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# Environmental and climatic history in the NW Argentine Andes (24° S) over the last 2100 years inferred from a high-altitude peatland record

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## Abstract

High-altitude cushion peatlands are versatile archives for high-resolution palaeoenvironmental studies, due to their high accumulation rates, range of proxies and sensitivity to climatic and/or human-induced changes. Especially within the central Andes, the knowledge about climate conditions during the Holocene is limited. In this study, we present the environmental and climatic history for the last 2100 years of Cerro Tuzgle peatland (CTP), which is located in the dry Puna of NW Argentina, based on a multi-proxy approach. X-ray fluorescence (XRF), stable isotope and element content analyses ($\delta^{13}$C, $\delta^{15}$N, TN and TOC) were conducted to analyse the inorganic geochemistry throughout the sequence, revealing changes in the peatland's past redox conditions. Pollen assemblages give an insight into substantial environmental changes on a regional scale. The palaeoclimate varied significantly during the last 2100 years. The results reflect prominent late Holocene climate anomalies and provide evidence that Northern Hemisphere temperature oscillations were extensive and affected the southward migration of the Intertropical Convergence Zone (ITCZ), and hence, the intensity of moisture flux within the South American Summer Monsoon (SASM) belt. Volcanic forcing at the beginning of the 19th century (1815 Tambora eruption) seems to have had an impact on climatic settings in the central Andes. In the past, the peatland recovered from climatic perturbations. Nowadays, CTP is heavily degraded by human interventions, and the peat deposit becomes increasingly susceptible to erosion and incision.

## 1 Introduction

Peatlands respond to climatic changes and anthropogenic disturbances in a very sensitive way, and therefore, can represent valuable archives for palaeoenvironmental studies. High-altitude cushion-plant peatlands are among the most unique and characteristic ecosystems of the Andes, but still remain relatively unexploited within palaeoenvironmental studies (Squeo et al., 2006; Schittek, 2014). They are capable of accumulating peat, although they are located near known hydrological and biological limits for plant growth (Earle et al., 2003).

Climatic changes affect the peatlands' hydrological regimes and the physiognomy of their natural surface. Fluctuations in water tables and redox conditions control the accumulation and mobilisation of heavy and semi-metals, which can serve as climate-sensitive proxies (Shotyk, 1988). When the peatland's surface is drying, increased decomposition provokes changes in organic geochemistry, which can be effectively measured. Further, micro- and macrofossils, archived in peat, represent a record of environmental changes in and around the catchment. Although, there still is a lack of knowledge concerning their ecological functioning, high-Andean peatlands can exhibit sensitive records of past moisture variations and offer the opportunity for multi-proxy palaeoenvironmental research.

Especially in the central Andes, the available information on palaeoenvironments clearly illustrates that the database for late Holocene palaeoclimatic reconstructions is yet not sufficient to draw valid conclusions for understanding the cause of climatic changes and its potential impact on ecosystems. Determining the mechanisms behind late Holocene climate variability will contribute to the understanding of present-day and future climates in the water stressed central Andes (Stroup et al., 2014). Climate and water availability are fundamental factors in sustaining these unique ecosystems (Squeo et al., 2006; Ruthsatz, 2008).

The investigated Cerro Tuzgle peatland (CTP) is one of the few archives in the central Andean region to provide a highly resolved, continuous record of the Holocene, allowing sub-centennial to decadal precision scales. We present first results of geochemical and micro-/macrofossil analyses spanning over the past 2100 years and compare these with regional and global high-resolution records of late Holocene climate variability. The aims of the presented study were to obtain a continuous palaeoclimate record to reconstruct late Holocene climate and landscape changes for the central Andes, to identify the timing and character of high-frequency shifts in the climate system and to explore the linkages between climate and human impact.

## 2 The study area

### 2.1 Geographical setting, regional climate and high-Andean vegetation

Located in the central Puna of northwest Argentina, the investigated CTP (24°09′ S, 66°24′ W; 4350 m a.s.l.) comprises an extended and diverse high-altitude peatland–shallow lake complex (Fig. 1). Cerro Tuzgle is an isolated, 5500 m a.s.l. high strato-volcano, which is situated in a north–south trending, thrust faults-bounded, intramontane depression, close to the "Calama–Olacapato–El Toro"-fault system (Norini et al., 2014). Here, the longitudinal stretching of the Puna depressions is less pronounced and chambered by various watersheds of volcanic origin (Werner, 1974). Several studies exhibit young volcanic activity ($< 0.5$ Ma BP) up to a possible lava flow unit of late Pleistocene/early Holocene age (Coira and Kay, 1993; Giordano et al., 2013; Norini et al., 2014).

The CTP is located in a tributary valley of Quebrada de Pircas, about 10 km to the southeast of Cerro Tuzgle, at the border between Jujuy and Salta provinces. The closest village is San Antonio de los Cobres (Salta province), about 15 km further to the southeast. The peatland is situated within an area dominated by outcropping Ordovician volcanic and sedimentary units and Cretaceous conglomerates. The catchment area of CTP is markedly small. As part of the Río San Antonio de los Cobres watershed, waters drain into the endorheic Salinas Grandes basin.

The Andes' meridional extension and their massively uprising mountain ranges constitute a distinct obstacle for moisture-bearing winds that are driven towards the eastern or western flanks of the orogeny. In the northwest Argentine Andes, the ranges of the eastern cordillera act as a climatic barrier, which block moist air masses that are transported by upper-level tropical easterly flow. This results in a very pronounced humidity gradient with increasing aridity towards the Puna plateau in the west. In mid-latitudes, the pattern reverses at approximately 37° S, where the western flanks of the principal cordillera receive extratropical rainfall originating from the Southern Hemisphere westerlies, leading to increased aridity in the lee towards the east. This distinct precipitation pattern characterises the position of the South American "Arid Diagonal". Its driest zone crosses the Andes at 28–32° S, where semiarid to arid conditions prevail (Garreaud et al., 2009).

In the study area, about 90 % of total precipitation is concentrated between November and March (Garreaud, 2000). Being located in the "dry Puna" (Troll, 1968) at the north-eastern margin of the "Arid Diagonal", the climate setting reflects a significant precipitation decrease towards the southwest. On average, 300–500 mm of annual precipitation falls along the eastern cordillera about 50 km to the northeast, while the annual mean decreases to values below 100 mm at about 50 km to the southwest. At CTP, annual precipitation varies between 100–300 mm (based on ERA-Interim climate data 1979–2013). The austral winter is characterised by a high insolation regime with little precipitation and cloud cover, cool temperatures and strong winds blowing from the west (Prohaska, 1976). Seasonal variability is driven by the southward shift of the Intertropical Convergence Zone (ITCZ) during austral spring/summer, the strength of the South American Summer Monsoon (SASM) and the resulting convection intensity in the tropical lowlands (Zhou and Lau, 1998; Vera et al., 2006; Vuille et al., 2012). Interannual climate variability is mainly related to El Niño Southern Oscillation. Circulation anomalies show a tendency for wet conditions during La Niña years and dry conditions during El Niño years in the central Andes (Lenters and Cook, 1999; Garreaud and Aceituno, 2001; Garreaud et al., 2009).

