Understanding the hydrochemical evolution of a coastal dune system in SW England using a multiple tracer technique

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Abstract An improved knowledge of the hydrology of coastal dune systems is desirable for successful management of their diverse ecology under a changing climate. As a near-pristine coastal dune spit system, Braunton Burrows (SW England) is an ideal location for the study of the natural processes governing recharge to the dune groundwater system and the evolution of its water quality. Whereas previous investigations have tended to focus on inter-dune slacks, this study has also given attention to infiltration through the high dunes. Cores were taken through dunes and the resulting sand samples processed to provide information on grain size distribution and porewater chemistry. Groundwater samples were obtained from beneath dunes and slacks. A variety of geochemical techniques were applied including hydrochemistry, stable isotopes and residence time indicators. The unsaturated zone profiles indicate the existence of piston flow recharge with an infiltration rate of 0.75–1 m/yr, although faster rates probably also occur locally. Groundwater beneath the high dunes gave ages in the range 13–16 yr, compared to the dune slack groundwater ages of 5–7 yr, and an age of 22 yr for groundwater from the underlying mudstone aquifer. The chemistry of waters in both unsaturated and saturated zones is dominated by Ca and HCO_3, supplemented by variable amounts of other ions derived from marine aerosols and limited reaction with sand grains and their coatings. The main chemical evolution of the porewaters occurs rapidly through the mobilisation of surface salt crusts and dissolution of shell carbonate. This situation changes little in the underlying groundwater, though an evolution towards reducing conditions increases the concentrations of redox-sensitive species such as Fe and Mn. The rapid chemical evolution of the infiltrating water means that its composition will respond quickly to changes in the supply of shell material and/or marine salts, which are possible consequences of climate change. However, the residence time measurements suggest the dune aquifer has a relatively long turnover time which will to some extent buffer such changes. The results of the present study should be transferable to natural dune systems in similar coastal situations.

Key words: dune, dune slack, wetland, hydrochemistry, stable isotopes, SF_6, unsaturated zone, groundwater.

1 INTRODUCTION

Within Europe, coastal dune systems are widely distributed along the Atlantic, Mediterranean, North Sea and Baltic littorals (Doody 2008). They include areas of open mobile sand and more mature vegetated and relatively static dunes. The elevation of the water table within the dunes partially dictates the morphology of the dune fields and determines the elevation at which wetland dune slacks, the flat-floored depressions that occur within the sand dunes, are formed (Stuyfzand 1993; Stratford et al. 2013). The slacks have a shallow water table in summer and may be flooded for much of the winter. The hydrological regime, coupled with the chemistry of the water, dictates the ecological status of the slacks which tend towards a rich and diverse assemblage including rare species (Grootjans et al. 1998; Curreli et al. 2013).

A conceptual understanding of the processes controlling the hydrological regime in dune systems is fundamental to conservation management. As the water table and water chemistry determine the abundance of many slack species and control the vegetation assemblages (Willis et al. 1959) knowledge of the hydrochemical processes and their stability is key to informing management strategies to protect the slack ecosystems. Key questions are:

1. Does infiltration reach the water table exclusively by piston flow?
2. How does water quality evolve in the unsaturated and saturated zones beneath the high dunes?
3. What kind of timescales are involved in the water movement and evolution?
4. Is water quality stable with time or could it change?

Conservation management also has to cope with coastal erosion and accretion which impact groundwater base levels, changes in rainfall and other natural and sometimes catastrophic events (Robins et al. 2013).

While there have been a number of studies of dune hydrology based on physical parameters such as water levels (e.g. Van der Hagen et al 2008, Vandenbohede et al 2008, Clarke et al. 2010, Davy et al. 2010), there are fewer examples of dune water quality being applied to a better understanding of hydrology and ecology (Stuyfzand 1993; Grootjans et al. 1996; Sival et al. 1999). These studies either tended to focus on dune slacks or, particularly in the case of

63 pioneering work on dune system geochemistry (Stuyfzand 1993, Stuyfzand 1989), on
64 systems impacted by processes such as artificial recharge, salinization, decalcification and
65 anthropogenic drainage works. In contrast, this paper describes a study of the
66 hydrogeochemistry of a more natural dune groundwater system at Braunton Burrows in North
67 Devon, England, based on data gathered from unsaturated zone profiles and piezometers
68 beneath both dune ridges and slacks. The techniques used include hydrochemistry, stable
69 isotopes and trace gas age indicators.
70
71 Investigations at Braunton Burrows, as at many other coastal dune wetlands, have
72 concentrated mainly on understanding the ecohydrology of the dune slacks with less attention
73 being given to the high dunes. This reflects the importance of the slack ecosystems and their
74 conservation management compared to the sparsely-vegetated high dunes (Davy et al. 2006;
75 2010). However, understanding the hydrology of dune systems requires knowledge of
76 processes operating across the whole site rather than just the more ecologically complex
77 zones. The present study, therefore, focuses on both the hydrogeochemical processes beneath
78 the dune slacks and the high dunes. The objective is to provide supporting evidence for the
79 understanding of dune spit hydrology in order to better inform the needs for conservation
80 management.
81
82
83 **2 BACKGROUND**
84
85 Braunton Burrows is a dune spit wetland on the North Devon coast in south-west England
86 (Fig. 1), rising in elevation to 38 m above Ordnance Datum (aOD) with an area some 10 km^2
87 (Stratford et al. 2013). The spit comprises a series of N–S oriented dunes and slacks which
88 evolved in response to the dynamics of the prevailing wind and sea (Saye and Pye 2007). A
89 narrow zone of low fore-dunes, up to 5 m high, adjacent to the beach is succeeded inland by
90 sand hills up to 15 m high separated by a discontinuous belt of slacks. The highest dunes
91 occur just inland from these slacks beyond which is a broad, but poorly defined, belt of
92 lower-lying ground with scattered hillocks and many ephemeral and some permanent pools.
93 Further inland are lesser dunes followed by flat sands with a few scattered small dunes which
94 merge towards cultivated fields. The slacks mainly remain dry in winter with ephemeral wet
95 weather pools (Davy et al. 2006; 2010).
96

The dunes rest on an estuarine clay layer forming the base of the small rain-fed aquifer in the sand (Burden 1998). The underlying Pilton Mudstone Formation (Devonian) forms a low-yielding aquifer, with little to no hydraulic contact between this and the sand aquifer. Groundwater level data from the piezometer network has been used to identify a groundwater divide within the sands parallel to the beach some two-thirds of the way inland towards the rear of the dune-field (Fig. 2). Groundwater discharges both to the beach beneath the fore-dune and inland to estuarine deposits which form low-lying meadows. The water table reaches a maximum elevation of 8 m aOD in winter along the axis of the groundwater divide (Stratford et al. 2013). There has been a decline in rainfall over the last 40 years which has caused a reduction in water table elevation which in turn has degraded the slack ecosystems (Robins and Jones 2013). Comparison with other west coast dune sites in England and Wales indicates that Braunton Burrows has been most impacted by change due to the decline in effective rainfall, making a better understanding of its hydrology a priority.

3 SAMPLING AND ANALYSIS

Three new uncored shallow dipwells (BB1, BB2 and BB3, see Table 1, Fig. 1) were hand-augered into the dune slacks to supplement an existing groundwater level monitoring network and to provide access for groundwater sampling. Subsequently a trial 'deep' cored dipwell (D1) was hammer drilled to a depth ~6 m on a high dune at the eastern end of the main slack transect in October 2011. Core was delivered in 1 m lengths within a polythene sleeve; recovery varied between 90 and 95%. The core was sub-sampled at 0.1 m intervals by slicing through the sleeve with aliquots stored in airtight glass vials later being used to test an offline preparation method for deuterium (δ^2H) analysis (see 4.3 below). The hole remained open during drilling with only the upper ~0.3 m being dry and friable. The remainder of the sand was moist and comprised consistently fine-grained to silt-grade material. The hole did not reach the water table but was lined with 36 mm diameter plastic pipe and capped top and bottom to allow future access if required.

