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ORIGINAL RESEARCH

The Geochemistry of Amazonian Peats

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Abstract The chemical, physical and palaeobotanical composition of peat can be used to infer the history of a peatland and the processes presently operating within it. Here we present new data on the geochemistry of a peat sequence from a lowland palm swamp, Quistococha, in Peruvian Amazonia. We show, through comparison with subfossil pollen data from the same sequence, that changes in the depositional environment cause changes in peat properties including lignin content, C/N ratios, and the abundance of several metal cations, but that these properties are altered by post-depositional processes to a large extent. An upward trend in the top 1.5 m of the sequence in the concentrations of N, K, Ca, Mg and Na probably reflects nutrient uptake and cycling by the standing biomass. Upward trends in Mn and Fe concentrations suggest that limited oxygenation of the peat may occur to a similar depth. Comparison with other published records suggests that such deep biological alteration may be characteristic of tropical forested peats.

Keywords Inorganic geochemistry · Lignin · Cations · Nutrient cycling · Water table · Pollen

Introduction

Tropical peatlands are estimated to store c. 89 Gt of carbon, or 14–19 % of the total global peatland carbon pool (Page et al. 2011a). They are vulnerable to degradation, which can lead to substantial emissions of greenhouse gases and loss of other ecosystem services (e.g. Page et al. 2002, 2011b; Jauhiainen et al. 2008; Anshari et al. 2010; Hooijer et al. 2010, 2012; Hergoualc'h and Verchot 2011). Improving our understanding of tropical peatland processes is important for predicting their response to climate change and human intervention, and in developing sustainable management practices.

One way to gain insights into the processes operating within tropical peatlands is to analyse the composition of the peats (e.g. Shotyk 1988; Gorham and Janssens 1992). This may allow us to identify ways in which tropical peatlands (particularly those in lowland settings, under warm climatic conditions) may function differently from temperate, boreal and montane peatlands. From first principles we might expect differences stemming from the following factors:

1. Biological differences, especially the dominance of trees in many tropical peatlands, including taxa with no close functional analogues in extratropical peatlands (e.g. palms with pneumatophores [breather roots]), which may mean (*inter alia*) a greater role for lignin in the overall makeup of tropical peats and greater oxygenation at depth.
2. Hydrological differences, such as the more vigorous hydrological cycle (high rainfall and year-round high evapotranspiration) associated with many tropical climates, and the higher hydraulic conductivity of wood peats relative to many temperate/boreal moss peats (Kelly et al. 2013), both of which would be expected to lead to rapid responses of peatland water-tables to seasonal or interannual variation in rainfall. In turn, large-amplitude water-table variations may lead to greater oxidation of

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the upper peats, and hence faster decomposition, which may limit the rate of peat accumulation.

3. The lower availability of plant nutrients at the landscape scale in heavily weathered lowland tropical terranes, which means that base-rich fens are probably restricted to the floodplains of 'white-water' rivers bearing sediments from geologically-young mountain ranges (i.e. in Amazonia, from the Andes).
4. Higher temperatures, which are likely to encourage high rates of litter production, vigorous microbial activity and rapid litter decomposition.

Geochemical studies of ecosystems can also be valuable in helping us to understand how chemical species are distributed within landscapes, and how chemical species (including important plant nutrients such as K, Ca, and Mg) are cycled and transported (Fortescue 1992; Benjamin and Honeyman 2000; Viers et al. 2005). Landscape-scale geochemical patterns and processes offer explanations of biogeographical patterns, such as the distribution of biodiversity (e.g. Quesada et al. 2009; Higgins et al. 2011).

There have been a number of surveys of the spatial and stratigraphic variation in major elements in other tropical peatlands in Indonesia (Polak 1975; Cameron et al. 1989; Neuzil et al. 1993; Brady 1997; Neuzil 1997; Shepherd et al. 1997; Weiss et al. 2002; Page et al. 2004), Malaysia (Cameron et al. 1989; Wüst 2001; Wüst and Bustin 2001, 2003; Wüst et al. 2002), Australia (Muller et al. 2006), and the Republic of Congo (Brncic et al. 2009), along with studies of aspects of peatland organic geochemistry in Burundi (Aucour et al. 1999) and Madagascar (Bourdon et al. 2000; Disnar et al. 2005). These studies have shown that there is considerable variation in the properties of tropical peats, although a systematic review is currently lacking. This variation in peat properties (as at higher latitudes) is likely attributable to some combination of variation in climatic factors, basin formation processes, hydrological regimes, and vegetational communities.

Here we present a new multi-proxy dataset from a peat and sediment sequence from a palm swamp at a site called Quistococha, in Amazonian Peru. Our detailed study of a single core, supported by published pollen data from the same sequence (Roucoux et al. 2013), complements more extensive but less detailed surveys of the carbon, nitrogen and selected metal cation concentrations of cores and near-surface peat samples from several sites in the same region of Amazonian Peru and western Brazil (including five samples from a separate core at Quistococha: Lähteenoja et al. 2009a, b, 2013; Lähteenoja and Page 2011).

Our principal aim in this paper is to interpret the characteristics of our peat and sediment sequence in terms of past and present environmental conditions and peatland processes. We apply our findings by critiquing previous analyses of peat composition in the Amazon and elsewhere in the tropics, and identifying further research directions. This is the most detailed multiple-proxy study of peats yet undertaken in Amazonia, and significantly, the first to use pollen data from the same sequence to constrain interpretations.

Materials and Methods

Quistococha is a palm swamp–lake complex situated on the floodplain of the Amazon near the city of Iquitos in NE Peru (Fig. 1). Core QT-2010-1 was collected using a stainless steel Russian-type corer (Jowsey 1966) from an area of peat 500 m south of the lake of Quistococha (3.840° S, 73.319° W), adjacent to a core separately analysed at lower resolution for carbon accumulation rates and cation chemistry by Lähteenoja et al. (2009b). The core is 632 cm long and extends well into the sediments underlying the peats. The core was shipped to the UK and stored under licence at 4 °C (a duplicate core was archived at the Instituto de Investigaciones de la Amazonía Peruana in Iquitos). The stratigraphy was described following Troels-Smith (1955). The present vegetation is described by Roucoux et al. (2013) and Kelly et al. (2013).