CTP is fed by several hillside springs, which might have emerged due to a thrust that crosses the peatland's headwater zone. The springs' discharge is permanent and increases during the rainy season. Ionic concentrations of the springwater have been measured since 2004 (Ruthsatz, 2008; Schittek, unpublished data). Low electrical conductivity of the spring water ranging between 200 and 300 µS $\mathrm{cm}^{-3}$ lead to the presumption that the local aquifer is maintained by precipitation and shallow groundwater(s) with short residence times.

In contrast to many high-altitude peatlands in central-western Andean mountain areas, which are exposed to repeated allochthonous sediment input through tributary stream channels during extreme rainfall events (Schittek et al., 2012), CTP represents a rather protected, and therefore, seldom found feature. It receives minor colluvial sediment input from the steep slopes to the north and south. A southern tributary valley currently does not transport water or sediment to the peatland area, but had formed an alluvial fan in the past, which enters the southernmost section.

The peatland is characterised by three main sections. (1) The headwater section, which is the only part with a very slight inclination. It is dominated by the Juncaceae *Distichia muscoides*, which forms mighty cushions within the spring water areas. The Cyperaceae *Zameioscirpus muticus* prevails areas, which are exposed to more frequent water-level changes. (2) A shallow lake occupies the middle section, with lowstands in winter and during dry years, surrounded by *Deyeuxia eminens* reeds and partially densely colonised by stonewort (*Chara* spec.). (3) The lower and most extensive section is dominated by the Juncaceae *Oxychloe andina*, which is forming large, stable mats. *Oxychloe* effectively accumulates peat as its shoots continue to grow at their tops but die off from the bottom (Schittek et al., 2015).

CTP is surrounded by stands of *Festuca argentinensis* and *Parastrephia phylicaeformis*. The characteristic regional vegetation of the Altoandean altitudinal belt (Ruthsatz, 1977; Werner, 1978), here, is dominated by *Festuca orthophylla* var. *eriostoma*, a tussock grass, which inhabits the dry and sandy plains at the foot of the mountains and the less debris-covered slopes (Werner, 1974). The overall vegetation cover, nowadays, usually is below 30 %.

## 2.2 The impact of human occupation

In the Argentine Puna, only few investigations focus on the ecological interrelationships between human strategies and their natural environment, especially concerning the past 2000 years (Kulemeyer, 2005; Morales et al., 2009). Evidence of first sedentary village societies appears by 100 BC. In the dry Puna, their economy was largely based on llama pastoralism, and was typically located in direct physical association with productive resources (Leonie and Acuto, 2008). Olivera et al. (2004) suggest a strong relationship between residence placement and the availability of water and pastures. Regional dry periods triggered the temporal abandonment of many sites, which is very noticeable during the timeframe coinciding with the Medieval Climate Anomaly (MCA) (Rivolta, 2007; Morales et al., 2009). The inclusion of the area into the Inca Empire, after AD 1400, introduced improved techniques of agriculture and led to a population growth (Braun Wilke et al., 1999). The Spanish conquest, after AD 1536, ended the Inca realm. The introduced European hoofed animals induced an intensified damage on pasture grounds compared to the llamas with their soft footpads (Ruthsatz, 1983). Overgrazing results in increasing erosion due to the destruction of the protective vegetation as an effect of trampling by the animals (Schittek et al., 2012; Schittek, 2014). CTP is continuously exposed to overgrazing by llamas, which has resulted in vegetation loss and the consequent erosional effects. In the lower section, the peatland is in danger to become incised due to an increase of channelled water runoff. A further contemporary severe thread is an earth road (ruta 40), which laterally affects the sensitive ecosystem by causing a heavy input of sediment. The most destructive impact was the laying of a glass-fibre cable sideways to the road directly into the peat sediments in 2014, which, to a huge extent, destroyed the peatland's surface. The cable duct was re-filled with loose dugout peat material, lacking measures against erosion to protect the fragile water resource.

## 3 Methods

The fieldwork was conducted in late December 2012. For selecting a suitable coring site, areas with thick peat accumulation and little through-flow in the peatland's lower section were chosen. Four sediment long-cores were recovered by using a percussion coring equipment. The retrieved sediment was immediately sealed in plastic tubes with a diameter of 4 cm. Several short-cores with a length of 20 cm were extracted to measure the water content of the peat.

This study focuses on the upper 2 m of the deepest core (Tuz 694), which reached a depth of 8 m and covers the past 8400 years. In the Palaeoecology Laboratory of the Seminar of Geography and Geographical Education (University of Cologne), the core was split into two core halves, photographed and described sedimentologically. One core half was subsampled at 1 cm intervals. To obtain qualitative element counts for major and trace elements, the other core half was analysed in 2 mm resolution using an ITRAX X-ray fluorescence (XRF) core scanner (Cox Analytical Systems; Croudace et al., 2006) at GEOPOLAR (University of Bremen). XRF-scanning was performed with a molybdenum (Mo) tube at 30 kV and 10 mA, using an exposure time of 10 s per measurement.

For stable isotope and element content analyses, subsamples at 2 cm intervals were selected. Subsamples were freeze-dried and milled with a high-speed mill grinder (Retsch, MM 400). Element contents and stable isotope composition were determined within the same run separately for carbon and nitrogen at the Stable Isotope Laboratory of IBG-3 (Research Center Jülich). For the analyses of the stable isotope ratios of nitrogen ($\delta^{15}$N) and organic carbon ($\delta^{13}$C) and nitrogen (TN) and carbon content (TC), samples were weighed into tin capsules and combusted at 1080 °C in an elemental analyser (EuroEA, Eurovector) with automated sample supply linked to an isotope ratio mass spectrometer (Isoprime, Micromass). Isotope results are reported as $\delta$ values [‰] according to the equation

$$\delta = (R_\mathrm{S}/R_\mathrm{St} - 1) \cdot 1000 \tag{1}$$

where $R_\mathrm{S}$ is the isotope value ($^{13}$C/$^{12}$C, $^{15}$N/$^{14}$N) of the sample and $R_\mathrm{St}$ is the isotope value of the international standard. Calibrated laboratory standards were used to control the quality of the analyses and to relate the raw values to the isotopic reference scales (VPDB for carbon, AIR for nitrogen). The analytical uncertainty (SD based on replicate analyses of samples) is lower than 0.1 ‰ for both $^{15}$N and $^{13}$C.

Total carbon (TC) and total nitrogen (TN) contents were calculated according to the amounts of $CO_2$ and $N_2$ released after sample combustion (peak integration) and calibrated against elemental standards. As stated in Ruthsatz (1993), the amounts of inorganic carbon and nitrogen in peats from the high Andes typically are very low. Indeed, various own tests for the occurrence of carbonates in the CTP core samples with 5 % HCl proved that decarbonisation was not necessary, neither for the determination of organic carbon content nor for $\delta^{13}$C measurements. Therefore, the TC content is treated as an equivalent of the apparent total organic carbon content (TOC$^*$) and is used for the calculation of the TOC$^*$/TN ratio.

Pearson correlation coefficients were calculated to describe the parameter relations. Correlation coefficients are always based on $N = 65$ and the level of significance always is $p \geq 0.05$.

