Ground air: a first approximation of the Earth's second largest reservoir of carbon dioxide gas

James U.L. Baldini[1*], Rachel A. Bertram[1], and Harriet E. Ridley[1]

[1] Department of Earth Sciences, University of Durham, Durham, DH1 3LE, UK.

*james.baldini@durham.ac.uk

It is becoming increasingly clear that a substantial reservoir of carbon exists in the unsaturated zone of aquifers, though the total size of this reservoir on a global scale remains unquantified. Here we provide the first broad estimate of the amount of carbon dioxide gas found in this terrestrial reservoir. We calculate that between 2 and 53 PgC exists as gaseous CO_2 in aquifers worldwide, generated by the slow microbial oxidation of organic particles transported into aquifers by percolating groundwater. Importantly, this carbon reservoir is in the form of CO_2 gas, and is therefore transferable to the Earth's atmosphere without any phase change. On a coarse scale, water table depths are partially controlled by local sea level; sea level lowering therefore allows slow carbon sequestration into the reservoir and sea level increases force rapid CO_2 outgassing from this reservoir. High-resolution cave air pCO_2 data demonstrate that sea level variability does affect CO_2 outgassing rates from the unsaturated zone, and that the CO_2 outgassing due to sea level rise currently occurs on daily (tidal) timescales. We suggest that global mean water table depth must modulate the global unsaturated zone volume and the size of this carbon reservoir, potentially affecting atmospheric CO_2 on geological timescales.

Keywords: caves, carbon reservoirs, ground air, carbon dioxide, vadose zone

1. Introduction

The presence of a reservoir of carbon within the unsaturated zone of karst aquifers is now well-established (e.g., Mattey et al., 2016; Noronha et al., 2015). Calculations based on groundwater geochemistry have long suggested that groundwater may equilibrate with air that has pCO_2 substantially higher than soil air pCO_2, implying a deeper source (Atkinson, 1977). This early research concluded that microbial oxidation of mechanically transported organic material within aquifer permeability generates CO_2 within the unsaturated zone of karst aquifers (Atkinson, 1977; Wood, 1985). This air reservoir, termed 'ground air', is characterised by very high CO_2 concentrations. Recent studies from cave sites (e.g., Baldini et al., 2006; Bourges et al., 2001; Whitaker et al., 2010) have shown that cave air pCO_2 values generally increase in smaller or more sheltered passages, with values sometimes considerably higher than local soil pCO_2, suggesting the presence of ground air. However, direct measurements of borehole air confirm that a reservoir of extremely high pCO_2 air exists within the unsaturated zone of aquifers in a variety of different lithologies (Benavente et al., 2010; Hendry et al., 1993; Hendry and Wassenaar, 2005), not just karstic aquifers. For example, research on the gas content of siliciclastic deposits of the Ogalla aquifer in south Texas concluded that aerobic microbes oxidized organic carbon transported to intergranular porosity by recharge water, producing CO_2 (Wood and Petraitis, 1984). Furthermore, radiocarbon measurements support the concept that this CO_2 is derived from the decay of old carbon that was probably transported into the aquifer (Bergel et al., 2017; Lechleitner et al., 2016; Noronha et al., 2015; Wood et al., 2014), rather than CO_2 produced in the soil zone and then diffused downward. Considered together, existing geochemical evidence suggests the presence of a substantial carbon dioxide reservoir at depth that has largely escaped quantification. Access issues have meant that this reservoir is most easily identified in cavernous and karstified environments, but ground air is found in any lithology with even small-scale permeability.

Here we use new laboratory and field data combined with published estimates of mean global depth to groundwater (Fan et al., 2013; Serrano-Ortiz et al., 2010) to estimate the size of the global ground air carbon reservoir. A strong link between sea level and CO_2 outgassing from this reservoir is observed in a new cave air pCO_2 dataset, which implies that vertical groundwater shifts associated with local sea level push ground air out of the subsurface during a rising tide and pull atmospheric air into the subsurface during a falling tide (i.e., that the water table acts as a piston). We suggest that eustatic sea level increases on geological timescales potentially also forced CO_2 out of the ground air reservoir and into the atmospheric reservoir, potentially accounting for a portion of the observed atmospheric CO_2 increase.