Four additional deep cored dipwells were hammer-drilled using a Cobra TT percussion drill along the line of the main slack dipwell transect (Fig. 1) to depths up to 9m (Table 1) during November 2011. Continuous sampling of the unsaturated zone was achieved in the first three dipwells (D2, D3 and D4) with partial sampling in D5 nearest the shore. Small sub-samples

taken at 0.1 m intervals from the D2 and D4 cores were transferred into airtight glass vials for δ^2H analysis of the sand moisture. All cored sections from D2, D3, and D4 were then sliced into 0.2 m intervals from which about 40 mm was deposited into pre-weighed sealable containers to measure gravimetric moisture content and the remainder transferred to sealed plastic bags and refrigerated for subsequent centrifugation in the laboratory. Dipwells D3, D4 and D5 penetrated the water table, below which coring ceased to be effective. Piezometers were completed and cased to below water level, where possible, with 1 m of permeable casing at the bottom of the hole.

Owing to a problem of sand fall-in during drilling which affected the top sample of many of the core runs, several samples from each piezometer had to be discarded, leaving a number of small gaps in each of the resulting profiles (Section 4.3).

The sites were chosen to minimize the influence of disturbance by trees and their roots. Details of vegetation at each site have been recorded (Table 1) from a vegetation survey that took place in 2012.

Sand moisture contents were calculated from the weight loss observed after heating subsamples to 75°C for 48 hours. The dried samples from D3 and D4 were subsequently used for grain size analysis.

The bagged sands were refrigerated and centrifuged soon after returning from the field. Sub-samples were transferred to centrifuge buckets made from inert material and centrifuged at 14,000 rpm for 25 minutes. The drained waters were passed through 0.45 μm filters and split between two HDPE bottles per sample. One of each pair of bottles was acidified to 1% with Aristar nitric acid for determination of cations. In addition, aliquots were taken for standard δ^2H and $\delta^{18}O$ analysis from those samples which yielded sufficient volume. Specific electrical conductivity (SEC) was determined on the unacidified sample splits.

Owing to ingress of fine silty sand during an initial attempt to sample groundwater standing in D3, D4, and D5 the piezometers were re-drilled to a depth of 9.2 m (Table 1) and completed with a 1 m, 36 mm diameter screen wrapped in a geotextile filter membrane section at the bottom of the piezometer. This enabled low turbidity samples to be obtained from $D_{new}4$ and $D_{new}5$, but the water column in $D_{new}3$ was too small to sample.

All piezometer groundwater samples, beneath both dune slack and high dune, were pumped using a portable peristaltic pump and where feasible pH, Eh, and dissolved oxygen were determined by electrodes in a flow-through cell. SEC and temperature (determined by thermistor thermometer) were also measured. Sampling commenced when purging was completed as indicated by stable field measurements, which sometimes involved emptying the piezometer and allowing it to refill before sampling. Alkalinity as HCO_3 was measured on site with a digital titrator. The bedrock borehole was artesian during sampling and was sampled using the same methods as the piezometers.

The groundwaters from $D_{new}4$ and $D_{new}5$ along with shallow slack dipwells 1, 2 and 3, PR2 and the underlying Pilton Mudstone formation were sampled for major and minor ion chemistry, stable isotopes and sulphur hexafluoride (SF_6).

Samples of groundwater were collected in pairs of HDPE bottles, one of which was acidified to 1% with nitric acid, before refrigeration and transfer to the laboratory. Unfiltered groundwater samples were collected for $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$ analysis. Samples for SF_6 (sulphur hexafluoride) measurement were collected by the displacement method into glass bottles contained within metal cans to minimise atmospheric contamination (Oster 1994).

Grain size analysis was carried out on a Mastersizer 2000, which uses laser diffraction to measure particle sizes. Selected grain samples were analysed by SEM. Determination of major and minor ions was carried out using ICP-MS for cations and ion chromatography for anions. Ionic balances were found to be within ±10%, a relatively wide error band but most likely due to the dilutions necessary for the analysis of these low-volume samples. Stable isotopes were measured by isotope ratio mass spectrometry following offline preparation by CO_2 equilibration ($\delta^{18}O$), zinc reduction ($\delta^{2}H$) and acidification with H_3PO_4 ($\delta^{13}C$-TIC), with precisions of ±0.1‰, ±1‰ and ±0.2‰ respectively. SF_6 analysis was performed by GC-ECD following cryogenic pre-concentration, with a detection limit of 0.1 pmol/L.

4. RESULTS

4.1 Grain size and mineralogy

The grain size analysis profiles for D3 and D4 are consistent with a well-sorted average D_{10} and D_{90} of 120 µm and 280 µm respectively, i.e. 'very fine to medium sand'. No anomalous silt or clay layers were penetrated. The full range of grain sizes within the profiles D_{10} and D_{90} are from 97–320 µm (Fig. 3).

SEM analysis of selected grain samples (2.2 to 2.4 m in D2, 2.4 to 2.6 m in D3 and D4) are consistently dominated by calcite derived from shell debris. The samples comprise Ca and Mg-rich shell fragments and fossils, quartz grains coated with illite, smectite, chlorite and thin iron coatings, with potassium and plagioclase feldspars and some faecal pellets.

4.2 Unsaturated zone moisture content

The gravimetric porewater profile in the unsaturated zones in the high dune (Fig. 4) shows that dipwell D2 has a moisture content in the range 3–9% while D3 has 5–12%. The unsaturated zone porewater profile for D4 is 5–11% to within ~0.5 m above the standing water level, below which moisture content rises to between 21–24 % through the capillary fringe.

4.3 Unsaturated zone hydrochemistry and isotopes

The major ion chemistry of the dune porewaters (Table 2) is variable, with total dissolved solids (TDS) within the range 245–635 mg/l. The chemistry of the porewaters is dominated by Ca and HCO_3 from the dissolution of shell debris, and is supplemented by variable proportions of Na and Mg (cations) and Cl and SO_4 (anions) from marine aerosol sources.

Most stable isotope results for the unsaturated sands are restricted to δ^2H because the small amount of sample usually available was only sufficient for the direct reduction technique (based on that of Turner and Gailitis, 1988). These results are shown in Fig. 5. However, in some cases both δ^2H and $\delta^{18}O$ could be measured on centrifuged water using standard

preparation methods. Values of δ^2H obtained in this way are included in Fig. 5, showing that the results are generally comparable within measurement error to the direct reduction data.

4.4 Saturated zone hydrochemistry, stable isotopes and sulphur hexafluoride

The analytical results for the groundwater samples collected from below the dune slacks and high dunes are supplemented by a sample from the bedrock (Pilton Mudstone Formation) which is hydraulically isolated from the dune aquifer by estuarine clay. The major ion chemistry for all groundwater samples shows anions are dominated by HCO_3 (Table 3). The cations are dominated by Ca below the slacks 1, 2 and PR2, with increasing Na dominance below high dune samples $D_{new}4$ and $D_{new}5$, dune slack 3 and the bedrock borehole.

O, H and C stable isotopes were measured on samples from the saturated zone in the high dune $D_{new}4$ and $D_{new}5$ dipwells, dune slack PR2 and bedrock (Table 3).

SF_6 values (Table 4) are corrected for excess air (Darling et al. 2012) on the assumption that this is present at 1.5 ccSTP/l, based on sand-column experiments of Holocher et al. (2002). An excess air correction of 2.5 ccSTP/l is used for the sample from the Pilton Mudstone Formation because of some uncertainty about the recharge mechanism. The SF_6 residence times assume a mean annual air temperature of 10°C.

5 DISCUSSION

5.1 The recharge process

5.1.2 Unsaturated zone

Unsaturated zone Cl (Fig. 6) and δ^2H profiles (Fig. 5) appear to reflect the rate of infiltration into the high dunes. A high Cl pulse normally occurs at the beginning of each autumn rainfall period flushing dry deposition consisting mainly of Cl, Na and SO_4 from the summer period into the newly infiltrating rain-fed recharge (Malcolm & Soulsby 2001). While Na and SO_4 are affected by sorption and other exchange processes Cl is more conservative and tends to remain in the profile as a peak. However, the conventional pattern of dry summers and wet

winters is not consistent with recent notably wet summers in 2007 and 2008, and a particularly wet July in 2009, all of which are likely to have perturbed the normal sequence to some extent.

While there may be some ambiguity in the interpretation of the observed Cl peaks as infiltration rate indicators, stable isotopes can also be used in this role. Colder winter rainfall tends to have a more negative δ^2H composition than generally warmer summer rainfall. The record from the nearest rainfall isotope monitoring station at Wallingford demonstrates this (Fig. 5), with particularly negative compositions during the winters of 2008/09 and 2009/10. Although Wallingford is approximately 150 km to the east (Fig. 1) and its rainfall has undergone some relative depletion by the 'continental effect' (Darling and Talbot 2003), it is likely to be broadly similar to the magnitude of the cyclicity at Braunton Burrows. Significant variations in the δ^2H profiles due simply to near-surface evaporative fractionation appear to be ruled out by the centrifuged porewater samples, whose δ^2H and $\delta^{18}O$ values plot on a slope of ~6 (Fig. 7) rather than the 2–3 typical of soil moisture evaporation (Barnes and Allison, 1988).