The hydrostatic pressure in a dipwell close to the core site at Quistococha was monitored from July 2011 to July 2012 using a self-logging pressure transducer, set to take measurements every two hours. A separate log of atmospheric pressure was used to convert the measured hydrostatic pressures to water table position relative to the peat surface.

Chemical analyses were conducted on samples of bulk peat. Total carbon and nitrogen analyses were carried out at 16 cm intervals using a Eurovector EA 3000 series combustion analyser at 950 °C. Each sample was dried at 40 °C, milled, weighed into tin caps, and mixed with V_2O_5 to ensure adequate oxidation, following Pella (1990). Using a range of internal replicates and accredited reference materials (B2150, B2152, ES4 and NJV942), reproducibility was estimated to be better than ±0.25 wt.% for N and ±0.9 wt.% for C at 1-σ.

The lignin content of the ash-free organic matter fraction was estimated at c. 16 cm intervals following Rowland and Roberts (1994). Each sample was washed through a grade 2 sinter using, successively, hot deionised water, acetone, and 72 % H_2SO_4, and the residue was ashed at 550 °C. The non-ash component of the residue is taken as a proxy for the lignin content of the ash-free peat. Using four internal replicates, reproducibility was estimated at ±4.4 wt.% at 1-σ.

The concentration of selected metal cations (Al, Ca, Fe, Mn, Mg, K and Na) was determined at 16 cm intervals using a Perkin Elmer 5300DV ICP-OES. The extraction method followed British Standard BS 7755 (1995), reducing the quantities of reagents appropriately for the sample size (3 g). Each sample was refluxed on a hotplate for two hours with 1 ml of deionised water, 21 ml of concentrated HCl, and

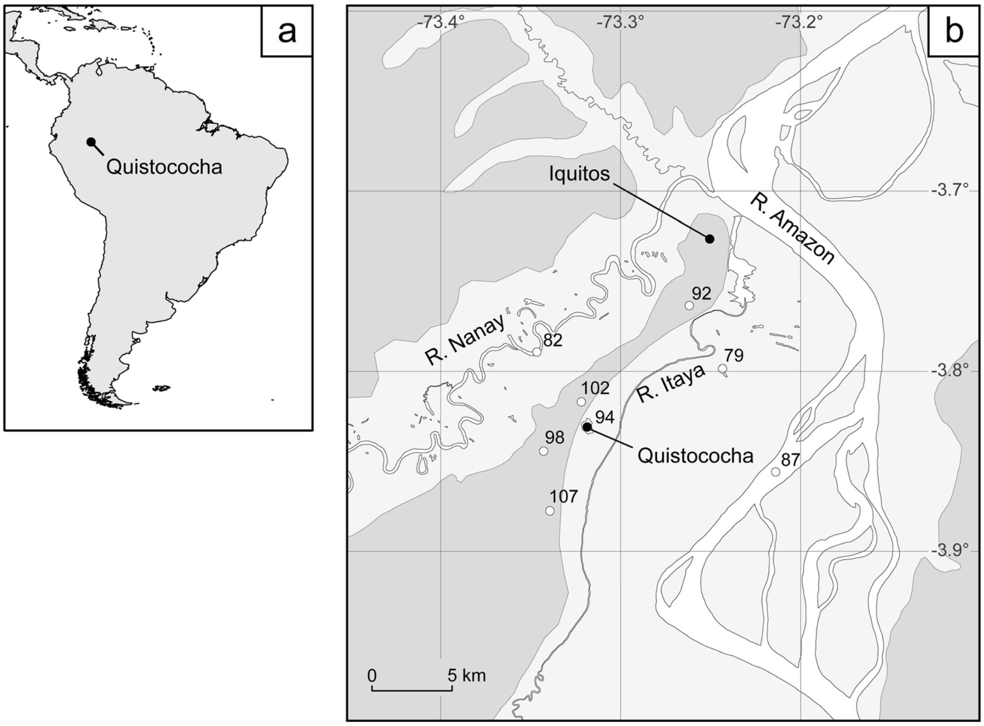

Fig. 1 Location of sites mentioned in the text. (**a**) Location of Quistococha relative to South America. (**b**) Local location map showing the lake at Quistococha in the context of local geomorphology. Core QT-2010-1 was taken 500 m south of the southern lake margin, in the palm swamp surrounding the lake. Selected spot heights are shown, derived from Shuttle Radar Topography Mission (SRTM) data, from areas without forest canopy. The boundary between active floodplains (*pale grey*) and *terra firme* (*dark grey*) is tentatively indicated based on interpretation of SRTM data and satellite imagery

7.5 ml of concentrated HNO_3, then cooled, filtered through Whatman 542 papers, and diluted to a final volume of 100 ml with deionised water. This extraction process, which is not a total extraction because it does not involve digestion of silicate minerals in HF, was chosen because it is more representative of the cation content of the organic material in the peat, and of the cations available to plants, than would be a total extraction. Reproducibility was estimated at ±6–12 wt.% for all cations except Al (no data) using four replicates, and detection limits were estimated at 107, 531, 188, 54, 13, 4, and 25 mg kg^{-1} for Al, Ca, Fe, K, Mg, Mn and Na respectively, using LGC6138 standard reference material.

Particle size distributions were measured at 16 cm intervals in the clayey silts underlying the peat. Samples were oxidized in 30 % H_2O_2 until no further reaction was observed, then suspended in 4 % $Na_4P_2O_7$. Aliquots were measured in triplicate using a Beckman-Coulter L230 particle size analyser. Measurements on four replicates indicate that reproducibility of the proportion of each size class (clays, silts, fine sands) was better than ±1 vol.%.

