyC abundances were checked for normal distribution with a Shapiro test, and found to be not normally distributed. Therefore, the Wilcoxon test was used to determine significant differences in means, and Levene's test for homogeneity of variances. We tested differences in variances to determine differences between individual, non-bulked, samples within plots, and between different plots, and different soil depths. Differences in means were tested between different plots and different soil depths. Moran's I test was used to check for spatial autocorrelation between plots based on Euclidean distance using plot coordinates. Linear interpolation was used to the approximate depths at

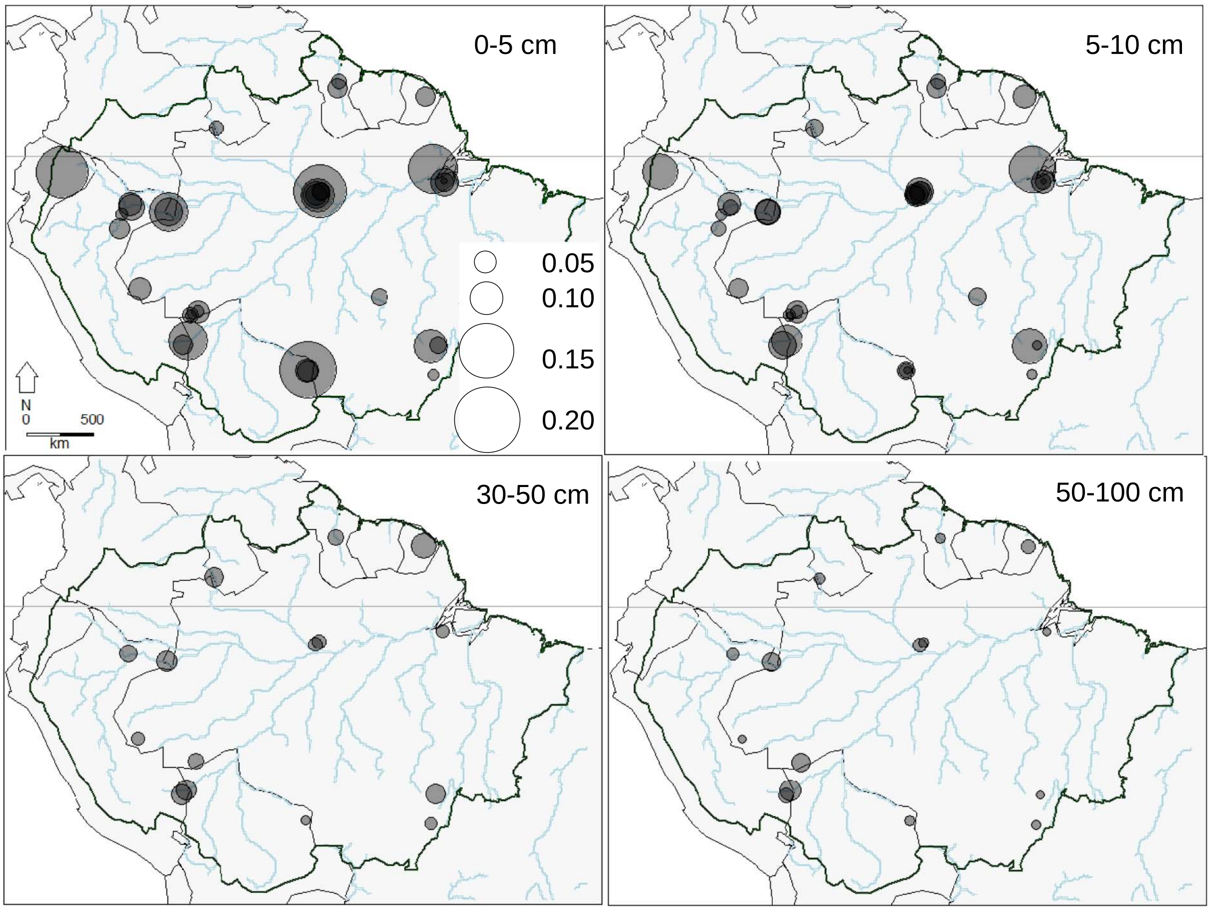

Fig. 1. Spatial variability of PyC in 0–5 cm, 5-10 cm, 30-50 cm and 50-100 cm, in 37 one hectare forest plots, with no known recent fire or anthropogenic disturbance, sampled in the Amazon Basin (delineated by green line). Points are scaled to the amount of PyC in percentage. Symbols are semi-transparent to allow visualization when overlapping. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

which 50% of TOC or PyC within 200 cm soil profiles was reached. All analyses were performed in R (R Core Team, 2014).