Based on their apparent cyclicity, both the δ^2H and Cl profiles from D2 and D4 suggest a moisture infiltration rate of 0.75 to 1 m/yr (Figs 5 and 6). Diffusion tends to blur the annual cycles at greater depth. The cyclicity in the upper parts of the profiles clearly confirms that a key transport mechanism in the unsaturated zone is piston flow (as new water arrives at the top of the column, old water is displaced at the bottom and the whole column moves uniformly downwards). The infiltration rate indicated by the Cl and δ^2H profiles in dipwells D2 and D4 suggests that it would take 6–7.5 yr and 5–6 yr for infiltration to reach the water table at D4 and D5 respectively.

However, the moisture infiltration rate of 0.75 to 1 m/yr suggested by the δ^2H and Cl profiles from D2 and D4 should also be considered in the context of the moisture content data (Fig. 4) and local meteorological data. The median moisture contents of D2 and D4 are ~6% and 8% by weight respectively, implying volumetric water contents of ~10% and 13% based on a dry bulk density for dune sand of ~1600 kg/m^3 (Ritsema and Dekker, 1994). These volume percentages translate to water contents of 100–130 mm for an infiltration rate of 1 m/yr. Rainfall at Chivenor (5 km E of the dunes) over the five years preceding the month of sampling averaged 925 mm/yr (based on data from

http://www.metoffice.gov.uk/climate/uk/stationdata/chivenordata.txt). Actual evapotranspiration data from the local MORECS (Meteorological Office Rainfall and Evapotranspiration Calculation System) Square 165 for the same period gives an average effective rainfall of 45%, implying an effective rainfall of ~400 mm/yr on the dunes, nearly all of which should theoretically infiltrate owing to the very limited potential for runoff. The calculated profile water contents would then amount to some 25–33% of the effective rainfall/recharge. While there is some uncertainty over the true value of actual evapotranspiration for the dunes, it is unlikely to be significantly different from the MORECS average. The disparity may be explained by preferential flow, which can include macropore flow but also (and probably more significant for sand) 'unstable wetting': for example a homogeneous dune sand lysimeter experiment by Hendrickx and Dekker (1994) found that at a depth of ~0.5 m, the sand volume was only patchily wetted after 4 months of rainfall totalling 400 mm. The existence of such 'fingering' in natural dune sands seems likely but it would take many more than the three profiles reported here to characterise satisfactorily.

The existence of preferential flow implied by the meteorological data would mean that much of the infiltration to the water table was moving rather faster than the maximum rate of 1 m/yr implied by the profile fluctuations in Figs 5 and 6. This could still be occurring via piston flow; the rather wetter profile D4 indicates a somewhat faster infiltration rate than the drier D2 (Figure 5), so it may be that the rate rises proportionally with moisture content in wetter fingers of sand.

5.1.3 Groundwater

Groundwater recharged during the past four decades can in principle be dated on the basis of its SF_6 concentration given certain assumptions about likely recharge conditions, principally mean annual air temperature but also the amount of excess air (EA) incorporated during recharge (4.4 above). The residence times in Table 4 have been calculated on a 'piston flow' model of groundwater flow (Darling et al., 2012), though in reality most pumped groundwater is a mixture of waters from all the flow lines reaching the discharge point, so the ages given in Table 4 should be regarded as mean residence times (MRTs).

The results show that groundwater below the sampled high dunes had MRTs of ~13 and ~16 yr, and below the dune slacks of ~6 yr. The greater thickness of the unsaturated zone

beneath the high dunes seems one obvious reason. There is, however, some uncertainty about the lag on the SF_6 'clock' during transit through the unsaturated zone (Darling et al. 2012), therefore, some mixing with older stored waters could also be contributing. Simple binary groundwater age mixing can often be detected by plotting SF_6 versus CFC (chlorofluorocarbon) concentrations. However, owing to the reducing conditions in most of the groundwaters, CFC analyses were not undertaken because of probable degradation effects (Sebol et al. 2007).

The MRTs in the dune system can be compared to that of the Pilton Mudstone aquifer as sampled at the Saunton Sands Golf Club (Bedrock BH, Fig. 1), which gives an MRT of ~22 yr. As a locally confined aquifer this would be expected to contain older water than the overlying dune system. While the calculated age is not much greater than those of the dunes water, little is known of the turnover of the Pilton Mudstone aquifer or its excess air content (see 4.4 above), which if higher than estimated would result in an older age.

5.2 Evolution of water quality

5.2.1 Unsaturated zone

The chemistry of the unsaturated zone porewaters (Table 2) derives from a variety of inputs. Much of the Na, Cl and SO_4 must be derived from deposition of marine aerosols, but superimposed on this are contributions from the mineralogy of the sand including calcareous shell debris and fossiliferous calcite, quartz coated with illite, smectite, chlorite and Fe compounds as well as potassic and plagioclase feldspars. Variable dissolution of these minerals accounts for most of the fluctuations in the minor element hydrochemistry of the dune porewaters. The lack of any rise in SO_4 with depth confirms the rather limited mineralogical evidence (see 4.1 above) for the absence of pyrite in the dune sands, which would tend to oxidise to sulphate.

The carbonate system is more consistent. The Mg/Ca molar ratios found in the porewaters of piezometers D2, D3 and D4 increase with depth (Fig. 8) reflecting increasing Mg dissolution. The near-constant Sr/Ca ratios (Fig. 9) suggest that incongruent dissolution of calcite is not the cause and that the increased Mg is coming from another source, probably the Mg-rich shell debris.

5.2.2 Groundwater

The groundwaters in the shallow sand aquifer continue to show the influence of mineralogy and marine aerosols. The carbonate system again dominates the chemistry seen in the groundwaters, most markedly at the slacks BB1, BB2 and PR2. These groundwaters are more carbonate-dominated than the porewaters. Increasing influence of marine aerosols as Na and Cl is seen below the high dunes and slack BB3 putting them closer within the main group of porewaters (table 2). Dune slack BB3 is seen to behave slightly differently to the others slacks; its higher marine aerosol signal may be due to its proximity to the sea.

The Mg/Ca molar ratios for the D4 and D5 groundwaters (Fig. 8) highlight their consistency with the porewaters as they plot as a continuation of the porewater series. Mg is seen to increase with depth as with the porewaters. The Sr/Ca ratios of the groundwaters (Fig. 9) are, however, lower than those of the porewaters with an increase in Sr possibly consistent with the occurrence of incongruent dissolution of calcite.

The high Fe and Mn present in the groundwaters beneath the slacks (PR2, BB1 and BB2) and high dunes are a consequence of the reducing conditions illustrated by the dissolved oxygen and Eh values. Both Fe and Mn are found as dissolved ions due to the reduction of iron oxide and manganese oxide mineral coatings and minerals found within the sand grains. This is in contrast to the low Fe and Mn concentrations found in the porewaters. The exception to this is the dune slack groundwater BB3 with Fe and Mn concentrations comparable to the dune porewaters. Although the dissolved oxygen is again low in this sample, the redox is elevated, this together with the low Fe and Mn points to a more oxygenated sample as with the porewaters. It is likely that a greater amount of recharge occurs through the flooded slacks than beneath the dunes (D Clarke, personal communication), and this may be a more recent recharge signal (BB3 gives the youngest MRT). The proximity of BB3 to the sea may account for the raised SEC and increased marine aerosol signal.