Pollen, magnetic susceptibility and loss-on-ignition data from the same sequence are presented in Roucoux et al. (2013) and summarized here in Figs. 2 and 3. We also use the age model established by Roucoux et al. (2013), which is based on a curve fitted between six AMS radiocarbon dates, four from discrete plant macrofossils and two from bulk peat samples with visible roots removed (Table 1).

The pollen zones established by Roucoux et al. (2013) are indicated in Figs. 2 and 4. Two samples fall within the clayey silts (pollen zone QT-1). Both are very rich in well-preserved grains of readily wind-transported taxa including *Cecropia*-type and Moraceae, with a diverse range of accessory taxa, which indicates deposition in anaerobic sediments under open-water conditions. The peats above 413 cm vary in palaeobotanical composition. Between 393 and 413 cm the peat includes numerous fragments of Cyperaceae leaves and stems; wood fragments are common between 185 and 230 cm; and above 185 cm, the peat contains numerous roots of the palm *Mauritia flexuosa*, and is increasingly fibrous. The palynology of the sequence follows a similar pattern and allows a more detailed assessment of the palaeovegetation. Cyperaceae pollen is abundant in zone QT-2 (376–408 cm), and the palaeovegetation here is inferred to be lake-marginal sedge fen or floating meadow. Above this, in zones QT-3 (296–376 cm) and QT-4 (152–296 cm), several different forms of mixed flooded forest of a type known locally as *tahuampa* occurred. In zone QT-5 (72–152 cm) pollen of *Mauritia*-type, dominantly representing the palm *Mauritia flexuosa* and to a lesser extent *Mauritiella armata*, began to expand, and dominated the pollen assemblage in zone QT-6 (0–76 cm). *Mauritia flexuosa* remains the most abundant taxon by basal area at the site today (Roucoux et al. 2013).

Results

The QT-2010-1 sequence consists primarily of peat (0–413 cm) with low ash content and low magnetic susceptibility, overlying clayey silts (413–632 cm) (Fig. 3). Magnetic

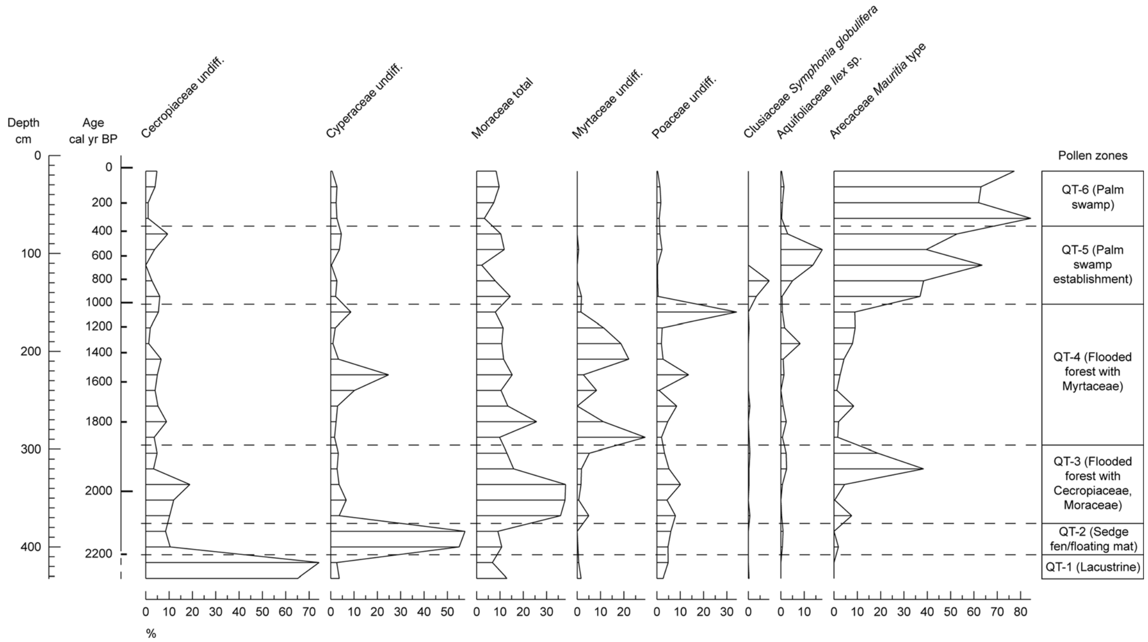

Fig. 2 Pollen diagram showing percentages of selected pollen taxa from core QT-2010-1 (from Roucoux et al. 2013)

susceptibility is highest below 600 cm, gradually declining upwards through the clayey silts, approaching zero at the base of the peat at 413 cm. The clayey silts are coarsest towards the base of the core, with up to 7.9 vol.% fine sand (63–350 μm) and only c. 10 vol.% clay (<2 μm); the sediments fine upwards so that just underneath the peats, at 420 cm, they contain 40 vol.% clay and no sand. The transition from clayey silts to peat occurs over a short interval, with a step-like transition between the two major units visible in the ash content between 380 and 413 cm.

The clayey silts below 413 cm contain little organic matter (mean 6.7 wt.%), which has a low C/N ratio (mean 10.7; see Table 2 for summary data). The concentration of all measured metal cations (Fig. 4) is high in the clayey silts relative to the rest of the sequence. The cations can be divided into two groups: those whose concentrations decrease upwards through the clayey silts (Ca, Fe, Mn, Na), and those whose concentrations increase (Al, Mg, K).