For macrofossil and microfossil sample preparation, subsamples at 8 cm intervals were selected. After KOH treatment for deflocculation, the samples were sieved in order to separate three size fractions (> 2 mm, 2 mm–250 µm, > 125 µm) for the study of macrofossils. After spiking with *Lycopodium* markers, the further pollen preparation followed standard techniques described in Faegri et al. (1989). Microfossil samples (< 112 µm) were mounted in glycerine and pollen was counted under ×400 and ×1000 magnification. For pollen identification, own reference collections and published atlases and keys were used (Heusser, 1971; Markgraf and D'Antoni, 1978; Torres et al., 2012). Regional pollen types were counted to sums of 300 in each sample. Macrofossils were disaggregated in deionised water. Plant tissues were determined in the 2 mm-fraction under a dissecting microscope, while seeds, charred particles and zoological remains were determined in the 2 mm–250 µm and > 125 µm-fractions (Schittek, 2014).

Microfossil and macrofossil data were subjected to numerical zonation using binary splitting techniques (Hammer et al., 2001), which highlighted three main zones. Principal component analysis (PCA) was used to decipher the main components of variability

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of the geochemical data after standardisation of the data to omit rows with missing values.

For age control within the first 2 m of the core, a total of 6 bulk sediment samples were AMS radiocarbon-dated at Poznan Radiocarbon Laboratory (Table 1). All radiocarbon dates were calibrated using CALIB 7.0.4 and the IntCal13 data set for Northern Hemisphere calibration (Reimer et al., 2013). The Northern Hemisphere calibration was used because during the austral spring and summer seasons, the south shift of the ITCZ brings atmospheric $CO_2$ from the Northern Hemisphere to the Andes, which is taken up by the vegetation during the growing season. Southern Hemisphere calibration is therefore more applicable for regions south of the thermal equator (McCormac et al., 2004). The age-depth model was plotted by applying the MCAgeDepth software (Higuera et al., 2009), which is based on a Monte Carlo approach to generate confidence intervals that incorporate the probabilistic nature of calibrated radiocarbon dates. Through a multitude of simulations, the program generates a cubic spline through all the dates. The final probability age-depth model is based on the median of all simulations. The software was modified to calculate values at 1 mm-resolution. All reported ages are calibrated ages, if not mentioned otherwise.

## 4 Results

### 4.1 Peat characteristics and chronology

The sedimentary deposits of the upper 2 m of the CTP sequence consist of homogeneous peat, showing a faint layering with regular changes between dark-brown and greyish dark-brown strata. Throughout the sequence, the peat matrix shows variable contents of embedded silt.

The retrieved 20 cm short-cores show that the water content of *Oxychloe* peat in the section 0–10 cm is 87 % ($\sigma = 0.91$ %, $n = 5$) and 73 % ($\sigma = 3.2$ %, $n = 5$) in the section 10–20 cm. Due to the high water content, the retrieved peat cores were compacted by the coring procedure. Apparently, compaction does not significantly render uncertainties in the stratigraphic sequence, as high Andean Juncaceae peats are characterised by a more or less flaky texture. For developing an age-depth model, core depth was adjusted for compaction by multiplying the compacted length by a correction factor (core length/compacted length). The age-depth model is based on six AMS radiocarbon dates (Fig. 2). Sample resolution is between 7–18 years $cm^{-1}$ and is highest at AD 400–850.

## 4.2 Inorganic geochemistry

Periods with enhanced allochthonous sediment input are considered to be outlined by high ratios of titanium (Ti) and the coherent (coh) scatter peaks of Mo (Ohlendorf et al., 2014). For this purpose, the intensities of the coh-peak are used as denominator, because it represents effects arising from sediment matrix variations (Rothwell et al., 2006; Guyard et al., 2007). Ti is considered to be immobile in peat (Muller et al., 2006, 2008). Therefore, following Thomson et al. (2006), the presented XRF-scanning data of iron (Fe), manganese (Mn) and calcium (Ca) were normalised to Ti to better reflect the variations in autochthonous in-peatland dynamics.

The Ti/coh ratio (Fig. 3) reflects very well the layering of the sequence, with the more greyish layers enriched with detrital minerogenic matter. Especially between AD 800 and AD 1600, the Ti/coh ratio shows a significant variability on sub-centennial time scale. Maxima occur at around AD 0, 350, 450, 1000, 1350, 1475 and 1800. The Ca/Ti ratio shows distinct peaks at AD 250 and generally higher values between AD 550 and AD 775. After AD 950, Ca/Ti values remain at a lower level.

Peaks in Fe/Ti and Mn/Ti ratios are interpreted as indicators of changes in in situ redox conditions due to water table fluctuations. Periods of significant enrichment in Fe are observed at 50 BC to AD 50, AD 825, AD 1000–1100, AD 1250–1350, AD 1500 and AD 1600–1700. Mn shows high values at AD 800–1000, AD 1625–1725 and AD 1800–1850. A sustained period of low values in both Fe and Mn is found at AD 250–550.

Changes in the Mn/Fe ratio are mainly linked to the strong precipitation of $Fe^{3+}$-oxide in the upper aerated layers under oxic conditions. High values, indicating a stable water table and prevailing anoxic conditions, are observed at AD 250–550, AD 850–900, AD 950–1000, AD 1100–1150 and AD 1700–1950. During the period of AD 1150–1700, Mn/Fe values remain highly variable.

## 4.3 Organic geochemistry

TOC* contents range between 21 and 41 %, reflecting the variable dilution effect of in situ-grown plant material with input of allochthonous sediment (Fig. 3). Investigations of living *Oxychloe andina* specimens, sampled in February and October 2013, revealed a mean carbon content of the whole plant (leaves and roots) of about 41 %. Thus, values of 40 % TOC* found in the archive already represent the upper boundary of carbon content for the Tuzgle cushion peat. Maximum values of $> 30$ % are reached episodically between 150 BC and AD 50, as well as between AD 700 and AD 1750. Lowest values of $< 25$ % prevailed at AD 300–600 and during the past 100 years. TN values range between 1.6 and 2.8 % and are closely related to TOC* values with an apparent correlation of $r = 0.85$. Accordingly, TN contents show their maxima and minima during the same periods as outlined for TOC*. TOC*/TN ratios vary between 12.0 and 19.0 with a mean value of 14.4. In comparison, TOC/TN values of leaves and roots of living *Oxychloe andina* showed ratios of about 20 and 65, respectively. TOC*/TN ratios in the core remained relatively stable between 150 BC and AD 600 with values mainly between 12 and 14. Peaks are observed at AD 800–900 and at around AD 1150 with values larger than 15. Between about AD 1450–1700, TOC*/TN values are frequently higher than 15, but afterwards constantly decline towards the present.

The $\delta^{13}C$ values of the peat core range between −26.4 and −24.5 ‰ with a mean value of −25.3 ‰. The topmost $\delta^{13}C$ value of the core (−25.8 ‰) fits well with the respective value of −25.9 ‰ for living *Oxychloe andina*. Between AD 200–600, $\delta^{13}C$ values almost constantly remain at a level higher than −25.0 ‰. Minimum $\delta^{13}C$ values around −26.0 are observed at around AD 850, AD 1125, AD 1300, AD 1375, AD 1500 and since the past ∼ 50 years, where the latter phase of depleted values can be due to the fossil fuel effect. The $\delta^{15}$N values vary in a range between 1.2 and 3.7 ‰ with a mean value of 2.4 ‰. Leaves of modern *Oxychloe andina* show values between 1.9 and 3.9 ‰, whereas roots seem to be comparably depleted with values of about 1.4 ‰. In the peat core, values below 2 ‰ are observed at 125 BC-0 AD, repeatedly at AD 600–900, around AD 1500 and around AD 1950, while maxima with values > 3 ‰ occur repeatedly at AD 100–550, at AD 950, AD 100, AD 1275 and at AD 1850.