3. Results

3.1. Pyrogenic carbon stock

TOC and PyC decrease by 99% from 0 to 5 cm to 150–200 cm soil depth (Fig. 2, Table 1). The PyC/TOC ratio increases with depth from an average 0.025 in the top 0–5 cm to 0.11 in 150–200 cm soil (Table 1).

Combining our data with TOC estimates for the Amazon Basin (Batjes and Dijkshoorn, 1999), we estimate the total PyC stock for the Amazon Basin forest soils at 1.10 Pg over 0–30 cm soil depth (1.44 Mg PyC ha^{-1}), and 2.76 Pg over 0–100 cm soil depth (3.62 Mg PyC ha^{-1}). PyC stock estimates for the 0–30 cm depth interval sampled in the Amazon Basin forest soils vary per soil type, from 26 Tg for Arenosols, to as high as 246 Tg for Ferralsols, and from 102 Tg for Plinthosols to 645 Tg for Ferralsols in the 0–100 cm depth interval (Table 2).

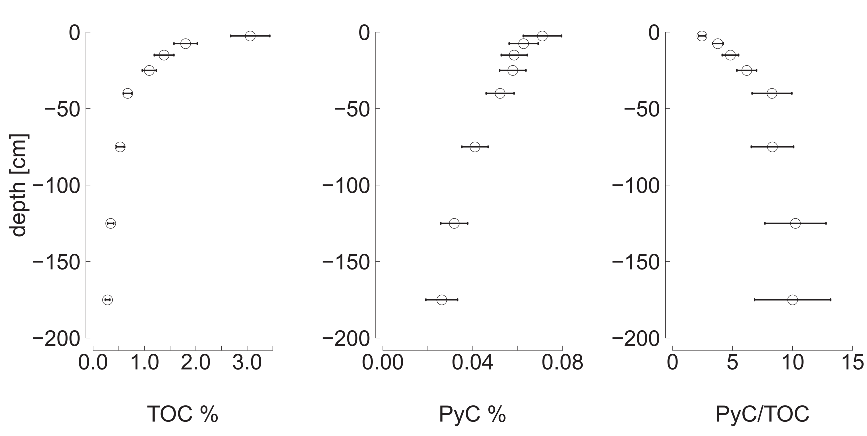

Fig. 2. TOC, PyC and PyC/TOC average values and 2SE error bars with depth for 37 1 ha forest plots, with no known recent fire or anthropogenic disturbance, sampled in the Amazon Basin.

Table 1
Average TOC and PyC in g kg^{-1} per soil depth, PyC/TOC per soil depth, standard errors (se) and coefficients of variation (CV).

depth	TOC	PyC	PyC/TOC	se TOC	se PyC	se PyC/TOC	CV TOC	CV PyC	CV PyC/TOC
0–5	31.9	0.76	0.025	0.197	0.004	0.165	0.50	0.49	0.47
5–10	17.8	0.63	0.039	0.130	0.004	0.296	0.52	0.42	0.49
10–20	14.3	0.60	0.048	0.104	0.003	0.488	0.57	0.40	0.59
20–30	11.1	0.59	0.062	0.081	0.004	0.549	0.52	0.42	0.55
30–50	7.0	0.52	0.082	0.016	0.006	1.079	0.27	0.29	0.46
50–100	5.2	0.41	0.084	0.075	0.005	1.064	0.32	0.34	0.49
100–150	3.6	0.35	0.106	0.044	0.004	1.730	0.37	0.45	0.54
150–200	2.7	0.28	0.110	0.045	0.000	0.780	0.31	0.50	0.61