Groundwater samples from the dipwells D4 and D5 and dune slack piezometer PR2 gave $\delta^{13}C_{TIC}$ values of –9.5, –9.3 and –8.9 ‰ respectively. The similarity of the values suggests rather consistent carbonate system conditions in the dune groundwaters. The total inorganic carbon (TIC) in the groundwaters beneath the dunes is likely to arise from reaction between shelly fragments in the sand and the CO_2 generated by soil bacterial respiration. Reaction

between soil CO_2 (~–26‰) and marine-derived calcite (~0‰) initially results in a $\delta^{13}C_{TIC}$ value of ~–13‰. Subsequent dissolution-reprecipitation processes will tend to drive the value towards the calcite composition, making it less negative as observed in the dune sand groundwaters. However, this can only occur under closed-system conditions, i.e. no further supply of soil CO_2. This is consistent with the commencement of the SF_6 "clock" well above the water table lying at the base of the unsaturated zone (5.1.2 above). The evolution of the $\delta^{13}C_{TIC}$ from initial equilibrium of ~–13‰ requires a certain amount of time, so the MRTs indicated by SF_6 (13 and 16 yr respectively) are consistent with this interpretation. Methanogenesis, an alternative explanation for the shift in $\delta^{13}C_{TIC}$ via co-produced isotopically heavy CO_2 (Stuyfzand 1993) can be ruled out on the basis of detectable NO_3 and absence of evidence for SO_4 reduction (Table 3), backed up by measurements of dissolved CH_4 in two slack groundwaters (PR2 and Orchid) which were both extremely low at <1 µg/L.

By comparison, the Pilton Mudstone formation gave $\delta^{13}C_{TIC}$ values of –13.6 ‰ which would be consistent with relatively young groundwaters in a locally confined aquifer.

Nitrate concentrations in the unsaturated zone and the groundwaters are generally low, the only exception to this being the top (0–200 mm) section of D2 and D3 which have 33 and 120 mgl^{-1} NO_3 respectively. (The top 50 mm of D4 was unavailable for sampling which may explain the lack of a high NO_3 concentration being found in this profile.) The elevated NO_3 at the top of the soil zone may be a consequence of atmospheric deposition along with plant and animal inputs as all material was used to provide porewater. Nitrate concentrations within the underlying bedrock aquifer (Pilton Mudstone Formation) are also low.

6 CONCLUSIONS

This study of a coastal dune system in SW England has used a range of environmental tracers to address the four key questions posed in the Introduction.

First, while this study has found evidence for the existence of piston flow through the unsaturated zone, the imbalance between indicated and likely recharge rates points to the existence of some preferential flow, probably mainly due to unstable wetting rather than macropore flow, which would seem less likely to be significant in a dunes context. It may be

436 the case that even in locally wetter zones, piston flow still predominates, but at a faster rate.
437 To get a better indication of this, a higher density of unsaturated zone profiling would be
438 required.
439
440 Second, water quality in the unsaturated zone of the dunes aquifer is predominantly the result
441 of the deposition of marine aerosols and the dissolution of shell fragments. There appears to
442 be relatively little reaction with the sand matrix. Saturated zone water quality largely matches
443 porewater compositions at the base of the unsaturated zone, implying that if faster infiltration
444 routes exist, the chemistry of these waters has already evolved a similar chemistry.
445
446 Third, it appears that the main hydrochemical evolution of unsaturated zone porewater occurs
447 very rapidly, in months rather than years. This is because comparatively rapid processes like
448 the mobilization of surface salt crusts and the dissolution of shell calcite tend to dominate the
449 water quality. However, minor changes like the slow build-up of Mg take longer because of
450 the reaction kinetics. The main change in the underlying groundwater is that the low-O_2
451 conditions appear to be slowly reducing the concentrations of ions like SO_4 and NO_3 and
452 increasing the concentrations of Fe and Mn, while also favouring the mineralisation of
453 carbon. Incongruent mobilisation of Mg continues. Measured mean residence times of up to
454 16 yr indicate that dissolved O_2 is relatively persistent with time, suggesting that the bacterial
455 mediation of reducing reactions is not highly developed.
456
457 Fourth, while this study did not include a water quality monitoring element, certain
458 conclusions can be drawn about the effects of secular changes in conditions, whether climatic
459 or morphological. Gradual changes in mean rainfall and temperature are unlikely to affect
460 water quality significantly, but changes in the supply of marine salts (e.g. via much stormier
461 conditions) or the supply of shell fragments (e.g. because of dune migration) could have a
462 rather greater impact on water quality.
463
464 The results of this study are applicable to other unmodified dune spit systems and hence their
465 future environmental management.
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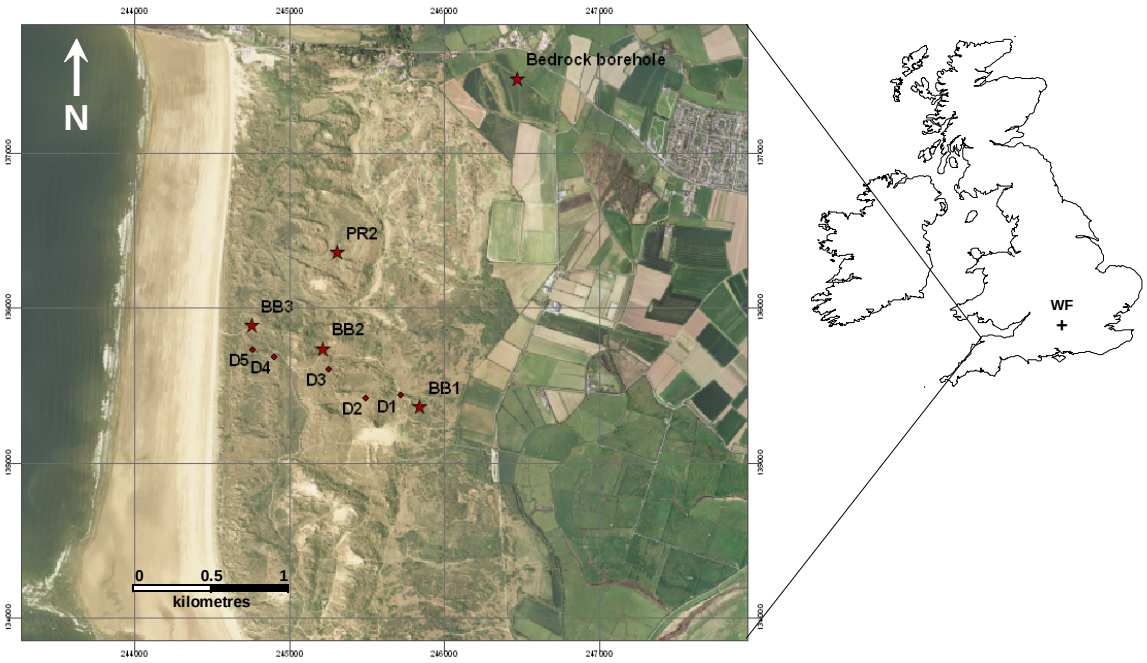

Figure 1. Map of Braunton Burrows, SW England, with key sites marked. Location of Wallingford (WF) shown on inset map. Based upon aerial photography from © NextPerspectives.

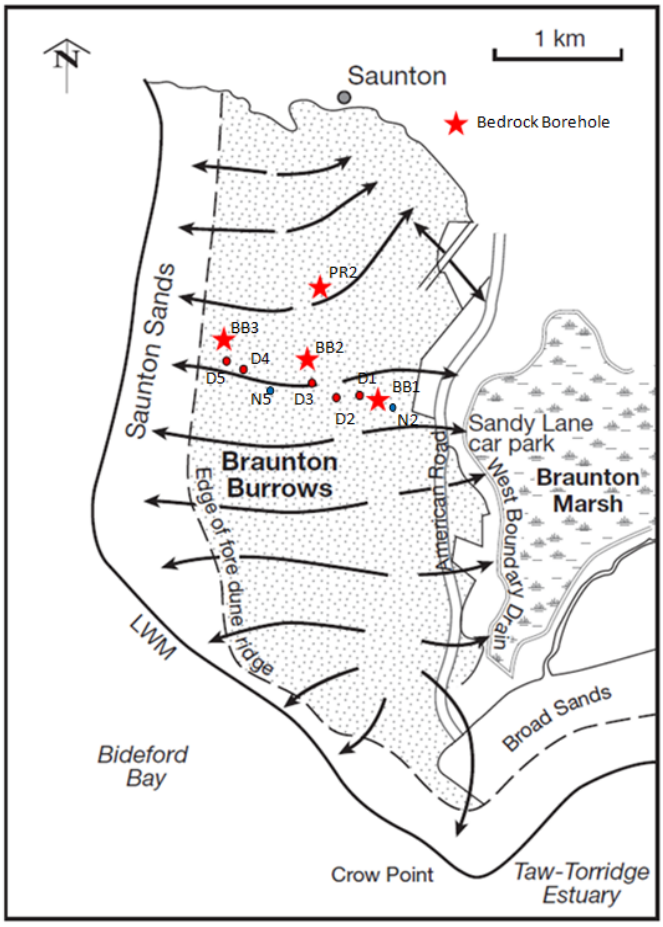

Figure 2. Conceptual groundwater flow at Braunton Burrows from Stratford et al (2013).