Between the stable isotope variables $\delta^{13}$C and $\delta^{15}$N, we observe only a weak correlation ($r = 0.22$). Still weak but stronger is the negative correlation between the TOC*/TN ratio and $\delta^{13}$C ($r = -0.35$) and $\delta^{15}$N ($r = -0.34$). In addition, $\delta^{13}$C is correlated with TOC* ($r = -0.36$) whereas no correlation is evident for $\delta^{15}$N, respectively. In this context, the strongest correlation is observed between TOC* and TOC*/TN ($r = 0.69$), while the respective correlation with TN is weak ($r = 0.21$).

### 4.4 Principal component analysis of the geochemical data

The PCA of the inorganic and organic geochemical variables shows that component 1 explains 38.9 % of the total variance, whereas component 2 explains an additional 18.3 % (Fig. 4). Ti/coh contributes negatively to component 1, while mainly Fe/Ti, Mn/Ti, TN and TOC* are at the opposite. Component 2 is mainly characterised by Mn/Fe, Ca/Ti, $\delta^{13}$C and $\delta^{15}$N at the positive end opposite to TOC*/TN.

### 4.5 Micro- and macrofossil analysis

All samples within the past 2100 years yielded sufficient pollen for counting (Fig. 5). Overall, the diversity of pollen is very low, reflecting the relatively simple, grass-dominated vegetation structure of the Altoandean vegetational belt (4150–4950 m a.s.l.; Cabrera, 1957; Werner, 1974; Ruthsatz, 1977). Poaceae dominate the pollen spectrum and make up 30–95 % of the regional pollen assemblage. The second most abundant pollen types are *Senecio*-type Asteraceae and Chenopodiaceae with percentages exceeding 20 %. The remaining pollen flora is composed of herbaceous taxa in the families of Apiaceae (including *Azorella* and *Mulinum*) and Caryophyllaceae (including *Pycnophyllum* and *Melandryum*), besides the Asteraceae *Perezia*. Werner (1974) had described these species as typical elements of the flora in the Cerro Tuzgle area. *Ephedra* and Chenopodiaceae represent the Puna vegetational belt (3350–4150 m a.s.l.), with the later (mainly represented by *Atriplex*) dominating the shores of closed basin lakes. Cyperaceae (including *Carex* and *Zameioscirpus*), *Hypochoeris*, Gentianaceae and *Plantago* represent local peatland vegetation (Ruthsatz, 2008) and were excluded from the pollen sum. Other pollen types comprise Brassicaceae, Cactaceae, Fabaceae, Malvaceae, Portulacaceae, Solanaceae and extra-regional tree species (*Alnus*, *Celtis*, *Podocarpus* and *Polylepis*) from the eastern Andean forests below 3500 m a.s.l., which occurred only sporadically in low abundances. Green algae (*Pediastrum* spec.), testate amoebae shells (*Arcella* spec.) and the coprophilous fungal spores IBB-15 (Montoya et al., 2012, 2010) and RVV-69 (Rull and Vegas-Vilarúbia, 1999) represent further microfossils other than pollen.

Charred particles were counted in microfossil preparations (< 112 µm), as well as in the sieved macrofossil samples (> 125 µm). *Oxychloe* and *Zameioscirpus* remains represented the most abundant plant macrofossils. *Oxychloe* is abundant throughout the record. Zoological macrofossils comprise egg capsules of flatworms (Neorhabdocoela), chironomids and oribatid mites, which were counted in total, but still not determined to species level.

Zone CTP-1 (150 BC-AD 700) is characterised by high percentages of Poaceae, which prevail at about 90 % between 150 BC and AD 400. A decrease to 60 % at around AD 550 coincides with an increase of *Senecio*-type Asteraceae. From here, *Zameioscirpus* remains become evident in the macrofossil samples. Zoological macrofossils show high abundances at around AD 300–500. The concentrations of charred particles, both in the < 112 and > 125 µm fraction are highest of the whole record, and only since AD 650 remain at significantly lower values.

Zone CTP-2 (AD 700–1450) is marked by a steady decline of Poaceae and a coinciding rise of *Senecio*-type Asteraceae percentages. Chenopodiaceae first peak at around AD 950 and then decline. Cyperaceae show their highest values at around AD 1150–1250. Fungal spores remain highly abundant within the zone. *Zameioscirpus* remains are not evident after AD 950. Within the transition from zone CTP-1 to CTP-2, zoological macrofossils, *Pediastrum* palynomorphs and *Oxychloe* seeds show their highest concentrations in the record. Charred particles diminish after AD 800 to constant low levels.

Zone CTP-3 (AD 1450–1900) begins with an increase of Poaceae pollen, while *Senecio*-typeAsteraceae stay at medium percentages. Chenopodiaceae percentages significantly decline during this period, whileCyperaceae reach their highest abundance of the record at around AD 1900. Neorhabdocoela and chironomids also show an increase at the same time.

## 5 Discussion

### 5.1 Geochemical proxies for tracking palaeoredox conditions

With the investigation of Cerro Llamoca peatland in the high Andes of southern Peru (Schittek et al., 2015), it has been shown that high-Andean peats are effective collectors of inorganic components. For CTP, this can be confirmed also, and especially the Mn/Fe and Fe/Ti ratios are proved as applicable palaeoredox indicators (Lopez et al., 2006). High Fe/Ti ratios indicate an upward movement of $Fe^{2+}$ from the anoxic peat to the upper aerated layers, followed by precipitation as $Fe^{3+}$-oxide (Damman et al., 1992). Thus, Fe is enriched and precipitates in the zone of water table fluctuations under oxic conditions, and therefore, is indicative for climatic conditions with the occurrence of episodic droughts, which affect the saturation of the peatland (Shotyk, 1988; Margalef et al., 2013). Under any naturally occurring pH-Eh conditions, ferrous ions are more easily oxidised than manganous ions (Krauskopf, 1957). At the expected pH ranges, Fe compounds are much more insoluble than Mn compounds. Further, a high concentration of Fe ions within the zone of water table fluctuations results in a displacement of Mn ions from exchange sites on the peat matrix (Kelman Wieder and Lang, 1986). Whereas Fe accumulates, Mn decreases rapidly under an unstable water table regime (Damman, 1978). Hence, the Mn/Fe ratio lowers during more oxic conditions, being mainly linked to the autochthonous precipitation of Fe-oxides. A higher presence of Mn might be related to increased leaching from the catchment zone, due to enhanced weathering under a wetter and colder climate (Kabata-Pendias, 2011). Krauskopf (1957) mentions that Mn in solution may be deposited as carbonate or silicate where the environment is reducing.

Nonetheless, any presumption on the complex behaviour of especially Mn and its compounds must remain speculative pending the collection of more geochemical and ecological data. Furthermore, Mn is highly associated with activities of microbes and plays a key role in the transformation and degradation of organic and inorganic compounds (Megonigal et al., 2003; Tebo et al., 2004).

The PCA plot clearly illustrates that Fe/Ti is tied opposite to Ti/coh. Ti is of lithogenic origin and brought to the peatland by run-off, where it is incorporated as particulate sediment (Margalef et al., 2013). Ti/coh, therefore, is an indicator for episodic allochthonous sediment input due to enhanced rainfall. Here, the amplitude of input is controlled by the erodibility of the water catchment area (Schittek et al., 2012), and not necessarily acts as a measure for the amount and duration of precipitation.