Table 2
Pyrogenic carbon stocks in Tg per soil type for 0–30 cm and where available for 0–100 cm, estimated from weighted pyrogenic carbon to total organic carbon ratios and total soil organic carbon stocks in the Amazon Basin after Batjes and Dijkshoorn, and *terra preta* PyC stocks inferred from Glaser et al. using 3% coverage of the Amazon Basin.

soil type	pyrogenic carbon 0–30 cm	N	pyrogenic carbon 0–100 cm	N
Acrisol	216	8	577	4
Alisol	48	2		
Arenosol	26	1		
Cambisol	123	4	271	3
Ferralsol	246	13	645	3
Plinthosol	45	7	102	3
Regosol	37	1		
Terra Preta	229		171	

3.2. TOC and PyC variability

Within plots, for all samples, 34% of individual sample TOC values and 35% of individual sample PyC values are within 1 standard error difference of the mean. All (100%) TOC and PyC individual sample values are within 2 standard error difference of the mean. Variances of TOC and PyC were not significantly different between individual samples (Table 3). Sample means of individual samples per plot for TOC and PyC in the 0–30 cm interval are not significantly different from bulked sample means (Table 3). Between plots, no spatial auto-correlation of TOC and PyC in the topsoil samples (0–5 cm) is observed (Table 3, Fig. 1). Means and variances of TOC and PyC between plots are significantly different (Table 3).

3.3. TOC and PyC differences with depth

TOC and PyC differ significantly between soil depths, both for plots analysed to 200 cm and for plots analysed to 30 cm depth (Table 3). Over the full 200 cm sampled, 50% of TOC in the soil profile is found in the upper 23 to 55 cm, and 50% of PyC is found in the upper 44 to 71 cm (Fig. 3). By linear interpolation, soil must be sampled to a depth of at least 71 cm to quantify 50% of PyC in the full profile, and to at least 127 cm to sample 75% of PyC.

Table 3
P-values and degrees of freedom (DF) of the statistical tests performed. Significant test results with $P < 0.05$ are in bold text.

	TOC		PyC	
	P value	DF	*P* value	DF
Levene between individual samples	0.85	2	0.28	2
Kruskal-Wallis between individual and bulk samples (0–30 cm only)	0.87	1	0.67	1
Levene between individual and bulk samples (0–30 cm only)	0.44	1	0.73	1
Kruskal-Wallis between plots	**9.20E–08**	36	**< 2.20e–16**	36
Levene between plots	**6.66E–03**	36	**1.49E–04**	36
Moran's I spatial autocorrelation between plots	0.16		0.98	
Wilcoxon between depths 0–200 cm	**< −2.20e–16**	7	**< 2.20e–16**	7
Levene between depths 0–200 cm	**2.24E–08**	7	**7.94E–03**	7
Wilcoxon between depths 0–30 cm	**< 2.20e–16**	3	**< 2.20e–16**	3
Levene between depths 0–30 cm	**1.65E–03**	3	0.15	3