2. Methods

2.1. Quantifying the global ground air reservoir

To constrain the global ground air CO_2 reservoir we estimated: *i)* mean ground air pCO_2, *ii)* mean global depth to groundwater, *iii)* mean global net (primary and secondary) permeability of the unsaturated zone, and *iv)* global land surface area (Table 1). Considerable variability exists in all these parameters, and we therefore necessarily report a broad range of ground air carbon reservoir sizes. We believe that the true value lies within this range, and future studies should focus on better constraining the variables defining this range.

The current global unsaturated zone volume was estimated here using published exposed land area and the Global Mean Water Table Depth (GMWTD: the mean distance from the surface to the water table over all points on land) values; the minimum GMWTD (26 m) was calculated using data presented in Fan *et al.* (2013) and the maximum (100 m) uses the value reported in Serrano-Ortiz *et al.* (2010)). The land area estimate does not account for ice cover because of substantial uncertainties in both the amount and distribution of subglacial carbon. Bedrock permeability values range considerably (Freeze and Cherry, 1979). We use a conservative mean global value of 10%, consistent with previous estimates (Serrano-Ortiz et al., 2010). This includes both primary and secondary permeability, and accounts for decreasing permeability with depth (Williams, 2008). Ground air pCO_2 values were assumed to range from 12,000 ppmv to 70,000 ppmv based on the results of the laboratory and field experiments conducted here and published data (see Supplementary Content). The minimum value is probably very conservative, but given the substantial uncertainties involved in this first estimate of the global ground air carbon reservoir size we feel that the broad range of estimates is justified.

2.2. Cave air *p*CO_2 monitoring

Cave air *p*CO_2 measurements were made in Conch Bar Caves, Middle Caicos, Turks and Caicos Islands (21°49′34″N, 71°47′28″W) to gauge the response of ground air to local sea level fluctuations. The cave is a flank margin cave, developed in Cretaceous and Tertiary aged carbonate platform sediments. The cave has numerous entrances, is well ventilated, and has a number of saltwater pools fed by direct connections to the sea (Supplementary Figure 3) (Smart et al., 1992).

The *p*CO_2 logger was placed in a small cave chamber with good airflow 180 meters from the nearest entrance, 20 meters below the surface, and two meters above mean sea level (Supplementary Figure 3). The majority of the chamber floor was flooded during high tide, except for a few isolated ‘islands’ of bedrock or secondary calcite (< four meters in diameter) that remained above sea level. The *p*CO_2 logger was placed on one of these, and was always at least one meter above the water level in the chamber. Cave air *p*CO_2 was measured automatically every three hours for 318 days from April 17, 2011, to February 28, 2012, using a calibrated Vaisala GMP343 infrared carbon dioxide probe connected to a Vaisala MI70 indicator (±7 ppmv) (Ridley et al., 2015). Data were corrected for barometric pressure (also measured on site, using a Barotroll barometric pressure logger) using the method outlined in Spötl *et al*. (2005). Spectral analysis of the *p*CO_2 dataset was conducted using PAST software (Hammer et al., 2001).

2.3. Beach transect CO_2 measurements

Measurements of ground air in the unsaturated zone were made at five sandy beaches across the UK (July-September 2013). Each site was divided into three zones (intertidal, high beach, and dune) and measurements were taken within each. Measurements were made across transects orthogonal to the shoreline, crossing all three zones at each of the five beach sites. At each location, a calibrated Vaisala GMP343 combination CO_2 and temperature probe (uncertainties of ±0.04% for CO_2 and ±0.05°C for temperature) was buried to a depth of one meter (or to just above the water table if the water table was shallower than one meter). CO_2 values stabilised at all sites within 100 minutes. The intertidal zone represents an area where the ground air CO_2 signature is 'reset' to atmospheric values once the tide recedes from the zone and atmospheric air is drawn into the subsurface by the dropping sea level. The sea occasionally affects the high beach zone environment during storms and unusually high tides, but not on daily timescales. The dune zone was not submerged in the recent past, and is overlain by typical halophytic vegetation and by a thin (< 5 cm), immature soil zone consisting almost exclusively of an O-horizon directly above the quartz sand substrate. The dune zone provides a contrast to the other two zones due to the presence of soil organic material, and because there would have been sufficient time for the organic material to infiltrate the sand substrate and oxidise. The dunes thereby provide an environment where ground air in the unsaturated zone is reasonably accessible. Time-series monitoring was conducted in the dune environment of Camber Sands and Greatstone Beaches, Kent, UK, where data was logged automatically every 15 minutes over several days.