Well-saturated, undisturbed high-Andean peatlands, dominated by Juncaceae like *Oxychloe*, *Distichia* and *Patosia*, are characterised by an interspersal with clusters of small and shallow pools (Coronel et al., 2004). This is also the case for CTP, but the degradation of the vegetation due to grazing and trampling by animals led to a levelling of the peatland's superficial structure, which results in a loss of structural diversity. With a higher abundance of shallow pools, a higher biological productivity in pools, which depends on climate conditions, can lead to a higher consumption of $CO_2$, which increases pH, and hence, triggers the precipitation of calcium carbonate (Boyle, 2001).

At CTP, higher Ca/Ti ratio values are contemporaneous with higher abundances of *Pediastrum* and Neorhabdocoela, which typically inhabit small water bodies (Pinto Mendieta, 1991). Therefore, it is presumed that, under certain environmental conditions, a high Ca/Ti ratio might indicate the presence of shallow water bodies on the peatland's surface.

The carbon isotope composition ($\delta^{13}$C) of vascular plants like *Oxychloe* and *Zameioscirpus* principally depends on the concentration and the isotopic composition of their inorganic carbon source, i.e. atmospheric carbon dioxide, and the fractionation occurring during the assimilation of $CO_2$. This biological fractionation is strongly controlled by the opening and closure of the stomata regulating the ratio between the intracellular to extracellular $p$$CO_2$ (Farquhar et al., 1982), and in general, leads to depleted values in the plant relative to the inorganic source. The aperture of the stomata is regulated according to the plant-available moisture. Therefore, the water table level in the cushion peatland is a key variable where a low water table could induce water stress for the cushion plants, leading to a reduction of the aperture and comparably enriched carbon isotope composition of assimilates and plant biomass. In this respect, local precipitation and air temperature are determinants for the $\delta^{13}$C composition of the cushion plants because they regulate the water inflow, respectively the amount of evaporation and transpiration. Thus, it has been suggested by Skrzypek et al. (2011) and Engel et al. (2014) that growing season temperature might be a determining factor for $\delta^{13}$C in a high-Andean peatland in Peru. In the CTP record, we observe a basic pattern of increased TOC$^*$ and increased TOC$^*$/TN coupled with decreased $\delta^{13}$C values. This could be interpreted as a pattern representing favourable conditions for cushion plants where high water availability fostered plant growth with less water stress, thus, high biomass production and low carbon isotope composition. This finding is opposite to the positive correlation between carbon content and $\delta^{13}$C reported by Engel et al. (2014) for their Andean peat record.

The plant nitrogen isotopic composition ($\delta^{15}$N) is determined by the isotopic composition of the nitrogen input and peatland-internal processes. Fractionation processes during plant uptake and assimilation are presumably less important (Evans et al., 1996). The difference between the depleted plant $\delta^{15}$N composition and the enriched inorganic N-source is generally small and can be less than 1 ‰ (Evans et al., 1996; Reinhardt et al., 2006). Besides nitrogen from chemical weathering and biomass decomposition, the inorganic nitrogen pool of the catchment is fed by wet and dry atmospheric deposition. This nitrogen reaches the peatland via direct deposition or through surficial and groundwater transport. Precipitation contains nitrogen as co-existing ammonium and nitrate with $\delta^{15}$N values of $NH_4^+$ being depleted by several per mil (4–5 ‰) compared to $NO_3^-$ (Kendall, 1998). A further nitrogen source for plant growth in the peatland is mineralisation of organic matter and formation of $NH_4^+$ and, subsequently, $NO_3^-$ with a $\delta^{15}$N signature equal or similar to that of the source material (Reinhardt et al., 2006). The peatland internal nitrogen pool can be altered via denitrification occurring under anoxic conditions leading to an isotopic enrichment of the remaining $NO_3^-$. Further peatland internal processes that could impact the $\delta^{15}$N of peatland plants are mycorrhizal relationships and uptake of organic forms of nitrogen (DON) (Marshall et al., 1997).

Peatlands can be considered as N-limited ecosystems (Bragazza et al., 2005) under pre-industrial conditions, and therefore, are excellent scavengers for available nitrogen (Aldous, 2002). We argue that on our timescales the $\delta^{15}$N signal of the Cerro Tuzgle peatland reflects the isotopic composition of the plant available inorganic nitrogen pool and, thus, of peat plants, in spite of concomitant recalcitrant N-bearing organic compounds (Marshall et al., 1997). Variations in the $\delta^{15}N_{peat}$ composition, thus, can be induced by variations in deposition (wet and dry) and inflow, denitrification, and the availability of ammonium relative to nitrate. However, under N-limiting conditions, the impact of denitrification should be negligible. Thus, we suggest that our $\delta^{15}N_{peat}$ record is driven mainly by changes in nitrogen deposition, presumably precipitation, since this would result in increased inflow, better availability of nutrients, fostering plant growth in general, and an alteration of the $NH_4^+/NO_3^-$ ratio in the internal N pool in favour of the isotopically depleted ammonium. In peatland ecosystems of the Northern Hemisphere, the $\delta^{15}N$ signatures of peat plants were negatively related to the proportion of $NH_4^+$ in atmospheric deposition (Bragazza et al., 2005) and to a hummock-lawn gradient (Asada et al., 2005), with hummock plants having lower $\delta^{15}N$ signatures potentially due to better ammonium availability.

## 5.2 Palaeoenvironmental changes during the past 2100 years

The CTP record of the last 2100 years provides valuable information on climate variability and environmental changes in the high Andes of northwest Argentina. In Fig. 6, the past fluctuations of Mn/Fe ratio values are compared with contemporaneous changes in Ti values of the Cariaco Basin marine record (Haug et al., 2001), a Northern Hemisphere temperature reconstruction (Moberg et al., 2005) and a precipitation reconstruction from the western Altiplano, based on *Polylepis tarapacana* tree-rings (Morales et al., 2012). The investigation of late Holocene glacier fluctuations in southern Peru has shown that the onset of cold conditions was widespread in the mid- and low-latitude regions of both the Northern and the Southern Hemispheres during that period (Licciardi et al., 2009; Stroup et al., 2014). An increasing number of palaeoclimatic studies in the tropical/subtropical Andes underlines that changes in precipitation relate to shifts in the mean latitude of the ITCZ (Haug et al., 2001; Bird et al., 2011; Vuille et al., 2012). A cooling of the North Atlantic provokes a southward migration of the ITCZ, which can be explained as a thermodynamic adjustment in response to the enhanced northward heat transport required to balance the greater high latitude cooling (Broccoli et al., 2006). A more southerly position of the ITCZ triggers moisture flux into the tropical lowlands, which strengthens convection in the Amazon basin, and hence, intensifies the SASM. According to Vuille et al. (2012), SASM intensity is suggested to respond in a very sensitive way to changes in Northern Hemisphere temperature. The variation of Mn/Fe ratios at CTP clearly reveals that local moisture availability is strongly coupled to more southward positions of the ITCZ (Haug et al., 2001), which further corresponds to overall cooler conditions in the Northern Hemisphere (Moberg et al., 2005).