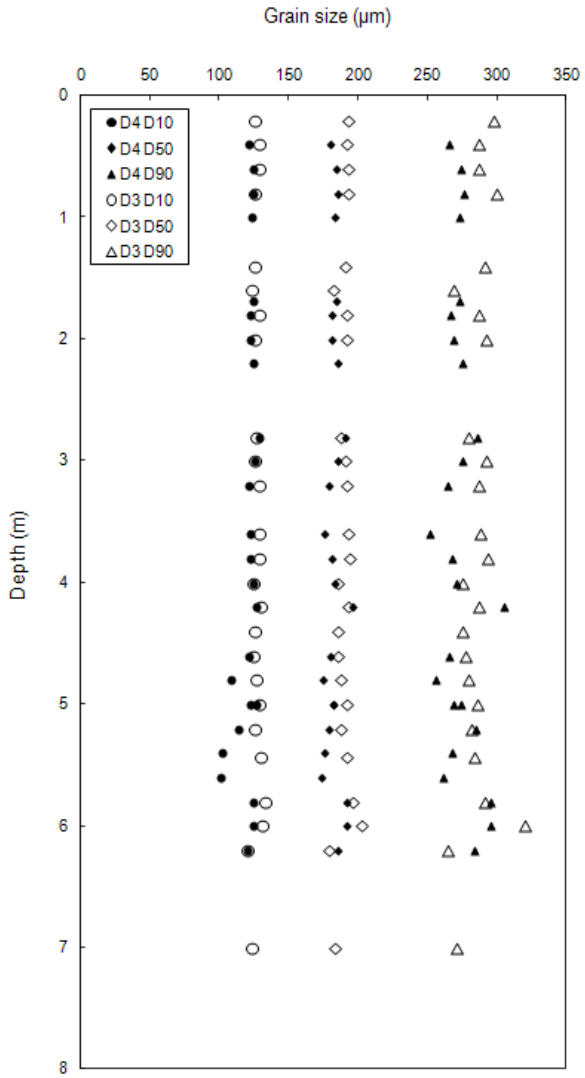

Figure 3. Results of grain size analysis for D4 showing D_{10}, D_{50}, and D_{90}.

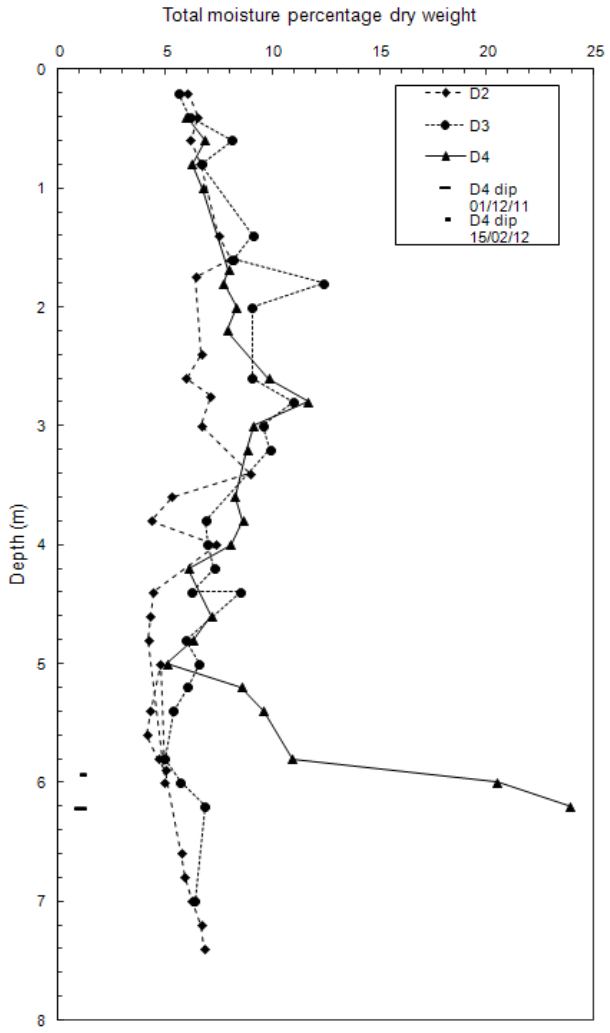

Figure 4. Moisture content depth profiles for piezometers D2, D3 and D4 showing water table in D4 in December 2011 and February 2012.

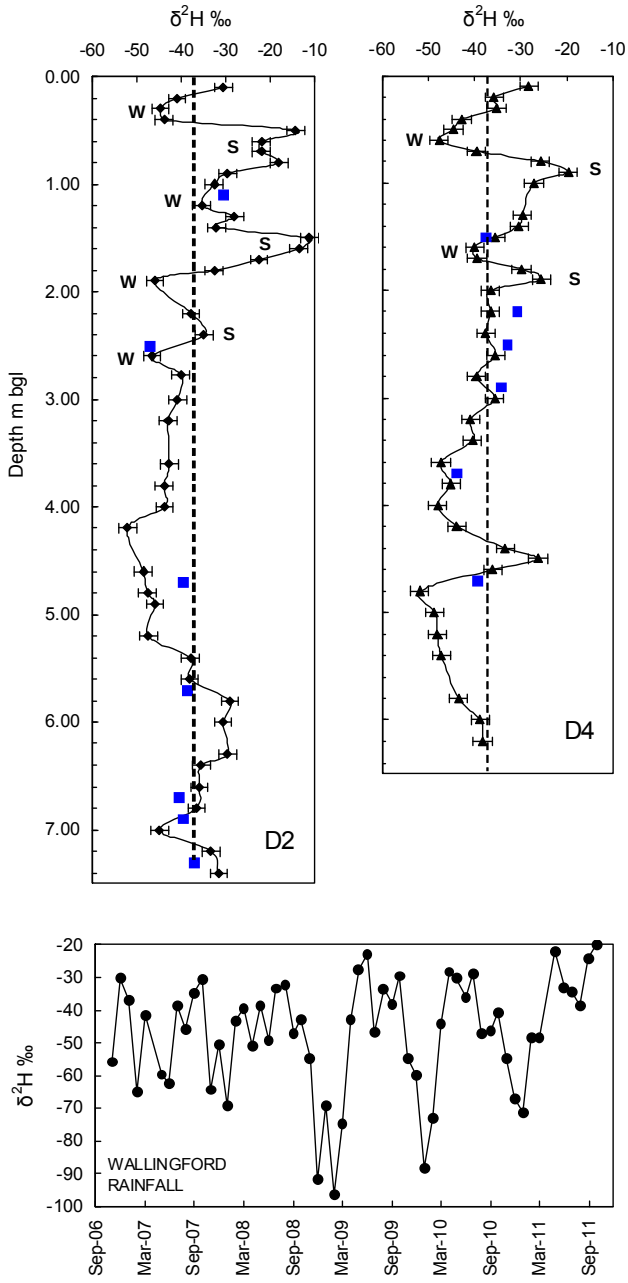

Figure 5. Profiles of δ^2H in sand moisture from piezometers D2 and D4, autumn 2011. Square datapoints represent analyses of water extracted by centrifuge, showing generally good agreement with the directly reduced sand moisture. Also shown is the rainfall isotope record from Wallingford (nearest rainfall isotope collection station) for the previous five years. The dashed vertical line shows the approximate δ^2H composition of the underlying groundwater. Probable summer (S) and winter (W) peaks and troughs are identified on the profiles.