3. Results and Discussion

3.1. Existing evidence for 'ground air'

The evidence for air within the vadose zone with substantially elevated CO_2 (and methane) concentrations is now strong. Laboratory mesocosm experiments (Hendry et al., 1993;

Hendry et al., 2001), new field data, and previously published data (e.g., Atkinson, 1977; Batiot-Guilhe et al., 2007; Denis et al., 2005; James, 1977; Mattey et al., 2016; Serrano-Ortiz et al., 2010; Wood and Petraitis, 1984) collectively indicate that a substantial CO_2 pool exists in the unsaturated zone of aquifers worldwide. Previous researchers have even suggested that the majority of cave air CO_2 is sourced from a deep biogenic source (Breecker et al., 2012), rather than the soil. We have compiled a representative collection of published measurements of unsaturated zone air pCO_2 and $\delta^{13}C$ (based on 14 different sites from different environments), which strongly suggest variable mixing between two end member pools of CO_2: one with low pCO_2 and high $\delta^{13}C$ and a second with substantially elevated pCO_2 and low (but locally variable) $\delta^{13}C$ values. The first pool is clearly the Earth's atmosphere, whereas the second represents a reservoir with pCO_2 that is up to two orders of magnitude higher than typical soil air pCO_2 (Murthy et al., 2003) (Figure 1). Because most of these elevated measurements are from regions with no known magmatic or hydrocarbon related CO_2, this strongly supports previous studies concluding that high CO_2 ground air exists in the unsaturated zone. Furthermore, if the second reservoir were simply soil air, mixing would reflect the photosynthetic pathway of the vegetation overlying the various sites (e.g., between -22 and -25‰ VPDB for C_3 vegetation and between -10 and -15 VPDB for C_4 vegetation). However, average mixing lines indicate that the CO_2 reservoir typically has a $\delta^{13}C$ of between -17 and -19‰ VPDB (although some individual sites clearly do reflect modern overlying vegetation, such as Obir Cave), suggesting that soil is not the main source of the CO_2. Possible sources for CO_2 found at depth in non-geothermal areas include: diffusion from the soil zone, microbial oxidation of organic material at depth (either material transported downward from the soil or carbon deposited with the rock), or degassing during calcite precipitation at the surface of the water table. The observed carbon isotope ratios may reflect mixing of organic material filtered by the aquifer over thousands of years, thereby integrating the $\delta^{13}C$ signal of a variety of vegetation, sometimes averaging C_3 and C_4 vegetation signatures. This is strongly supported by radiocarbon evidence from stalagmites and cave air suggesting the contribution of substantial amounts of very old carbon, and that soil carbon is often not the direct source of cave air pCO_2 (Noronha et al., 2015). The recent use of oxidative ratios of subsurface gases provides more strong support for the concept that the carbon in both caves and the vadose zone is at least centuries old (Bergel et al., 2017). Furthermore, studies on dissolved organic carbon within an aquitard demonstrate that C within connate pore water is approximately 15,000 years old (Hendry and Wassenaar, 2005). The high (compared to C_3 vegetation) $\delta^{13}C$ values typical of ground air may also reflect carbonate equilibrium chemical reactions involving both bedrock dissolution and calcite precipitation at the water table. Mattey et al. (2016) provide a comprehensive review of ground air in karstic environments and how advective and diffusive mixing of CO_2 derived from different sources, including soil air, occurs.

The natural environments with the highest ground air pCO_2 values are: *i)* inaccessible small-scale permeability within bedrock and *ii)* deep, unventilated cave and mine passages, which are inaccessible without breathing apparatus due to the high pCO_2 levels (known colloquially as ‘bad’ or ‘foul’ air amongst cavers (Smith, 1999)). Cave air pCO_2 measurements made in more accessible sections of caves reflect, almost without exception, a mixture of ground air with substantial amounts of outside (atmospheric) air and have pCO_2 values low enough to permit exploration of the passage. In one of the few examples from a poorly ventilated passage (in Lascaux Cave, France), Peyraube *et al.* (2013) measured pCO_2 values over 70,000 ppmv. Additionally, a growing number of borehole pCO_2 measurements (Affek et al., 1998; Benavente et al., 2010; Peyraube et al., 2013; Vadillo et al., 2010) with maximum values approaching 70,000 ppmv also indicate that ground air is present. It is intriguing that almost no measurements of ground air considerably above 70,000 ppmv exist. The reasons underlying this observation are unclear, but may reflect a reduction in metabolic rate of aerobic bacteria (and associated organic matter oxidation rate) once ground air oxygen levels drop below 14% (equivalent to the conversion of 70,000 ppmv O_2 gas to CO_2 gas from the presumed initial pO_2 value of 210,000 ppmv (21%, the concentration in the Earth’s atmosphere)).