Concerning the evolution of late Holocene environments in the Argentine Puna, earlier investigations, mainly based on palynological and sedimentological investigations (Markgraf, 1985; Zipprich et al., 2000; Schäbitz et al., 2001), revealed that palaeoclimatic patterns basically agree with the Lake Titicaca records (e.g. Baker et al., 2001). Schittek (2014) offered a 2200 year-spanning record of variations in local fire regimes, based on the analysis of charred particles extracted from a high-altitude peatland in the eastern cordillera of Jujuy province. Here, fire susceptibility at high altitude pointed to an upward shift of altitudinal vegetation belts due to a pronounced warm period at around 50 BC to AD 50. At CTP, low Mn/Fe ratios and elevated Fe/Ti ratios point to sustained oxic conditions during the same period, lasting until about AD 100. Drier conditions during that period have also been found by Schittek et al. (2015) and Chepstow-Lusty et al. (2003) in the Peruvian Andes. Increasing $\delta^{15}$N values, after a low at around 75 BC, might point to a constant increase in precipitation until AD 175.

After AD 100, Mn/Fe ratios also constantly increase and remain at a high level until about AD 550, which is concurrent with glacier expansions observed in the Peruvian and Bolivian Andes (Wright, 1984; Thompson et al., 1995; Abbott et al., 1997). According to Haug et al. (2001), the ITCZ continuously succeeded southward during that period. Higher Poaceae percentages at CTP suggest conditions that were more humid and point to a generally higher vegetation coverage in the surrounding area. More precipitation can also be suggested from higher $\delta^{15}$N values. This might have triggered the formation of more water bodies upon the peatland's surface, as evidenced by repeated peaks of Ca/Ti. The higher abundance of water bodies and higher levels of introduced detrital minerogenic matter might be the main reason for lower TOC$^*$ contents.

Starting at about AD 550, conditions begin to fluctuate between oxic and anoxic conditions, showing high amplitude changes especially from AD 800 to AD 900. Sustained drier conditions prevail at AD 1000 to AD 1100, as indicated by low Mn/Fe ratios, peaks in Fe/Ti ratios and low Poaceae percentages. *Zameioscirpus*, which is better adapted to frequent water level changes, becomes abundant in the macrofossil assemblages. For this time interval, Schittek et al. (2015), Schittek (2014) and Binford et al. (1997)

also observed a period of drought in the central Andes. Furthermore, Bird et al. (2011) evidenced drier conditions at Laguna Pumacocha in the Peruvian Andes at AD 900–1100 and linked this event with the Northern Hemisphere Medieval Climate Anomaly (MCA) and a considerable weakening of the SASM at the same time.

At CTP, a return to more humid conditions is evident at AD 1100–1150. Afterwards, conditions repeatedly fluctuated until the onset of a marked dry phase at around AD 1250–1330, most markedly evidenced by increasing Fe/Ti ratios and decreasing Poaceae pollen percentages. The timing is concurrent with a retreat of glaciers in the Cordillera Blanca in Peru (Jomelli et al., 2008). The climate history of the following centuries, as evidenced at CTP, is well comparable to the findings of Morales et al. (2012) (Fig. 6). The major trends in precipitation changes, as evidenced by seven merged *Polylepis tarapacana* tree-ring chronologies from the western flank of the Andean Western Cordillera in Bolivia and Chile, are reflected by simultaneous changes in Mn/Fe ratios at CTP.

Stroup et al. (2014) report re-advances of Qori Kalis outlet glacier at Quelccaya ice cap during the first decade of the 17th century and during the first half of the 18th century, which is time-equal with high Mn/Fe ratios at CTP and pluvial periods detected by the tree-ring record of Morales et al. (2012).

At around AD 1810–1830, the Mn/Fe data signify an abrupt increase, concurrent with the onset of a long-term wetter period, evidenced in tree-ring data (Morales et al., 2012). An extraordinary pluvial period in the early 1800s was further implied from fossil rodent midden data at Quebrada La Higuera (northern Chile) and increasing growth of the human population in the northern Chilean Andes (Mujica et al., 2015). The timing and the sudden onset of this climatic shift give reason to assume that increased volcanic forcing, most apparently by the AD 1815 eruption of Tambora volcano, could have modulated climate patterns within the monsoon-belt, which obviously affected site conditions at CTP. Until about AD 1870, Mn/Fe values remain highest, and afterwards, a persistent trend to significantly less anoxic conditions is observed towards the present. This trend is well comparable to the contemporaneous rise of temperatures in the Northern Hemisphere as modelled by Moberg et al. (2005) (Fig. 6).

### 5.3 Human-environment interactions

Morales et al. (2009) hypothesise that the MCA provoked changes in human organisational strategies, accompanied with an intensification of land use. The effective population growth during the “Late Ceramic Period” (AD 900–1470; Leonie and Acuto, 2008) fostered soil degradation and erosion, which affected the natural vegetation composition (Ruthsatz, 1983). Kulemeyer (2005) highlighted the onset of valley incision in the Puna highlands during that period, because of increased grazing.

With the near disappearance of charred particles after AD 1100, the CTP record gives evidence of a significant reduction in fire activity. A more fragmented vegetation structure, due to the impact of grazing, generally reduces the amount of burnable biomass, and hence, limits fire to spread in the high-Andean grasslands. Schittek (2014) proved a contemporaneous, ultimate decrease in fire activity, deduced from two peatland sites in the eastern cordillera of Jujuy.

Currently, overgrazing is a severe thread to the structural integrity of CTP, which causes an increase in erosion due to the destruction of the protective vegetation. The drying of the surface peat layer leads to heavy degradation and mineralisation. Where the vegetation cover once is destroyed, water run-off is rapidly bundled (Schittek et al., 2012). The laying of a glass-fibre cable longitudinally through the peatland in 2014 demonstrates shockingly, that environmental policy-makers still not give sufficient attention to the important water storing and regulating capacities of high-Andean peatlands. The effects of global warming and the growing exploitation by mining companies increase the intensity of stress factors on these sensitive ecosystems. If the destruction of high-altitude water resources continues, this will severely affect the economic development of certain regions in the near future.

## 6 Conclusions

High-Andean peatlands effectively accumulate both geochemical and biological proxies, which can be used for the reconstruction of past environmental conditions. The investigated CTP represents a continuous peat record, which, due to its sensitivity towards environmental changes, offers unique opportunities to investigate the timing and character of climatic shifts in the central Andes. Especially in the NW Argentine Andes, there is still a lack of palaeoclimatic archives, which serve to explore linkages between climate and human impact.

With the application of XRF-analyses, it is possible to detect past fluctuations of the peatland's redox conditions at a high temporal resolution. Here, in particular, the Mn/Fe ratio is a valuable indicator of past water table changes. Stable isotope values of organic carbon and nitrogen, as well as organic carbon and nitrogen contents, give further information to reconstruct relationships between the peatland's surface wetness and climate. Plant macrofossils indicate the local occurrence of the main peat-forming plant species. The macrofossil assemblages bear further information on the presence of fungal and invertebrate taxa. With the study of microfossils it was shown that climate variations and human activities had an influence on the abundance of dominating taxa, particularly on grasses.