Above 380 cm the peats have a low ash content and low magnetic susceptibility. Inspection showed that much of the

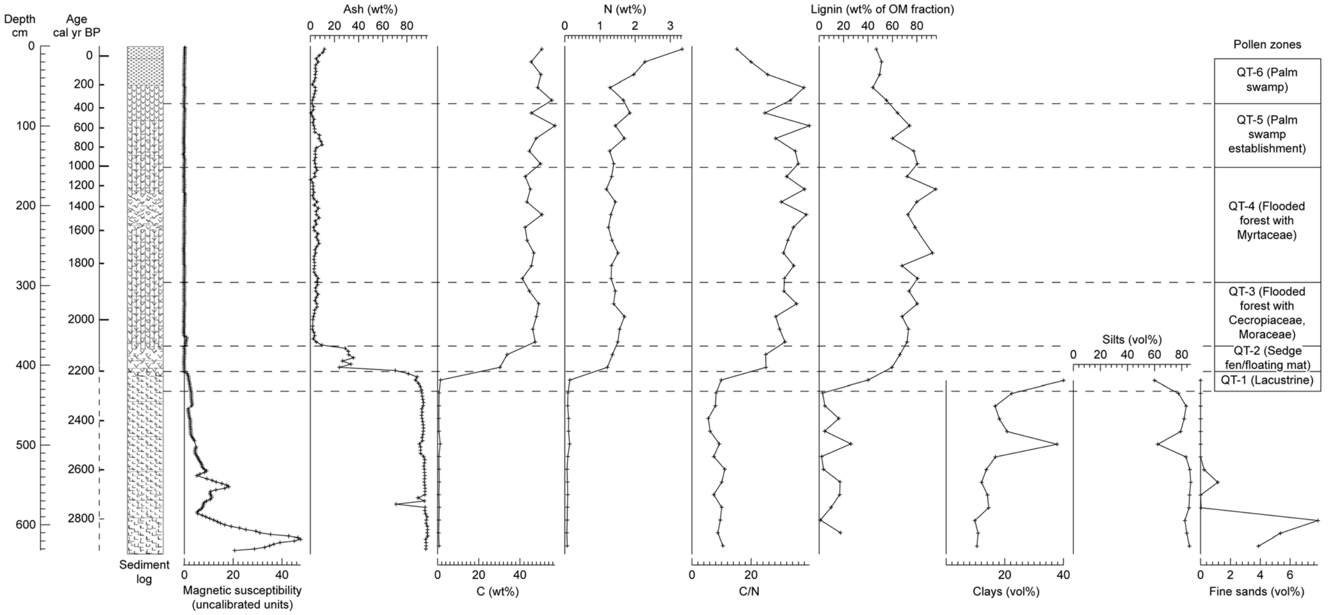

Fig. 3 Properties of core QT-2010-1. Left to right: depth and inferred age; radiocarbon dates; Troels-Smith sediment log; ash content; magnetic susceptibility; carbon and nitrogen concentrations, and C/N ratio; lignin concentrations; particle size data (clay: < 2 um; silt: 2–63 um; fine sand: 62–250 um); pollen zones, from Roucoux et al. (2013)

Table 1 Radiocarbon dates from core QT-2010-1 (after Roucoux et al. 2013). Sample UBA-18437 returned a radiocarbon date indistinguishable from 'modern' ($f^{14}C$=1.0010±0.0041; cf. Reimer et al., 2004)

Code	Depth (m)	^{14}C age	Error (1 σ)	$\delta^{13}C$	Material	Calibrated age range yr BP (2 σ)
UBA-20048	0.50–0.52	117	31	−32.2	<180 μm fraction	269 to 12
UBA-18437	0.80–0.81	Modern	Not applicable	−37.6	<425 μm fraction	252 to −7
UBA-18438	1.30–1.31	911	27	−29.3	Wood	915 to 745
UBA-18440	1.90–1.91	1411	28	−35.5	<425 μm fraction	1353 to 1287
UBA-18441	2.60–2.61	1867	27	−31.4	Leaves and seeds	1872 to 1727
UBA-18439	3.36–3.37	1997	29	−31.0	Leaves and seeds	1999 to 1882
UBA-18442	4.00–4.01	2161	33	−32.9	Leaves and seeds	2308 to 2056

ash is biogenic in origin (mostly plant phytoliths: cf. Wüst et al. 2002). Carbon concentration is stable throughout (mean 47.2 wt.%), N concentration is stable (mean 1.4 wt.%) except in the uppermost 36 cm where it rises to a maximum value of 3.3 wt.%, and the C/N ratio is also stable (31.4) except above 36 cm where it declines. Lignin concentrations rise rapidly through the transitional zone around 400 cm, matching the decline in ash content. Lignin concentrations peak around 180–300 cm (in pollen zone QT-4), then decline slightly towards the top of the sequence.

Metal cation concentrations all decline during the transition from clayey silts to peat, some (Al, Fe) more quickly than others. All metal concentrations are low in the low-ash peats, although some increase again towards the top of the sequence, notably Ca above 108 cm.

During the dry season, water levels varied from 27 cm below the peat surface to 9 cm above the surface (Fig. 5). During the wet season in 2012, the site was flooded to a height of c. 1 m above the peat surface. This extent of flooding is rare, with no similar events during the previous decade (V. Reategui, pers. comm. 2012). Excluding this event, wet season variation in the peat water table was from 5 cm below the surface to 18 cm above the surface.