4. Discussion

4.1. Pyrogenic carbon stock in Amazon forest soils

We provide a first estimate for the PyC stock in natural forest soils of the Amazon Basin of 1.10 Pg over 0–30 cm soil depth, and 2.76 Pg over 0–100 cm soil depth. For estimates of deeper layers more TOC stock data are needed. PyC stock varies strongly per soil type (Table 2), but PyC is present in all soils analysed. We found that the PyC content of Amazon forest soils is larger than previously approximated by Bird et al. (2015). They assigned a nominal 0.01 PyC/TOC for tropical wet climates in the 0–30 cm soil interval, and we found a range of 0.007 to 0.2 PyC/TOC for the 0–30 cm interval in our 37 forested non-*Terra Preta* plots across the Amazon Basin. Resistant C/TOC ratios increasing with depth were also observed by Paz (2011) in pristine Amazon forest soils, as for PyC/TOC in our study. Paz (2011) analysed dichromate resistant C, which likely represents the PyC fraction, and found that this resistant C is present in all soils analysed, although amounts varied with soil type. Our estimate is also similar to the 3.45 Mg charcoal ha^{-1} over 1 m soil depth observed in Amazon forest fragments by Turcios et al. (2016). Turcios et al. (2016) did not analyse total PyC so their estimate is conservative, but recent burnings within and nearby their forest fragments may account for higher charcoal than in our plots that were not recently burnt. Ferralsols nearby *Terra preta* soils contain 2.5 g kg^{-1} PyC in the topsoil to nearly 0 g kg^{-1} PyC at 50 cm depth (Glaser et al. 2001), which is considerably higher than in our soils. Our range is similar to PyC in North American prairie soils, reported to be between 4 and 18% (Glaser and Amelung, 2003), and smaller than the range found by DeLuca and Aplet (2008) of 0.1–43% for North American coniferous forests. Grassland ecosystems as analysed by Rodionov et al. (2010) have a higher range than our samples of 4–30% PyC of TOC. Thus, we corroborate the speculation that PyC is likely omnipresent in humid tropical Amazon Basin forest soils, as in many other ecosystems around the world.

Modern rainforest clearing in the Amazon Basin produces 2.5–6.5 t ha^{-1} PyC, and most of this PyC enters the soil pool (Kuhlbusch and Crutzen, 1995; Forbes et al., 2006), where it can remain over geological timescales (Knicker, 2011). Combustion completeness, the amount of biomass that is converted to gas, aerosols, and particulates by the combustion process (Carvalho et al., 1998), is around 20% following Amazon Forest clearing, but local differences in combustion completeness will affect the PyC stocks. Aerosol deposition of PyC from smoke can also contribute to soil PyC over long-term timescales, and be derived from different sources. Savanna (cerrado) ecosystems surrounding the Amazon forest burn frequently (Barbosa and Fearnside, 2005), potentially contributing to the Amazon soil PyC stock. Cerrado fires have increased since European settlement, as well as Amazon forest fires more recently, and fire management may have

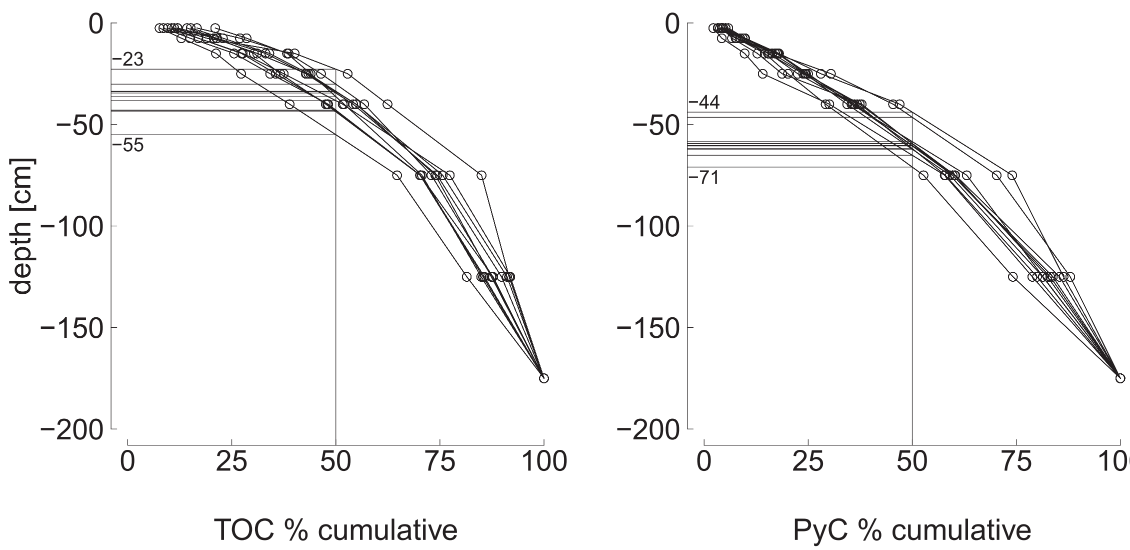

Fig. 3. Cumulative percentage of TOC and PyC with depth for all plots with individual sample analyses. Horizontal lines represent for each plot the interpolated depth where 50% of TOC or PyC is reached. Upper and lower limits of the interpolated depths are given.