Vuille et al. (2012) and Bird et al. (2011) hypothesised that Northern Hemisphere climate oscillations affect the SASM activity of the tropical/subtropical Southern Hemisphere. This hypothesis can be confirmed by our data. It turns out that, during the last 2000 years, Northern Hemisphere temperature variations (Moberg et al., 2005) and the concomitant shifts in SASM intensity had an impact on the redox conditions of CTP. Deviations appear during the "Little Ice Age", which, at CTP, is characterised by highly frequent climatic fluctuations.

Dry conditions prevailed from 150 BC to AD 100. A more humid phase dominated between AD 100 and AD 550. From AD 550 to AD 1250, the climate was characterised by several distinct changes between drier and wetter conditions, showing a pronounced dry period between AD 1000 and AD 1100. Afterwards, the climate repeatedly fluctuated. The CTP data give evidence of numerous humid (AD 1350, AD 1550, AD 1700–1750, AD 1800–1850) and arid (AD 1250–1330, AD 1500, AD 1590, AD 1750–1800) phases. Volcanic forcing in the beginning of the 19th century seems to have had a major influence on climatic settings in the central Andes, as evidenced by a sudden change in redox conditions at that time.

The high temporal resolution of CTP and the evident sensitivity of the applied palaeoclimate proxies confirm that high-altitude cushion-plant peatlands in the central Andes preserve valuable records of past climate dynamics. They provide important information for palaeoclimatological/palaeoecological and archaeological research. Experiences and findings provide good prerequisites for further investigating these highland ecosystems. For a sound interpretation of past processes and past environments, a better understanding of the contemporary ecological processes of these fragile ecosystems is highly demanded.

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**Table 1.** Radiocarbon ages of core Tuz 694 of Cerro Tuzgle peatland. The calibrated age ranges were calculated using CALIB 7.0.4 and the IntCal13 data set (Reimer et al., 2013). The modelled ages are the result of a probabilistic age-depth model using MCAgeDepth (Higuera et al., 2009). The range represents the 2$\sigma$ values, and the median ages are in parentheses.

| | core depth (cm) | compacted depth (cm) | measured $^{14}$C | measured error (±) | 2 $\sigma$ calibrated age (cal yr BP) | MCAgeDepth modelled age (cal yr BP) |
|---|---|---|---|---|---|---|
| Poz-56032 | 37.5 | 50.5 | 600 | 35 | 541–(603)–654 | 541–(602)–654 |
| Poz-56034 | 77.5 | 82.5 | 1095 | 30 | 938–(1001)–1060 | 941–(1000)–1061 |
| Poz-56035 | 103.5 | 152.5 | 1245 | 25 | 1082–(1211)–1268 | 1084–(1210)–1264 |
| Poz-66440 | 144.5 | 172.5 | 1620 | 30 | 1412–(1514)–1591 | 1419–(1514)–1588 |
| Poz-56036 | 160.5 | 180.5 | 1715 | 30 | 1557–(1620)–1700 | 1558–(1619)–1700 |
| Poz-66442 | 187.5 | 193.5 | 1960 | 30 | 1830–(1911)–1988 | 1836–(1910)–1984 |

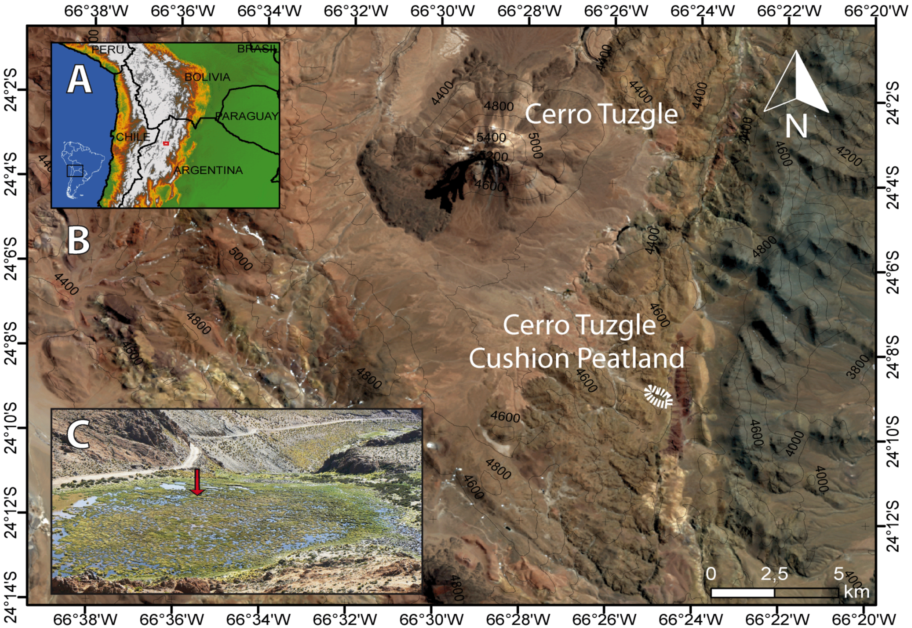

**Figure 1. (a)** Map of NW Argentina and adjacent countries (data source: GLCF World Data). **(b)** The location of Cerro Tuzgle peatland (CTP) south of Cerro Tuzgle volcano in the NW Argentine Puna plateau (data source: DGM-GTOPO30). **(c)** Panorama of the *Oxychloe andina*-dominated part of CTP and the location of the coring site (February 2013).

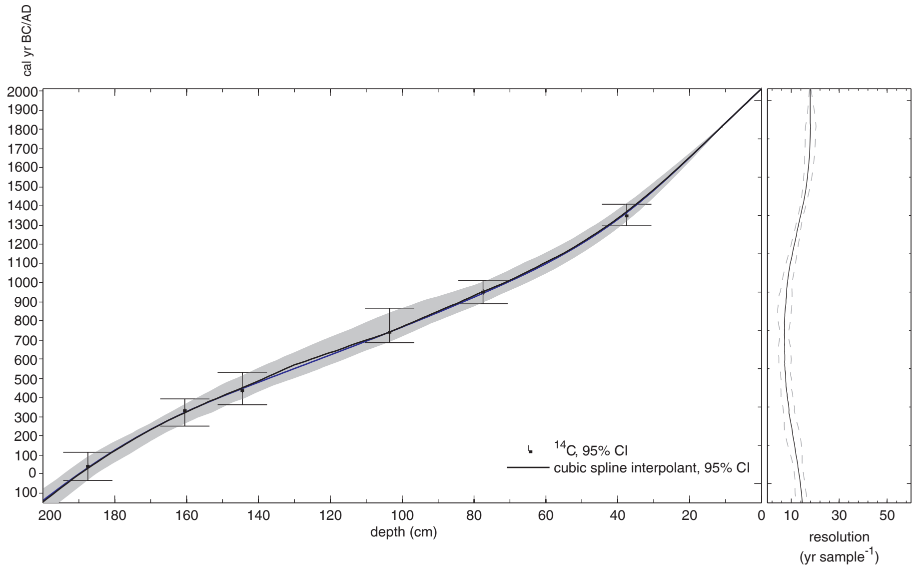

**Figure 2.** Age-versus-depth model for core Tuz 694 retrieved from CTP based on 6 $^{14}$C dates. The grey band represents the modelled range of dates and the black line the 50th percentile of all runs.