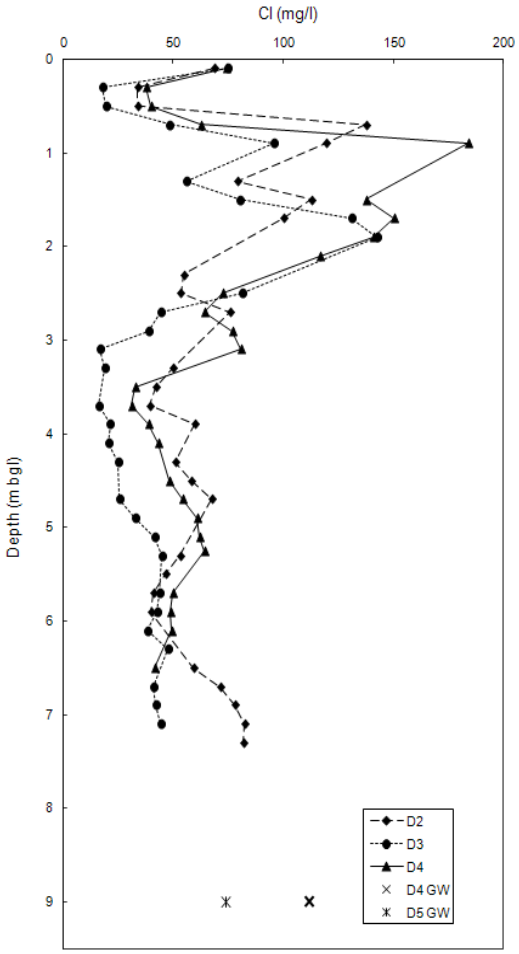

Figure 6. Concentration of chloride (mg/l) in the unsaturated zone below the high dunes. Data from centrifuged porewaters.

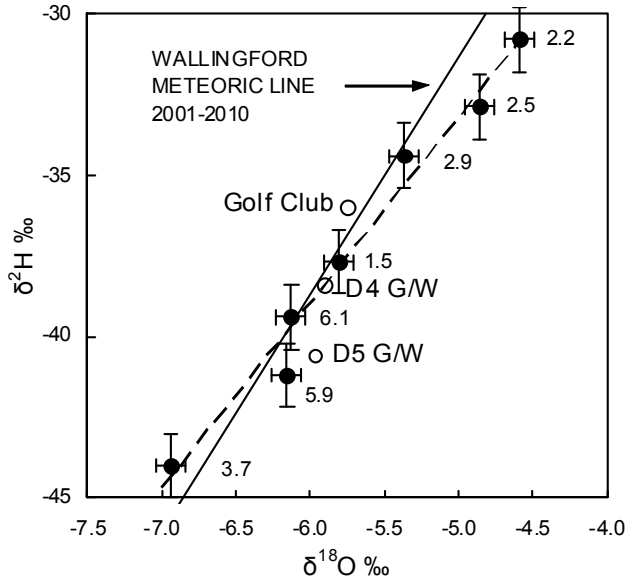

Figure 7. Isotopic co-plot showing the composition of centrifuged waters from the D4 profile compared to the meteoric line at Wallingford (WML), the nearest available GNIP network station (data from http://www.univie.ac.at/cartography/project/wiser/index.php). Sample depths are given in m bgl. Pumped groundwaters from piezometers D4 and D5 and the Golf Club (bedrock aquifer borehole are also included. The lack of significant deviation from the WML suggests that evaporation has little effect on the infiltrating water.

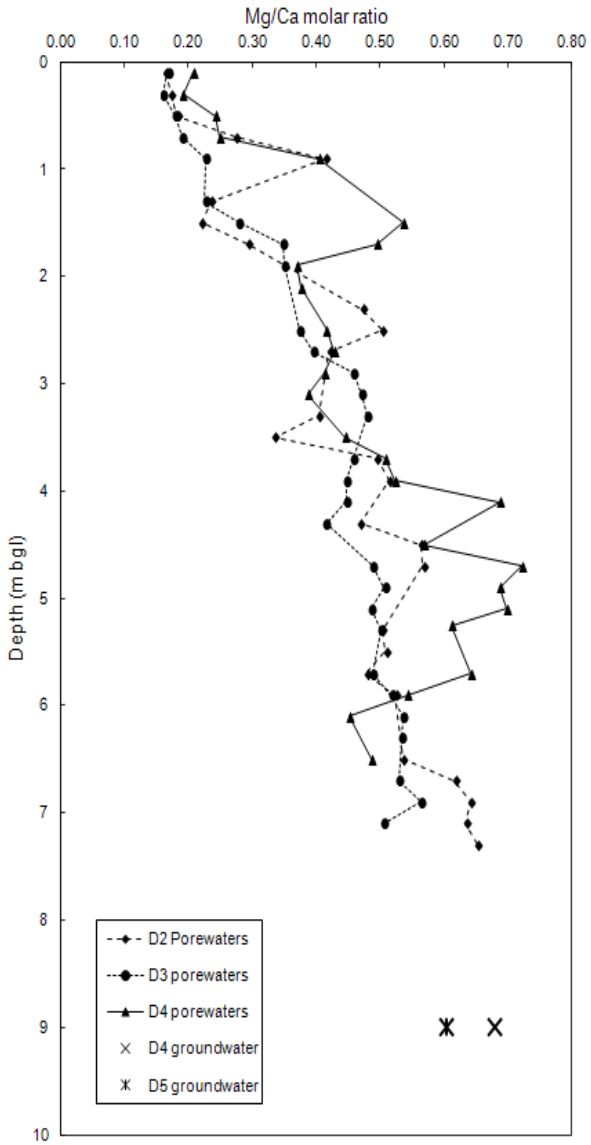

Figure 8. Mg/Ca molar ratios for the porewaters and groundwaters of the high dunes. Groundwaters were sampled from approximately 9 m bgl.

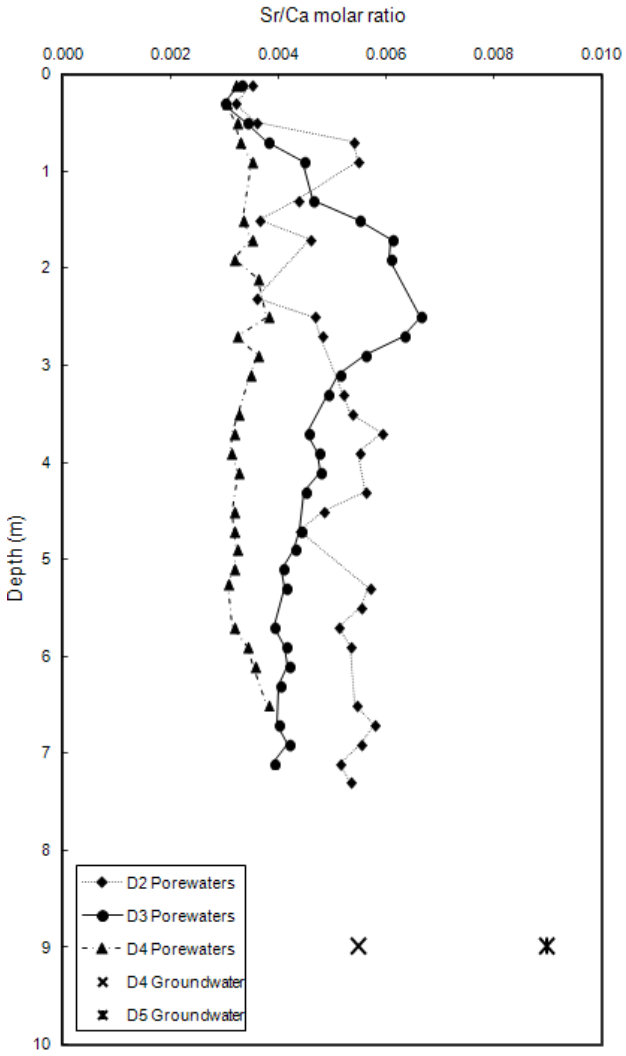

Figure 9. Porewater Sr/Ca molar ratio with depth.

Table 1. Construction details of sampled dune slack and high dune piezometers at Braunton Burrows, with water levels in m bgl (below ground level) at the time of sampling.

Dipwell	Surface elev. (m)	Drilled Depth (m)	Water level (mbgl)	Vegetation	Notes
BB1	9.75	1.97	top of casing	SD14 wet calcareous slack type	Dune slack
BB2	9.76	1.97	0.51	SD16 dry calcareous type	Dune slack
BB3	6.93	1.97	0.35	SD16 + SD14 slack–dry transitional	Dune slack
PR2	9.42	2.52	0.79	SD16 dry calcareous type	Dune slack
D1	16.14	6.00	Dry	Fixed dune vegetation	
D2	25.20	8.62	Dry	Fixed dune vegetation	
D3	17.03	8.62		Fixed dune vegetation	
Dnew3	17.03	9.20	8.38	Fixed dune vegetation	
D4	13.09	8.62		Fixed dune vegetation	Casing removed
Dnew4	13.09	9.20	5.93	Fixed dune vegetation	
D5	11.30	8.80		Fixed dune vegetation	Sediments risen to 5.93 mbgl by 17-Oct-12
Dnew5	11.30	9.20	5.1	Fixed dune vegetation	

Table 2. Major, selected minor and trace element analyses of dune porewaters from dipwells D2, D3 and D4.