triggered less frequent but more severe fires (Pivello, 2011). Smoke transport from Africa is an external source of PyC in the Amazon Basin that may account for 50 Tg of PyC transported with Westward winds to the Amazon Basin annually (Kaufman et al., 2005; Ansmann et al., 2009), probably deposited East to West over the region, although such a pattern is not discernible in our data. Therefore, PyC in Amazon forest soils potentially reflects both local fires over long and short time periods, influencing local PyC distribution, as well as long-term input from external sources, potentially influencing large areas. Another possible source of PyC could be biological transformation of TOC into polycondensed aromatic moieties, non-pyrogenic PyC, although the mechanisms and total amounts of polycondensed aromatic moieties within the PyC fraction remain unknown (Glaser and Knorr, 2008).

4.2. Variability of pyrogenic carbon in Amazon forest soils

We found relatively small variability in PyC within the 1 ha plots, but significant large scale variability between plots. Coefficients of variation of TOC for our samples are similar to those for TOC calculated by Batjes and Dijkshoorn (1999) for the Amazon region. Individual sample variance and coefficients of variation of PyC are similar to those of TOC in our samples (Table 1), thus rejecting the hypothesis that PyC is more variable than TOC in Amazon forest soils. Our data suggest that bulking 5 individual samples from 1 ha, incorporates the site heterogeneity observed in individually analysed samples. Bulking samples is thus a valid way to reduce sample numbers, whilst still capturing natural variability in soil PyC content, as has been shown for total soil organic carbon (Bird et al., 2004). Our results also suggest that three replicated samples from 1 ha capture most of the variability in TOC and PyC, and that bulking five replicates per 1 ha does not further reduce sample variance (Table 3).

Differences in PyC within the Amazon Basin likely represent different (historical) fire regimes (Preston and Schmidt, 2006), as aeolian deposition of PyC is likely more homogeneously distributed over large areas than local fires. Fire intensity affects the initial pool of PyC formed (Duffin et al., 2008), and soil properties determine the degradation of PyC (Knicker, 2011). Mean annual temperature and to a lesser extent exposure to oxygen are environmental factors influencing the stability of PyC in soils (Cheng et al., 2008a, 2008b). Similar to other forms of organic matter, PyC can be stabilized in soil by incorporation into stable aggregates through interaction with the soil mineral phase (Glaser et al., 2000; Brodowski et al., 2006).

4.3. Soil types and PyC

Our estimates cover a wide range of PyC stocks, and PyC stocks in individual soil types differ widely (Table 2), suggesting that in our plots soil characteristics may affect PyC persistence. Fertility and climate gradients in the Amazon Basin (ter Steege et al. 2006; Quesada et al., 2010) likely create different physical andchemical conditions for PyC to react with mineral soil and affect its biogeochemical cycling. The range of soil types that we sampled may thus also represent a range of soil properties affecting PyC stability over time. Soil properties that may influence PyC stability are texture (Paz, 2011), weathering grade (Quesada et al., 2010; Paz, 2011), and climate (Paz, 2011). PyC forms organo-mineral complexes with clay (Glaser et al., 2000; Knicker, 2011). Therefore, SOM and PyC stability is different between soil types with clay (e.g. Ferralsols) and sandy soils without clay fraction (Arenosols and Podzols) (Paz, 2011). Indeed, our results show the lowest PyC stock in Arenosols, although based on one profile only (Table 2), but we also observe large differences in PyC stocks between clayey soil types. We found no clear link between the fertility gradient from the more fertile soils just west of the Andes to the West of the Amazon Basin (Quesada et al., 2010), the PyC stock and soil type (Fig. 1). Soil forming processes associated with specific soil types could be of influence to PyC stability. For instance, clay accumulation at greater depth in Acrisols and Alisols can cause PyC to accumulate at greater depth, bound to the clay particles, while at the surface no clay-PyC complexes are found. Depending on the hydrological regime of the soils, clay accumulation horizons and plinthic layers may (temporarily) cause areas with little oxygen in which PyC is also protected from degradation through lack of oxygen. In Ferralsols iron and aluminium oxides may stabilise high amounts of PyC, as indicated by the high amounts of PyC in Ferralsols.