Available data suggest that ground air pCO_2 values are greatest near the capillary fringe and decrease upward towards the soil zone (Wood et al., 2014). This is due to enhanced CO_2 generation near the water table but also to dissolution and downward transport of CO_2 by percolation waters (Affek et al., 1998; Walvoord et al., 2005; Wood et al., 2014). Calcite precipitation at the water table could also partially account for the high concentrations adjacent to the water table, but mass balance considerations suggest that microbial oxidation of organic matter is a larger source (Walvoord et al., 2005). At some borehole sites, it is clear that high permeability, even without the presence of cavernous porosity, creates conditions favouring rapid air exchange between the surface and subsurface, and the residence time of vadose zone air is measurable in years to decades (Thorstenson et al., 1998). In these cases, such as at Yucca Mountain, Nevada, ground air pCO_2 values are moderated by exchange with the atmosphere, with very low values, typically ranging from 900 to 6,000 ppmv according to local permeability and depth (Thorstenson et al., 1998). This illustrates that ground air pCO_2 varies substantially both geographically and vertically. A number of different variables, including bedrock permeability, moisture content, rock type and organic content, local climate, and vegetation cover all affect ground air pCO_2 values. The maximum measured values for ground air pCO_2 used here (70,000 ppmv) are therefore likely substantially higher than mean values of the global unsaturated zone reservoir. Conversely, the minimum values (12,000 ppmv, derived from our lab and field data (see Supplementary Content)) are lower than most direct ground air pCO_2 measurements, and therefore are likely to underestimate the global mean.

3.2. Estimating the ground air reservoir size

Serrano-Ortiz *et al.* (2010) estimated the CO_2 contained in karstic regions, but did not consider non-karstic areas. However, no reason exists why only karst regions should host ground air and, as discussed previously, unsaturated zone pCO_2 measurements in other environments support ground air as a global phenomenon. We therefore suggest that elevated pCO_2 exists throughout the unsaturated zone globally, but that direct measurements are lacking due to the absence of accessible cave passage in non-limestone lithologies. In fact, non-karstic aquifers may actually have higher mean ground air pCO_2 values due to a reduced capacity for ventilation due to the absence of large passages (Covington, 2016). The presence of aerobic bacteria in the deep subsurface is currently not well constrained, but a number of studies now illustrate that aerobic bacteria are found in some of the harshest and least hospitable environments on the planet, including in ocean sediment at depth in the most nutrient-poor regions of the Pacific Ocean (D'Hondt et al., 2015), within caves (e.g., Tomova et al., 2013), and in bedrock (Personne et al., 2004). Specifically, studies on boreholes demonstrate that aerobic bacteria exist throughout subsurface and that their concentrations do not seem to decrease with depth (Hicks and Fredrickson, 1989). The current consensus appears to favour a model where the biosphere in the deep subsurface is both diverse and active (Fredrickson and Balkwill, 2006; McMahon and Parnell, 2014; Rempfert et al., 2017), so the presence at depth of microbes capable of oxidising organic matter is not surprising.