Discussion

Interpretation of the Data From QT-2010-1

Basal Sediments (413–632 cm)

The composition of the clayey silts below 413 cm is consistent with the site formation model proposed for Quistococha by Räsänen et al. (1991) whereby the lake-swamp complex

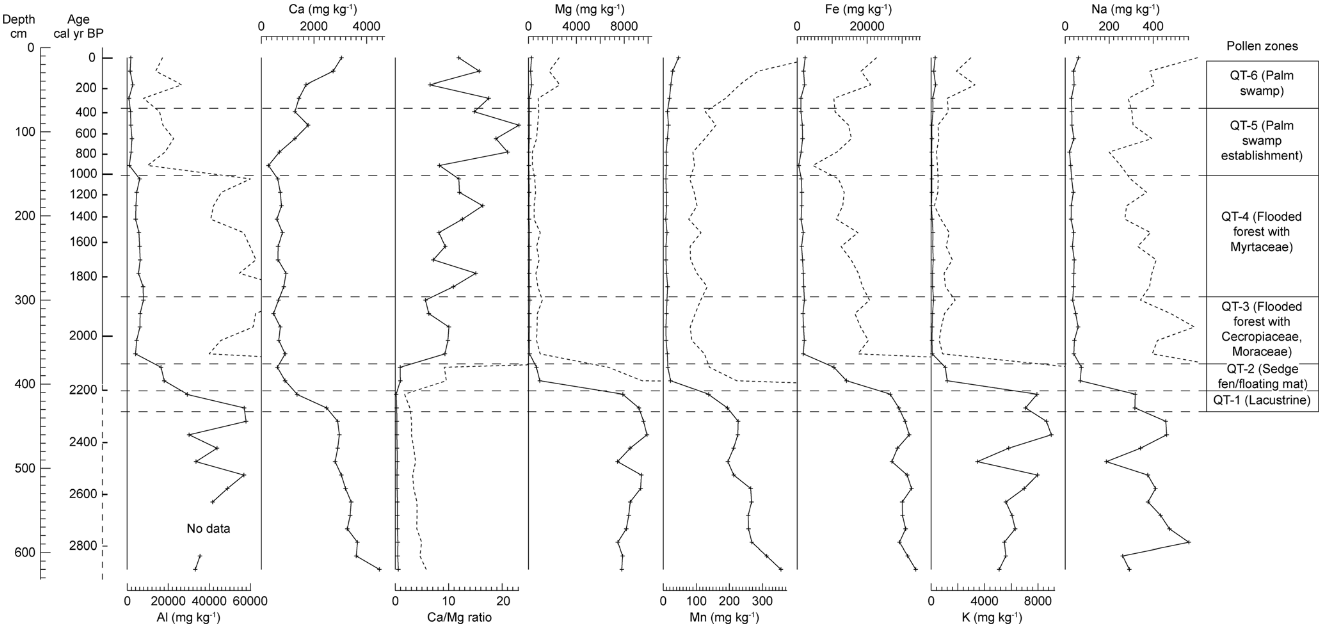

Fig. 4 Concentrations of selected cations in core QT-2010-1. Dashed curves show the data exaggerated by a factor of 10. See table S 1 for the full geochemical data

Table 2 Median values for selected parameters in the clayey silts (below 372 cm), lower peats (150–372 cm), and upper peats (above 150 cm); see text for a description of these units. For full data see Table S 1 (supplementary data)

	C (wt%)	N (wt%)	Lignin (wt%)	Ca (mg kg^{-1})	Mg (mg kg^{-1})	Al (mg kg^{-1})	Na (mg kg^{-1})	K (mg kg^{-1})	Fe (mg kg^{-1})	Mn (mg kg^{-1})
Upper peats	46.5	1.62	57.4	1,430	81.8	1,720	30.9	121	1,470	15.9
Lower peats	43.1	1.29	73.8	692	69.9	5,830	38.6	91.6	1,690	9.52
Clayey silts	0.72	0.08	5.27	3,000	8,280	35,400	359	5,930	30,000	226

occupies an abandoned arm of the Amazon. Today the main channel of the Amazon is 10 km southeast of our core site. Concentrations of all of the metal cations measured are higher in the clayey silts than in the overlying peats, and typically two orders of magnitude richer in Ca, Mg, Na and K than the Amazonian *terra firme* soils studied by Quesada et al. (2009). This presumably reflects transport of relatively unweathered mineral material from Andean source areas by the Amazon, and implies that during the initial period of peat formation, plants would have had exceptionally good access to nutrients. Over time, the chemical character of the sediments changed gradually, from very magnetically susceptible silts and fine sands that are relatively poor in the measured cations (presumably, rich in quartz), to less magnetically susceptible, more clay-rich silts. The fining-upwards sequence suggests that the sediments were deposited under a gradual decline in the depositional energy at the site, consistent with progressively less frequent, shallower flooding of the abandoned channel by a white-water river, and/or with increasing distance between the site and the main channel of the river (Mertes 1997). Sediments currently accumulating in the lake at Quistococha are highly organic with little clay or silt, so the inorganic nature of the sediments below 413 cm in QT-2010-1 indicates more regular transport of mineral sediment to the site than takes place today.

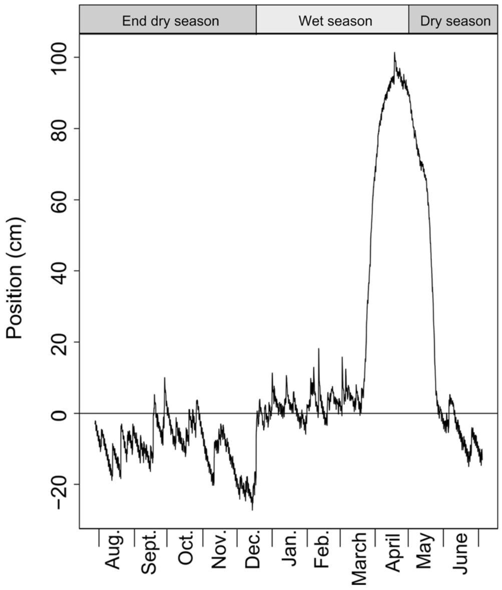

Fig. 5 Water table variation at Quistococha. The dipwell was adjacent to the site of core QT-2010-1. Water table position relative to the peat surface (0 cm) was recorded automatically every 2 h from July 2011 to July 2012

C/N ratios in lake sediments are generally thought to reflect the average C/N ratio of plant and animal material contributing to the sediment, with minimal diagenetic alteration after sedimentation (Meyers 1994; Meyers and Lallier-Verges 1999; see below for a discussion of diagenetic effects in peats). Making this assumption, the low C/N ratio indicates that the organic material is dominantly algal in origin rather than being derived from vascular plants (Meyers 1994), suggesting that periods of clay inwash (during wet season floods) alternated with periods of still, clear water allowing algal growth to occur. The pollen assemblages in the uppermost clayey silts are consistent with deposition under open-water conditions (Roucoux et al. 2013), supporting this interpretation.