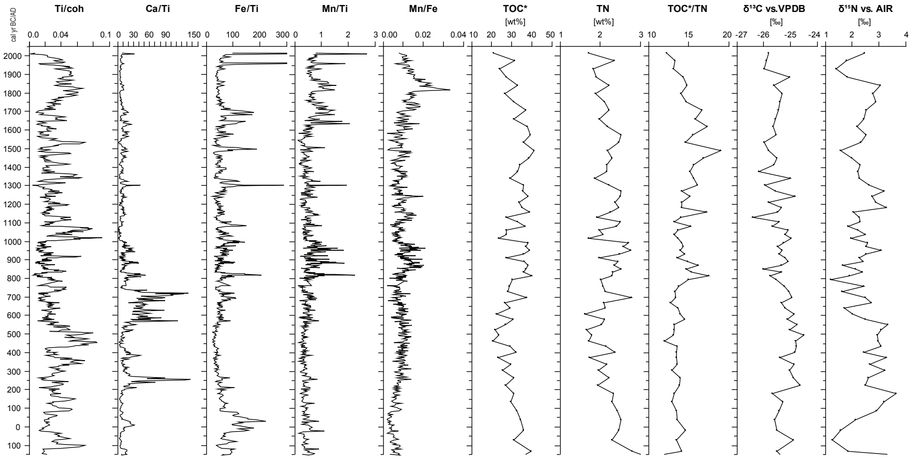

**Figure 3.** XRF-measured element ratios, elemental and stable isotope contents for core Tuz 694 of Cerro Tuzgle peatland, plotted against age.

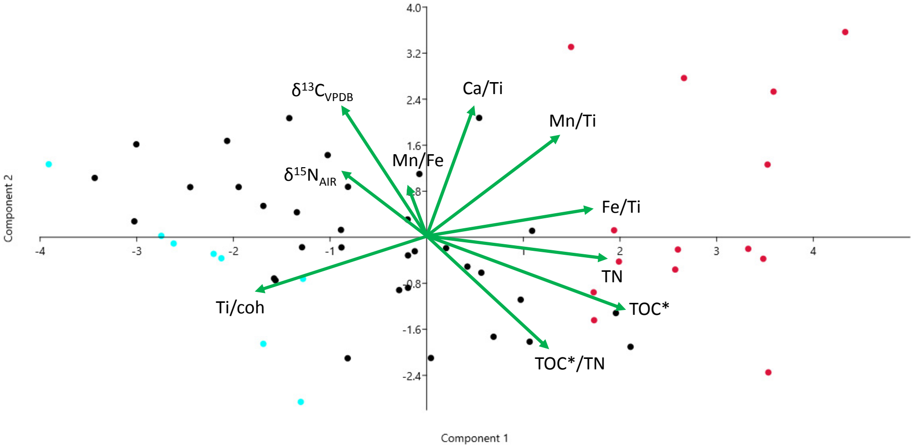

**Figure 4.** Principal component analysis of the geochemical data. Component 1 explains 38.9 % of the total variance and component 2 explains additional 18.3 %. Red dots: peak values of Fe/Ti (values > 85). Blue dots: peak values of Ti/coh (values > 0.05).

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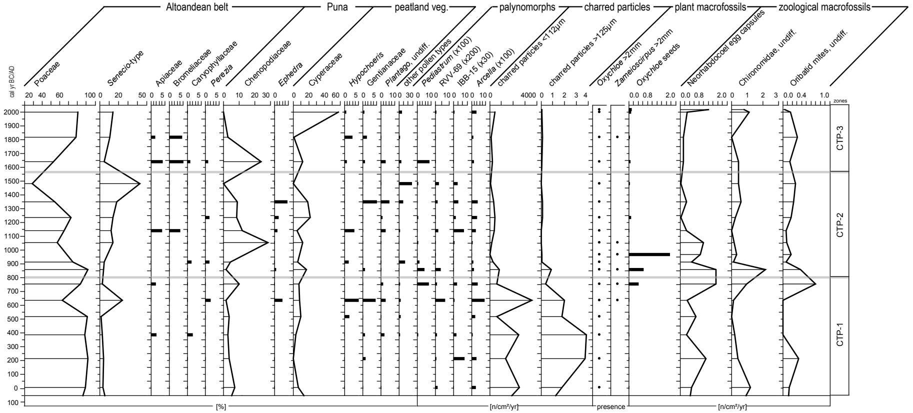

**Figure 5.** Pollen, palynomorphs, charred particles and macrofossils diagram for core Tuz 694 of Cerro Tuzgle peatland. Peatland vegetation was excluded from the pollen sum.

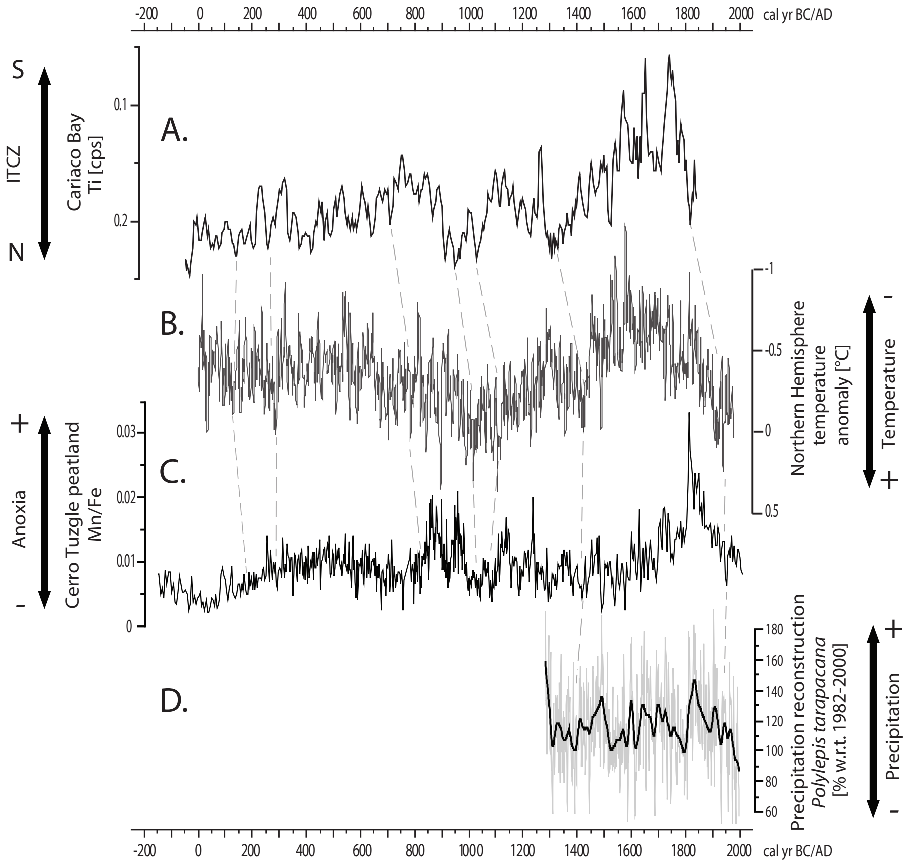

**Figure 6.** The late Holocene Mn/Fe ratio sequence of Cerro Tuzgle peatland compared with high-resolution marine and terrestrial records. **(a)** Bulk Ti content of Cariaco Basin sediments (Haug et al., 2001). **(b)** Northern Hemisphere temperature reconstruction (Moberg et al., 2005). **(c)** Mn/Fe ratio sequence of CTP. **(d)** Precipitation reconstruction for the central Andes based on *Polylepis tarapacana* tree-rings (Morales et al., 2012).

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