Using the estimated ranges in parameters affecting global unsaturated zone volume and ground air pCO_2 (Table 1), we estimate between 2 and 53 petagrams of carbon (PgC) are stored as ground air within the unsaturated zone of aquifers globally. This range is consistent with values of 2.0 PgC calculated by Serrano-Ortiz *et al*. (2010) calculated for just karst regions (representing ~15% of land area) using lower values of pCO_2 measured in caves (20,000 ppmv). This range is also consistent with the calculations suggesting 10-100 PgC exists in the deep biosphere as microbes (between 2 and 19% of the Earth's total biomass) (McMahon and Parnell, 2014; Whitman et al., 1998). Ground air CO_2 therefore represents a terrestrial C pool containing between 0.24 and 6.4% of the current atmospheric C content (830 PgC) (Le Quere et al., 2015). The calculation is most sensitive to the GMWTD, and simply changing the value from the Serrano-Ortiz et al. (2010) value (0.1 km) to the Fan et al. (2013) value (0.026 km) reduces the maximum ground air reservoir value from 53 PgC to 14 PgC. The lower estimate of GMWTD of Fan et al. (2013) is more comprehensive, and consequently it is likely that the total ground air reservoir is on the lower end of the range reported here. Critically however, unlike many other non-atmospheric carbon reservoirs, ground air C exists as gaseous CO_2, and does not require a phase change prior to entering the atmospheric pool. For example, carbon stored in the deep marine reservoir has a mean residence time of ~100,000 years, while carbon in limestone has a residence time of ~100 million years. Carbon within the biosphere is more mobile (mean residence time of living terrestrial biosphere = ~20 years), but with the exception of fires is not instantaneous. Consequently, variability in unsaturated zone reservoir magnitude could affect atmospheric CO_2 concentrations and ultimately global climate extremely quickly. Any major rise in sea level would necessarily be accompanied by ground air outgassing that reflects the rapidity of the sea level change.

3.3. Correlations between cave air pCO_2 and sea level

Evidence that even small tidal sea level fluctuations push high-pCO_2 air out of the unsaturated zone ground air reservoir and into cave passage is derived from new high-resolution pCO_2 time-series data from Conch Bar Caves (Turks and Caicos Islands) proximal to the Atlantic Ocean (Figure 3). Importantly, cave air pCO_2 increases with increasing local sea level, indicating that CO_2 is forced up from the bedrock permeability rather than down from the soil. The outgassing signature is remarkably clear despite the cave system having multiple entrances and an active ventilation system (Figure S3). The results are striking, with cave air pCO_2 tracking sea level, illustrating the ground air CO_2 'piston effect' well. Spectral analysis of both the Conch Bar Cave pCO_2 record and the tide gauge-derived sea level record illustrate in-phase 12- and 24-hour cycles (Figure 3), reflecting lunar tidal forces.

These observations have implications on longer timescales. GMSL reductions associated with low sea levels on geologic timescales (e.g., Ice Ages or glaciations) expose new land while simultaneously increasing GMWTD, thereby increasing the unsaturated zone volume. In most situations with unconfined aquifers, sea level acts as the local base level, and shifts in base level control the elevation of the water table further inland in accordance with the Dupuit equation (Fetter, 1994; Hiscock, 2005). In unconfined aquifers, basic hydrological principles dictate that water must flow from high hydraulic head to low hydraulic head; an increase in sea level is therefore propagated inland until it eventually affects the entire aquifer. Evidence does exist for sea level-induced water table lowering during periods when sea level was substantially lower. For example, substantial cave development ~100m lower than the modern water table in Florida may reflect local water table responding linearly to sea level rise during the last glacial termination (Wilson, 1988). In fact, cave development within the Floridan aquifer may reflect mixing of the fresh water table with high pCO_2 ground air during the LGM (Gulley et al., 2013). Abundant evidence for a lower water table during glacial conditions exists throughout coastal regions globally (e.g., Bard et al., 2002; Moseley et al., 2013). The simple assumption of unconfined flow is not directly applicable to some groundwater basins with complex geological structural controls (such as the Basin and Range province of North America), but is relevant in many cases. We further acknowledge that shifts in climate and regional recharge conditions on long timescales also impact the depth to the water table locally, but globally these shifts would tend to cancel each other out (i.e., shifting rainfall patterns will raise the water table in one area while lowering it in another).

Downward percolating water will transport organic matter into the newly exposed volume of rock (or sediment) where oxidation produces CO_2. In this manner, sequestration of atmospheric CO_2 will occur with sea level falls. On the other hand, sea level increases will cause flooding of land, reduced GMWTD, and a smaller ground air carbon reservoir (during low-ice volume intervals of Earth history). During transitions from high to low ice volume intervals, some CO_2 gas will necessarily transfer from the unsaturated zone into the atmosphere. Interestingly, the identification of this terrestrial carbon reservoir is consistent with recent results suggesting increased storage of carbon during the Last Glacial (~21,000 years before present) in an previously unidentified inert terrestrial pool (Ciais et al., 2012), which was apparently released into the atmosphere during deglaciation.