Transition Between Clayey Silts and Peats (380–413 cm)

The transition from clayey silts to peats records the period when the site began to terrestrialize and a Cyperaceae-dominated fen or floating meadow became established (Roucoux et al. 2013). Shortly thereafter, sediment transport to the site became much less important, as indicated by the lower ash content of the overlying peats, but the presence of many taxa indicative of seasonally-flooded forests in pollen zones QT-3 and QT-4 indicates that periodic flooding did not cease. The gradual infilling and shallowing of the basin would have reduced the energy of floodwaters reaching the site, but the abrupt nature of the two-stage decrease in ash content suggests the crossing of a threshold. The most likely scenario, taking into account the palynological and sedimentological evidence, is that the establishment of a sedge fen at the site increased the hydraulic roughness and slowed the progress of floodwaters, encouraging sediments to settle out before reaching the core site. Absolute concentrations of metal cations decline substantially across the sediment/peat transition.

C/N ratios in floristically homogenous peats are often interpretable as an indicator of degree of decomposition, with low ratios associated with greater decomposition of peat and loss of carbon (Malmer and Holm 1984; Kuhry and Vitt 1997;

Brady 1997; Biester et al. 2012). However, in our record the absence of a simple stratigraphic decline in C/N ratios through the peats above the transition zone, and the strong coincidence between other sedimentary indicators for environmental change (including the pollen data) and the C/N values, suggest that it is more parsimonious to interpret the increase in C/N ratios in this transitional part of the sequence as primarily reflecting a change in the original chemistry of the organic matter supplied to the sediments, rather than a change in decomposition rates. C/N ratios rise gradually through the transition zone, suggesting that algal material remained important for some time during the transition. Lignin concentrations rise along with the C/N ratios, suggesting that higher C/N ratios reflect a greater abundance of structural organic molecules. The pollen data suggest that herbaceous plants dominated at the site at this time, and the lignin in the peat may derive from root intrusion from later generations of woody plants (cf. Brady 1997: 108–111; Rodriguez Pereira et al. 2000).

Lower Peats (150–380 cm)

The peats above 380 cm all have a high C/N ratio (mean 31.4), typical of terrestrial plants (Meyers 1994). The peats are all rich in lignin, as would be expected in forested swamp peats, and the lignin values are comparable to those reported from peats and litter samples in forested peatlands in Sumatra by Brady (1997). The ash content of the peats in QT-2010-1 (mean 4.4 %) is towards the upper end of values reported by Lähteenoja et al. (2009b) and Lähteenoja and Page (2011) from sites in the region (although they also report much higher ash values for basal peats grading into the underlying sediments). More ombrotrophic sites typically yield lower values: e.g. Aucayacu (3.8 wt.%) and San Jorge (2.8 wt.%), Peru (Lähteenoja and Page 2011); core SA6.5, Sebangau, Kalimantan (0.5 wt.%; Page et al. 2004).

The generally low Ca (mean 706 mg kg^{-1}) and Mg (113 mg kg^{-1}) concentrations between 380 and 150 cm suggest, assuming negligible diagenesis and by comparison with other data from the region (Lähteenoja et al. 2009a, 2013; Lähteenoja and Page 2011), that the site was moderately poor in nutrients during this period. The floodplains of large rivers like the Amazon are complex hydrological zones where rainwater, groundwater and river water mix in varying proportions (Mertes 1997). The low Ca and Mg concentrations suggest that fluvial inputs were low and rainwater may have dominated during this period in the history of Quistococha. On the other hand, even lower Ca concentrations (based on digestion procedures including HF treatment, which should be more effective than the procedure used here at liberating cations from silicate minerals) have been reported from peats elsewhere in the tropics (e.g. Aucayacu [82.5 mg kg^{-1}] and Miraflores [62.5 mg kg^{-1}], Peru: Lähteenoja and Page 2011; core SA6.5, Sebangau, Kalimantan [63.2 mg kg^{-1}]: Weiss et al. 2002). Consideration of Mg concentrations and Ca/Mg ratios, which are higher than those of rainwater (cf. Weiss et al. 2002; Lähteenoja et al. 2009a; Lähteenoja and Page 2011), leads to the same conclusion, i.e. that the site was largely fed by rainwater, but with some groundwater influence. Kelly et al. (2013) showed through hydrological measurements and modelling that the high annual rainfall at Quistococha (c. 3,100 mm y^{-1}: Marengo 1998) probably exceeds the capacity of the peat to drain through groundwater flow alone, which supports this scenario: a stronger groundwater influence would be expected in a peatland which sheds rainfall more quickly.

Upper Peats (0–150 cm)

Above c. 150 cm the organic chemistry of the peat changes, with first lignin concentrations and then C/N ratios declining towards the top of the sequence. The beginning of the decline in lignin concentrations occurs in peats that are increasingly rich in pollen of *Mauritia*-type (probably mostly *Mauritia flexuosa*, with some *Mauritiella armata*: Roucoux et al. 2013). This may indicate that the peat formed under *Mauritia*-dominated vegetation is relatively less lignaceous than peat formed under other tree species. This may be significant in terms of the recalcitrance of the peat: lignin is generally considered to be relatively chemically stable and to decompose more slowly than other major constituents of peat such as cellulose and holocellulose (e.g. Bauer 2004) (although the concept of 'recalcitrance', and particularly the contention that lignin is inherently resistant to decay, has been challenged in the more general context of soil organic matter decomposition: Dungait et al. 2012). Alternatively, the decline in lignin concentration above 150 cm may simply reflect an increasing abundance of fresh litter and roots, and the correlation with *Mauritia*-type pollen may be coincidental. The marked declines in lignin concentrations and, especially, C/N ratios above c. 40 cm likely reflect limited decay or even live material in the youngest peats: less recalcitrant plant compounds are likely to still be relatively abundant. Brady (1997) found similar patterns of changing litter quality in near-surface peat sequences (up to 40 cm long) in Sumatra.