4.4. Pyrogenic carbon with soil depth

Interestingly, in our plots, 50% of PyC was found at depths > 58 cm on average. Furthermore, the ratio of PyC/TOC increases with depth in our plots. This is contrary to the assumptions made by Bird et al. (2015) for humid tropical forests of no PyC in soil deeper than 30 cm or that in the deep soil the PyC/TOC ratio is similar to the ratio in the 0–30 cm interval. Stable PyC likely translocates into deeper soil over time

(Knicker, 2011; Velasco-Molina et al., 2016), and with less organic carbon from litter, root or microbial necromass present in deeper soil layers compared to topsoil, the ratio of PyC to non-PyC therefore increases. Furthermore, PyC in deeper soil horizons is likely more stable than at surface horizons, stabilized in organo-mineral aggregates and protected from oxidation through less available oxygen (Cheng et al., 2008a, 2008b; Glaser et al., 2000; Brodowski et al., 2006; Velasco-Molina et al., 2016), whereas PyC at the soil surface is more likely to oxidize and degrade quickly. As recalcitrant PyC at depth accumulates and persists over time, this PyC is likely older than PyC at surface layers, as discussed by Pessenda et al. (2004, 2010). The main accumulation and cycling of TOC in the top 30 cm soil is also demonstrated by the high variability of TOC at this depth, and low variability deeper in the soil (Fig. 2). In contrast, PyC content remains variable over the entire 200 cm (Fig. 2). PyC content at depth depends on translocation of PyC from the surface and on the stability of the translocated PyC, with both factors leading to the observed high heterogeneity. The distribution and replacement of PyC along the soil profile depends on a continuous input of material from local burnings and external sources, and continuous bioturbation. It has been suggested that if PyC has been produced at its current rate since the Last Glacial Maximum, PyC should account for 25–125% of TOC, thus exceeding the observed amounts (Masiello and Druffel, 2003), and represent a large proportion of TOC in subsurface soils and sediments (Schmidt and Noack, 2000). Although we show that the PyC proportion of TOC is largest in the subsurface soil of Amazon forest soils, our total PyC stocks are much smaller than suggested by Masiello and Druffel (2003). PyC is continually lost from surface and subsoil through oxidation after disturbance such as uprooting after tree-fall and subsequent erosion, through leaching of dissolved PyC (Dittmar et al., 2012), and bioturbation (Preston and Schmidt, 2006; Knicker, 2011). Subsurface C was shown to be mineralized under the influence of root exudates (Fontaine et al., 2007), and it is likely that recalcitrant PyC is also degraded by plant roots and microbial activity over millennia (Kuzyakov et al., 2009). Thus, although deep PyC is more recalcitrant than surface PyC, it is probably involved in biogeochemical cycling and microbial degradation over millennial timescales.

4.5. Conclusion

We present a first estimate of Amazon Basin forest PyC stocks over 100 cm depth and show that these are much larger than previously approximated (Bird et al., 2015). Moreover, PyC represents a significant (11%) portion of TOC, especially in soil deeper than 30 cm. Considering that PyC in deeper mineral soil layers is likely more stable than at the surface, this can be an important carbon pool for long-term carbon storage. Nonetheless, the relevance of deep PyC in forest soils for biogeochemical cycling and soil fertility remains unknown and should be properly investigated. More PyC stock data from the Amazon Basin, and other ecosystems globally, will enable refining for different soil types and linking to other soil properties and influences on plant growth and forest biomass.

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Author contributions

T.R.F., M.B. and N.K. designed the study. N.K. carried out statistical analyses. J.H. analysed the PyC samples. N.K., T.R.F., M.B. interpreted the results and wrote the paper. C.Q. and E.O. sampled soil. All co-authors commented on the paper.

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