Depth	SEC	Ca	Mg	Na	K	HCO_3	Cl	SO_4	NO_3-N	NO_2-N	Si	Fe_{tot}	Mn	Sr	PO_4-P
mbgl	µS cm^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}
Dipwell D2															
0.1	605	79.8	7.99	33.9	11.8	171	68.4	74.7	8.90	0.088	1.93	33	13.7	612	180
0.3	478	45.5	4.78	52.0	3.09	182	33.9	19.7	4.46	0.045	2.07	9	2.7	318	<30
0.5	432	46.2	5.11	36.6	2.65	178	33.5	18.0	1.33	0.033	2.00	13	0.6	363	34
0.7	648	70.7	11.8	37.3	1.58	122	138	18.9	1.38	<0.006	3.00	4	3.8	834	<50
0.9	635	61.5	15.5	41.7	1.70	153	119	24.1	0.964	<0.006	3.15	<2	22	736	<50
1.3	522	56.6	8.11	29.9	1.31	133	78.9	13.4	0.773	<0.003	2.31	<2	4.8	539	<30
1.5	570	68.6	9.17	25.2	1.47	101	113	13.6	0.900	<0.006	2.32	3	3.1	545	<50
1.7	562	57.6	10.3	36.1	1.33	124	99.7	12.5	0.756	<0.003	2.00	<6	1.50	578	42
2.3	529	52.7	15.1	58.8	2.90	166	54.5	29.2	2.12	0.035	2.12	<2	4.2	414	45
2.5	491	37.7	11.5	49.0	1.69	155	53.4	21.4	0.959	0.029	3.24	<2	6.0	385	47
2.7	548	49.1	12.5	48.5	1.60	165	75.5	18.7	0.694	0.031	3.20	<2	14.9	514	<30
3.3	489	44.7	11.0	47.7	1.83	168	50.0	22.7	1.20	0.022	3.11	7	3.7	508	42
3.5	423	43.4	8.81	34.8	1.38	150	42.0	18.3	1.31	0.026	2.92	<2	6.6	507	42
3.7	463	37.4	11.2	44.5	1.73	158	39.4	26.9	2.07	0.029	3.12	2	5.6	483	46
3.9	505	38.8	12.1	48.9	2.20	161	59.5	27.6	1.19	0.033	3.00	<4	5.6	465	<30
4.3	512	40.9	11.6	51.7	2.14	174	50.7	27.0	1.69	0.037	4.00	<4	1.50	501	77
4.5	535	39.9	13.7	56.4	2.31	164	58.3	28.8	1.72	<0.003	4.00	<4	0.9	422	47
4.7	559	47.7	16.4	68.5	2.86	162	67.3	32.9	1.94	0.027	2.00	<4	1.6	459	55
5.3	497	43.3	13.2	44.8	2.17	162	53.0	23.3	1.64	0.031	3.46	<2	1.4	537	81
5.5	475	38.6	11.9	44.0	2.13	151	46.4	25.7	1.77	0.025	3.00	<4	2.4	467	58
5.7	470	53.1	15.4	51.3	2.51	182	40.8	23.2	1.59	0.025	4.00	<4	2.0	594	<30
5.9	428	36.8	11.7	37.4	1.86	147	40.0	23.7	1.21	0.029	3.26	<2	1.2	430	77
6.5	574	46.4	15.1	52.1	3.11	188	59.2	32.8	1.94	0.039	3.93	<2	1.2	551	65
6.7	538	38.7	14.5	51.4	2.68	150	71.5	27.8	1.52	<0.003	3.50	9	0.9	489	55
6.9	578	42.9	16.7	52.2	2.77	166	77.9	29.6	1.60	0.028	3.50	<2	0.9	519	49
7.1	598	44.1	17.0	53.2	2.42	156	82.5	32.1	2.11	0.027	3.21	4	1.3	495	68
7.3	600	45.2	17.9	53.9	3.01	167	81.8	32.1	1.47	0.024	3.62	<2	1.0	527	63
Mean	550	50.5	12.4	47.6	2.86	162	68.8	28.7	2.12	0.037	3.02	5	4.1	526	61
Min	423	36.8	4.78	25.2	11.8	101	33.53	12.5	0.69	<0.003	1.09	<2	0.6	309	<30
Max	873	90.1	17.88	68.5	9.60	238	137.6	74.7	8.90	0.153	4.00	33	22	966	81

Table 2 (contd). Major, selected minor and trace element analyses of dune porewaters from dipwells D2, D3 and D4.

Depth	SEC	Ca	Mg	Na	K	HCO_3	Cl	SO_4	NO_3-N	NO_2-N	Si	Fe_{tot}	Mn	Sr	PO_4-P
mbgl	µS cm^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}
Dipwell D3															
0.1	820	109	11.1	48.1	11.0	204	74.4	30.4	32.7	0.078	4.80	34	14.3	780	<30
0.3	427	45.4	4.94	27.8	4.2	188	17.8	14.8	6.00	0.027	2.21	4	1.0	381	61
0.5	362	49.9	5.77	39.3	2.6	169	19.3	11.6	1.53	0.025	2.42	2	0.6	337	67
0.7	466	57.4	7.94	42.4	2.0	168	48.4	14.7	0.724	0.024	2.37	<2	0.6	413	59
0.9	571	84.8	10.2	51.7	16.1	149	95.4	14.0	0.370	0.105	4.25	3	1.6	560	44
1.3	469	50.4	6.92	40.6	1.6	166	56.0	10.2	0.509	0.023	2.14	22	1.0	511	50
1.5	539	57.2	9.72	34.1	1.3	165	80.3	12.0	0.503	0.023	2.84	<2	0.9	684	47
1.7	585	60.8	12.9	28.0	1.4	135	130.7	16.5	0.616	<0.006	2.57	<2	0.6	809	88
1.9	646	68.1	14.4	32.2	1.8	145	142.3	15.6	0.615	<0.006	2.97	3	1.1	903	94
2.5	550	60.3	13.7	29.7	1.5	169	81.0	13.4	0.519	0.023	2.89	<2	0.4	874	42
2.7	491	55.1	13.2	26.7	1.4	173	44.3	10.5	0.362	<0.003	2.88	<2	0.3	761	62
2.9	439	44.0	12.2	24.9	1.3	192	39.0	12.1	0.445	0.023	2.72	<2	0.2	539	56
3.1	341	33.2	9.51	22.2	1.1	167	16.7	12.0	0.816	0.023	2.40	<2	0.7	372	48
3.3	372	39.1	11.4	24.2	1.4	183	19.0	11.6	0.375	<0.003	2.80	<2	0.7	420	49
3.7	370	35.9	9.97	25.5	1.5	183	16.1	14.1	0.940	0.024	3.07	<2	0.7	357	67
3.9	381	37.7	10.2	29.2	1.5	174	21.4	14.4	1.10	0.030	2.87	2	1.1	390	53
4.1	386	37.5	10.2	29.9	1.7	182	20.6	14.2	1.10	0.032	3.15	4	0.9	392	51
4.3	392	37.5	9.46	32.5	1.4	164	25.1	17.3	1.39	0.029	2.91	3	0.9	368	75
4.7	407	38.6	11.5	29.0	1.7	190	25.3	14.8	1.11	0.026	2.85	<2	1.4	371	51
4.9	451	43.1	13.3	33.0	2.0	201	32.6	15.7	1.04	0.026	3.05	<2	1.2	405	52
5.1	452	40.6	12.0	38.2	2.1	172	41.7	19.6	1.36	0.035	2.94	<2	1.5	362	55
5.3	460	40.0	12.2	33.3	2.1	170	44.6	19.2	1.07	0.040	2.75	9	1.2	360	49
5.7	492	42.7	12.7	42.6	2.4	194	43.7	21.1	1.26	0.040	3.23	3	0.9	366	69
5.9	456	40.1	12.6	44.1	2.4	166	42.6	21.9	1.40	0.034	2.97	7	1.3	361	59
6.1	463	38.3	12.5	39.0	2.5	184	38.3	19.0	1.14	0.031	3.10	<2	0.7	351	61
6.3	477	39.4	12.8	40.4	2.3	173	47.8	21.1	0.851	0.030	2.84	<2	0.7	346	64
6.9	467	38.9	13.3	41.3	2.6	176	41.9	21.6	2.03	0.029	2.95	3	1.1	355	64
7.1	487	39.6	12.2	42.6	2.8	180	44.0	23.6	1.57	0.031	3.30	<2	0.6	338	58
Mean	496	49.5	11.19	35.9	2.86	179	50.9	19.5	2.61	0.032	2.94	4.38	1.44	497.1	57
Min	341.1	33.2	4.9	22.2	1.1	135	16.1	10.2	0.36	<0.003	1.2	<2	0.2	337	<30
Max	820	108.5	14.78	54.5	16.1	261	142	70.4	32.65	0.105	4.80	34	14.3	902.5	94

Table 2 (contd). Major, selected minor and trace element analyses of dune porewaters from dipwells D2, D3 and D4.