Kuhry and Vitt (1997) discussed the relationship between C/N ratios and peat decomposition in detail, and also observed, in a 4 m *Sphagnum* peat sequence from Alberta, C/N ratios in coarse peat components to increase downwards to c. 40 cm depth (reflecting biological recycling of N), followed by a much slower decline in C/N ratios to the base of the *Sphagnum* peat, which they attributed to diagenesis (loss of C, but not N, through peat decomposition). At Quistococha, C/N ratios and lignin contents continue to vary throughout at least the top 150 cm of the peat, presumably due to a combination of root intrusion from above and past variations in litter quality, and there is little evidence of the smooth monotonic decline in C/N ratios in deeper peats that is widely held to reflect decomposition. This implies that decomposition rates are likely to be less predictable in complicated successional settings like Quistococha than in the simpler *Sphagnum* peatlands studied by Kuhry and Vitt (1997) and others (e.g. Malmer and Holm 1984; Malmer and Wallén 1999, 2004). It also implies that bulk peat C/N ratios are, in these settings, probably a poor guide to the extent of carbon loss through decomposition (cf. Malmer and Wallén 1999, 2004).

The concentrations of several cations also change in the top 150 cm. Of these, the increases in K, Ca, Mg and Na concentrations are particularly striking, especially in the uppermost sample measured (at 12 cm). One possibility is that inputs of sediment from river flooding increased, for example due to channel migration of the Amazon or its floodplain rivers. However, three lines of evidence suggest that bioaccumulation – the uptake and concentration of nutrients by organisms – is the dominant process at work in driving the changes in the chemistry of our sequence in the upper 150 cm. Firstly, a slight increase in the ash concentration occurs only in the uppermost 10 cm, which makes it unlikely that the increased cation concentrations across the whole of the upper 150 cm are due to increased sediment inputs. Secondly, K, Ca, Mg, and Na concentrations all increase towards the top of our sequence. K, Ca, and Mg (but not Na: see below) are all important plant nutrients, and a similar increase in the upper 200 cm of the SA6.5 peat core from Kalimantan was attributed to bioaccumulation by Weiss et al. (2002), and in cores from Batang Hari, Sumatra, by Cameron et al. (1989), as well as in several higher-latitude peat sequences (e.g. Shotyk et al. 1990; Jones and Hao 1993). Thirdly, Jobbágy and Jackson (2001) showed that, globally, the degree of bioaccumulation of major cations in soils (as reflected by the steepness of the vertical gradient in concentrations) occurs in the order K>Ca>Mg>Na, reflecting the fact that K is in greatest biological demand; K also shows the steepest gradient and Na the weakest in our data, being 5.2 and 1.5 times more abundant at 12 cm than at 108 cm depth, respectively.

One intriguing aspect of the data is the accumulation of Na towards the top of the sequence to a maximum of 60 mg kg^{-1}. Sodium is not generally accumulated by plants (Shotyk 1988; Jobbágy and Jackson 2001), so its upward increase is initially surprising. The same pattern is visible in the less well-resolved data of Cameron et al. (1989) from Sumatran peats (Na has not previously been measured in Amazonian peats). The concentrations of Na in the QT-2010-1 peats are typically lower by a factor of 5–10 than in more maritime records from higher latitudes (e.g. Shotyk et al. 1990; Chagué-Goff and Fyfe 1996; Bragazza et al. 2003), and are of the same order of magnitude as measured in soils across the central and western Amazon (Quesada et al. 2009, 2010). Kaspari et al. (2009) and Dudley et al. (2012) suggest that the western Amazon is starved of Na, being far removed from oceanic sources of Na-bearing aerosols, and they highlight the metabolic importance of Na in fungi and animals. Thus the relative increase in importance of Na towards the top of the QT-2010-1 sequence may be attributable to bioaccumulation and cycling by fungi and invertebrate decomposers such as termites, rather than by plants. Alternatively or additionally, some of the plant species present in the Quistococha palm community may in fact accumulate significant amounts of Na. Mean concentrations of 82–208 mg kg^{-1} have been observed in the mesocarpium of fruits collected from separate *Mauritia flexuosa* populations in Peru (Vásquez-Ocmín et al. 2009). Other palm species may have similar capabilities: Na concentrations on the order of 10^4 mg kg^{-1} have been observed in the pith of *Raphia* palms in Africa (Reynolds et al. 2009).

In temperate and boreal peats, the upward increase in abundance of plant nutrients in uppermost peats rarely extends over more than 10–20 cm (Damman 1978; Shotyk 1988; Shotyk et al. 1990). Similarly to our record, Weiss et al. (2002) observed an increased abundance of Ca, Mg and K (and additionally P and S) extending to 200 cm depth in their peat sequence from Kalimantan. The implication that biological alteration apparently affects deep peats in some tropical peat sequences could reflect (a) the importance of trees at these sites, as their long roots are more likely to introduce bioaccumulated elements deep into the peat (Weiss et al. 2002); and/or (b) high productivity causing rapid burial of nutrient-rich litter (which is still being scavenged for nutrients at depth), an inference which has some support from our age model (and also from several peat sequences in SE Asia where rapid accumulation in the uppermost layers has been documented: Maloney and McCormac 1995; Brady 1997; Weiss et al. 2002). Despite persistent waterlogging, greater biological activity may be permitted at depth in these peats due to adaptations such as pneumatophores (‘breather roots’) which occur in *Mauritia* and some other species typical of waterlogged environments in the tropics (Weiss et al. 2002).