5. Conclusions

Here we calculate that between 2 and 53 PgC exist in a terrestrial carbon reservoir located in the unsaturated zone of aquifers worldwide. This range is consistent with previous estimates of carbon dioxide content of karst aquifers alone and with estimates of microbial biomass within all aquifers. We agree with the recently expressed perspective (Bergel et al., 2017) that the increasingly clear presence of a 'ground air' reservoir may require a re-evaluation of the classic models of carbon dioxide formation within karst aquifers. Additionally, we propose that this reservoir is not restricted to karst aquifers, but is instead commonplace in all lithologies with any appreciable permeability. This global 'ground air' carbon reservoir is the second largest store of CO_2 gas on the planet, but remains largely unappreciated due to difficulties with access.

Assuming that the PCO_2 of ground air is (on average) temporally constant, the largest control on the carbon amount stored is the volume of the unsaturated zone. Variability in ground air carbon reservoir size represents a potential control on global atmospheric pCO_2 and consequently temperature. A new cave air PCO_2 dataset from a coastal cave illustrates that sea level is a fundamental control on the outgassing of CO_2 from the ground air reservoir. Changes in eustatic sea level will therefore directly influence the unsaturated zone volume and hence the global ground air reservoir, potentially affecting the amount of CO_2 contained within the Earth's atmosphere and, consequently, climate. It is worth noting that this mechanism may also have contributed to more pronounced climate shifts during geological intervals when continental shelves were larger, or expansive shallow seas were present, such as the late Neoproterozoic or the Ordovician. In these cases, a moderate sea level drop would have exposed considerable amounts of land, possibly resulting in considerable carbon storage in the unsaturated zone followed by substantial release of CO_2 during sea level rises.

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Figure Captions:

Figure 1: Keeling plot of published CO_2 measurements (in % atm) from the unsaturated zone and outside atmosphere. Cave air, soil air, atmospheric air, well air, and borehole air pCO_2 data from selected sites from around the world (Batiot-Guilhe et al., 2007; Benavente et al., 2011; Bourges et al., 2001; Breecker et al., 2012; Denis et al., 2005; Frisia et al., 2011; Kowalczk and Froelich, 2010; Mattey et al., 2010; Peyraube et al., 2012; Peyraube et al., 2013; Riechelmann et al., 2011; Spötl et al., 2005; Tremaine et al., 2011). Sites were chosen to illustrate ground air CO_2 in different environments, and are not comprehensive. Measurements from sites currently overlain by C_4 vegetation are represented by triangles and those overlain by C_3 vegetation by circles. Atmospheric values are for Mauna Loa Observatory (Keeling et al., 2001) (dark blue stars) and published values above some cave sites (light blue stars).

Figure 2: Carbon dioxide concentrations along transects perpendicular to the coast at five beach locations in the UK. Measurements of ground air in the unsaturated zones at five sandy beaches across the UK taken at different times between July-September 2013. Measurements were made across transects orthogonal to the shoreline, using a calibrated Vaisala GMP343 combination CO_2 and temperature probe buried to a depth of one meter (or to just above the water table if the water table was shallower than one meter). Two transects were conducted at Camber Sands on different days; these are labelled A and B respectively.

Figure 3: Cave air record at Conch Bar Cave, Turks and Caicos Islands, compared with tide data. (a) Cave air pCO_2 was measured from April 17, 2011, to February 28, 2012. One representative week (8-14 August 2011) of the cave air pCO_2 record is shown here, along with sea level data from the nearest tide gauge (Virginia Key, Florida, USA; 950 km to the NW). The time difference between the tide at Virginia Key and that measured live (no

logged data available) at Sandy Point, Turks and Caicos Islands, is less than one hour. (b) Spectral analysis of the full 318-day datasets (inset) illustrates the presence of statistically significant (at 90% confidence) 12-hour and 24-hour cycles within both the cave air pCO_2 and sea level datasets.

Table 1: Parameters used to estimate ground air carbon stores. The range of values used represents the uncertainty in the measurements. Land area values and global mean water table depth have varied over geological time; estimates are presented for the periods considered in this study.