Depth	SEC	Ca	Mg	Na	K	HCO_3	Cl	SO_4	NO_3-N	NO_2-N	Si	Fe_{tot}	Mn	Sr	PO_4-P
mbgl	µS cm^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}
Dipwell D4															
0.1	739	93.5	11.75	41.1	7.6	277.3	73.9	27.2	3.22	<0.003	2.46	38	19.1	654	106
0.3	581	67.1	7.81	44.1	2.7	258.2	37.4	17.0	3.68	0.034	2.16	6	1.3	445	92
0.5	490	48.7	7.17	54.8	1.7	195.9	39.7	17.7	1.43	0.033	2.76	3	1.1	343	69
0.7	619	55.8	8.4	61.6	1.4	224.1	62.4	21.0	0.886	0.032	2.37	2	1.0	400	59
0.9	762	71.2	17.44	46.0	1.5	137.3	184.0	12.9	1.20	0.047	2.65	3	2.5	547	93
1.5	715	59.7	19.44	52.3	2.3	163.6	137.6	16.4	0.804	0.044	2.86	<2	1.2	435	83
1.7	687	61.2	18.36	47.6	2.6	161.3	150.1	14.5	0.914	0.044	2.51	2	1.0	470	69
1.9	709	70.7	15.84	52.3	2.5	160.5	141.0	16.0	0.867	0.045	2.27	<2	1.4	489	87
2.1	639	65.6	15.01	34.2	2.3	147.9	116.4	15.4	0.579	0.044	3.08	<2	0.7	519	73
2.5	531	55	13.89	26.3	2.0	170.9	72.2	13.4	0.563	0.042	2.55	<2	0.3	457	66
2.7	483	47.3	12.27	33.6	2.2	162	64.0	15.3	0.831	0.044	2.79	3	0.9	335	93
2.9	531	53.9	13.52	36.8	2.3	170.5	76.6	13.4	0.654	0.043	2.27	3	0.4	427	82
3.1	524	54.8	12.87	30.2	1.8	148.7	80.4	14.7	0.621	0.043	3.45	<2	0.3	417	62
3.5	434	45.6	12.32	27.0	2.0	199.2	32.5	14.6	0.519	0.043	2.61	<2	0.5	324	69
3.7	412	41.7	12.85	26.7	2.4	188.6	31.0	16.5	0.907	0.045	2.82	2	0.6	288	98
3.9	458	44.9	14.25	33.5	3.1	195.2	38.5	17.5	1.87	0.044	2.80	4	0.4	307	75
4.1	513	41.2	17.18	39.5	4.0	215.5	42.9	20.6	1.85	0.046	3.91	2	1.0	293	69
4.5	518	45.7	15.74	39.5	3.4	203.4	48.1	22.5	1.62	0.045	2.68	<2	0.6	316	76
4.7	544	41.8	18.31	44.0	4.1	196.4	54.0	24.0	2.25	<0.003	1.94	7	1.1	290	83
4.9	604	47.6	19.86	48.7	4.8	203.1	60.7	31.8	3.06	<0.003	2.76	4	1.4	335	80
5.1	579	47.2	20	43.4	4.0	177.4	62.1	31.0	5.32	<0.003	2.87	3	0.8	328	80
5.25	562	43.9	16.31	42.9	3.9	157.1	63.9	29.5	5.22	<0.003	4.38	3	1.3	293	88
5.7	493	41	15.97	37.1	3.3	176.9	50.0	20.2	2.30	<0.003	3.05	3	1.1	283	82
5.9	474	42.2	13.91	37.9	2.7	192.4	48.7	14.6	0.882	<0.003	3.02	<2	<0.2	317	59
6.1	518	46.6	12.76	44.7	2.7	210.2	49.4	11.9	0.245	<0.003	3.00	<2	<0.2	361	59
6.5	439	37.6	11.1	39.8	2.40	157.6	41.3	22.0	1.71	0.044	13.8	<4	<0.4	312	117
Mean	594	55.0	15.08	45.1	3.35	188.4	79.49	23.57	1.873	0.0315	2.77	4.35	2.1	408.2	80
Min	412	37.6	7.17	26.3	1.43	137.3	30.99	11.95	0.245	<0.006	1.94	<2	<2	282.9	<50
Max	936	93.5	24.41	82.5	10.5	277.3	218.8	88.4	5.321	0.0517	4.38	38	19.1	653.5	117

Table 3. Major, selected minor and trace element chemistry and stable isotope composition of groundwaters from the Braunton dune system.

Site ID	Date	Temp (^{o}C)	pH	Eh (mV)	DO mg l^{-1}	SEC µS cm^{-1}	Ca mg l^{-1}	Mg mg l^{-1}	Na mg l^{-1}	K mg l^{-1}	HCO_3 mg l^{-1}	Cl mg l^{-1}	SO_4 mg l^{-1}	NO_3-N mg l^{-1}	NO_2-N mg l^{-1}	Si mg l^{-1}	Fe_{tot} µg l^{-1}	Mn µg l^{-1}	Sr µg l^{-1}	P µg l^{-1}	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰	$\delta^{13}C_{DIC}$ ‰
Dune slack																							
1	25-Feb-10	7.9	7.30	139	0.4	719	101.2	14.6	24.8	1.9	373	41.3	8.08	0.01	<0.006	5.23	928.2	972.6	1566	<30	nd	nd	nd
2	25-Feb-10	8.9	7.53	133	0.2	597	81.5	11.1	28.3	1.1	291	42.3	5.17	0.01	<0.006	3.29	613.2	244.8	725	<30	nd	nd	nd
3	25-Feb-10	8.3	7.67	248	0.2	835	68.3	22.0	68.0	3.8	307	94.5	20.47	<.01	<0.006	2.51	11.3	4.2	959	<30	nd	nd	nd
PR2	15-Nov-12	12.2	7.57	148	0.5	599	58.6	22.5	77.8	3.9	306	120.5	38.58	2.43	<0.006	3.94	106.4	163.0	nd	<30	-5.40	-34.9	-8.9
High dune																							
D4	15-Feb-12	10.4	7.93	-190	1.1	804	65.1	26.8	54.2	4.0	285	111.3	21.16	0.95	<0.003	3.66	231	470	779	<10	-5.90	-38.4	-9.5
D5	15-Feb-12	12.1	7.98	-318	0.5	687	62.6	23.0	43.7	2.8	330	73.2	15.99	0.01	<0.003	3.75	303	566	1230	<10	-5.97	-40.6	-9.3
Pilton Mudstone formation																							
Golf Club	14-Nov-12	12.0	7.20	231	0.9	877	72.4	16.7	28.4	1.5	254	43.02	7.15	0.02	<0.003	4.35	94.4	136.6	nd	<10	-5.82	-35.9	-13.6

Table 4. SF_6 concentrations as measured and also corrected for excess air inputs (see text), with calculated mean residence times (MRTs) for groundwater below dune slacks and high dunes.

Dipwell	Site type	Date	SF_6 (fmol/L)	SF_6 corr. (fmol/L)	MRT (yr)
D1	Dune slack	25-Feb-10	2.65	2.29	6 ± 2
D2	Dune slack	25-Feb-10	2.49	2.15	7 ± 2
D3	Dune slack	25-Feb-10	2.73	2.36	6 ± 2
Dnew4	High dune	15-Feb-12	1.76	1.52	16 ± 2
Dnew5	High dune	15-Feb-12	2.06	1.78	13 ± 2
Golf Club	Bedrock	14-Nov-12	1.31	1.04	22 ± 2.5