The relevance of the vegetation to the properties of the underlying peat may also be reflected in the Mn and, to a lesser extent, Fe profiles. Both elements increase in concentration towards the top of the sequence, especially above 150 cm. This likely reflects stratigraphic variation in redox conditions, because Mn and Fe occur in soluble forms under anoxic, low-pH conditions and thus are usually present in very low abundances below the water table (i.e. in the catotelm) due to leaching (Shotyk 1988: 155–156; Shotyk et al. 1990). Mn may be concentrated by plants (Shotyk et al. 1990) but this is less likely in the case of Fe. One possible explanation of the elevated concentrations of both Mn and Fe only above c. 150 cm is that the peat at Quistococha is at least partly oxygenated to that depth. Our hydrological data, although of limited duration, suggest that the peat at depths greater than c. 30 cm is unlikely to be routinely exposed to air due to water table changes alone, but oxygen transport through plant roots can produce patches of elevated oxygen availability below the water table (Armstrong 1964; Fritz et al. 2011). Forested peatlands may also be better oxygenated than open peatlands because of enhanced water uptake by trees, leading to greater drying of peats above the water table and, possibly, greater oxygen diffusion to peats below the water table (Boggie 1977; King et al. 1986).

Significance for Understanding Amazonian Peatlands

This study confirms the relevance of geochemistry to understanding the present and past ecology of tropical wetlands. Our detailed study of a single site adds substantially to the existing data on eleven other sites in western Amazonia (Lähteenoja et al. 2009a, b; Lähteenoja and Page 2011). Broadly, we are able to confirm the general model developed through that work, which is that most of these peatlands began as frequently-flooded, relatively nutrient-rich wetlands, and became increasingly isolated from fluvial influence over time. In the case of Quistococha, that does not (yet) mean that there is any indication that the site is trending towards ombrotrophy; concentrations of most elements actually increase upwards in the peats. However, we attribute this mainly to the effect of bioaccumulation, which may mask a longer-term trend towards nutrient depletion.

Lähteenoja and Page (2011) proposed that Amazonian peatlands fall into two main groups, one ombrotrophic and nutrient-poor, the other minerotrophic and nutrient-rich (Quistococha lies in the middle of this range). They noted considerable underlying variation in the trajectory of geochemical change at each site and wide diversity in the relative abundance of different elements. Our multiple-proxy dataset indicates that, at Quistococha, comparatively homogenous peats (in terms of their chemistry) were formed under markedly varying palaeoenvironments (especially in terms of vegetation). The high diversity of peatland types proposed by Lähteenoja and Page (2011) on the basis of their chemistry may well prove to be even greater, when ecological variation is taken into account.

Our data suggest that bioaccumulation is an important modifier of peat chemistry. This needs to be taken into account in interpreting geochemical data from near-surface peats. We also suggest that caution is needed in interpreting past changes from minerotrophy to ombrotrophy on the basis of, for example, Ca concentrations alone (e.g. Lähteenoja et al. 2009a), because such changes may be due to enhanced peat decomposition, not enhanced Ca accumulation. Consequently our study is important in showing that a more critical interpretation of geochemical data is needed, and that the developmental history of sites like Quistococha cannot be reconstructed using geochemical data alone. We suggest that palynology remains the best single approach to reconstructing the palaeoenvironments of peat formation, but multiple proxies provide a fuller reconstruction.

In the introduction we discussed four reasons why, *a priori*, tropical peatlands may be expected to differ from peatlands at higher latitudes. Our data suggest that some of these differences may indeed occur, at least at this site. There are differences in peat chemistry, including partial oxidation below 1 m and a deeper zone of nutrient enrichment in the uppermost peats than is typical in many northern peatlands, which may be explainable through biological differences, in particular, the prevalence of pneumatophores. Our water-table data show that the water-table does respond quickly to seasonal changes in rainfall. Our data also confirm that this peatland has been moderately nutrient-poor throughout much of its history, despite evidence for at least occasional deep flooding even at the present day, which fits our prediction of limited presence of minerotrophic systems in Amazonia. However, further research is needed to test the significance of our findings. In particular, investigation of the redox conditions of palm swamp peats and of the potential role of nutrient limitation of microbial communities is needed to gain a fuller understanding of the processes responsible for carbon accumulation in these environments. The peats at Quistococha accumulated remarkably quickly (averaging 1.8 mm y^{-1}) compared with peats in other tropical environments (e.g. SE Asia) or in many temperate and boreal bogs. The geochemical evidence presented here suggests that, even at depths of more than a metre, the peat may be occasionally or patchily oxygenated, which should encourage rapid microbial decay. If this is the case, then the rapid peat accumulation at sites like Quistococha is even more difficult to explain.

Conclusions

1. We have undertaken the most detailed study of the composition of an Amazonian peat sequence to date, which, in combination with published pollen data from the same sequence, provides new insights into the interpretation of geochemical data from similar settings.
2. Past changes in depositional setting and vegetation are accompanied by changes in the present composition and chemistry of the sediments and peats, albeit modified by post-depositional processes. In particular, C/N ratios do not show a monotonic decline with depth below their peak values, as reported for more palaeobotanically homogenous peats elsewhere. This means that using C/N ratios as an index of organic matter decomposition (e.g. Kuhry and Vitt 1997) is likely to be problematic at sites with complex successional histories.
3. Biologically-important elements including Ca, Mg, K and N occur at elevated proportions close to the peat surface,

which is consistent with expected patterns of nutrient cycling and bioaccumulation. The zone of enrichment appears to be deeper than in many temperate peats.

4. Chemical evidence (Mn, Fe) suggests that limited amounts of oxygen may penetrate over a metre into the peat, which would tend to encourage rapid decay. Further investigation is needed to better understand the chemical environment in peats at sites such as Quistococha, in order to explain adequately the high rates of peat accumulation observed.

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