Naturally-high nitrate in unsaturated zone sand dunes above the Stampriet Basin, Namibia

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ABSTRACT

Elevated groundwater nitrate levels are common in drylands, often in excess of WHO guidelines, with concern for human and animal health. In light of recent attempts to identify nitrate sources in the Kalahari this paper presents the first unsaturated zone (USZ) nitrate profiles and recharge rate estimates for the important transboundary Stampriet Basin, alongside the first rainfall chemistry records. Elevated subsurface nitrate reaches 100–250 and 250–525 mg/L NO3−–N, with NO3−–N/Cl of 4–12, indicating input above evapotranspiration. Chloride mass balance recharge rates range from 4 to 27 mm/y, indicating a vertical movement of these nitrate pulses toward the water table over multi-decadal timescales. These profiles are sampled from dune crests, away from high concentrations of animals and without termite mounds. Given low-density animal grazing is unlikely to contribute consistent spot-scale nitrate over decades, these profiles give an initial estimate of naturally-produced concentrations. This insight is important for the management of the Stampriet Basin and wider Kalahari groundwater. This study expands our knowledge about elevated nitrate in dryland USZs, demonstrating that it can occur as pulses, probably in response to transient vegetation cover and that it is not limited to long-residence time USZs with very limited downward moisture flux (recharge).

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1. Introduction

Nitrate pollution in the groundwater of arid and semi-arid areas remains an environmental issue of considerable concern, owing to the potential health hazards of nitrate to both human and animal populations (Canter, 1997; Carlson and Breeze, 1984; Colvin, 1999; Davidson et al., 1964; Sindelar and Milkowski, 2012). Elevated nitrate levels in groundwater seem to be a feature of the arid zone environment (e.g. Aranibar et al., 2003; Barnes et al., 1992; Edmunds and Gaye, 1997; Jackson et al., 2004; Stadler et al., 2012; Walvoord et al., 2003), with concentrations often exceeding the WHO (2003) guideline value of 50 mg/L as NO3− (11.3 mg as NO3−–N/L; all values will be given as NO3−–N). Elevated nitrate values in many dryland aquifers are widely attributed to anthropogenic nitrate pollution. For example, application of agricultural fertilisers is discussed in the Triffa Plain, Eastern Morocco (Fekkoul et al., 2013); Zeroud basin, central Tunisia (Salem et al., 2012); the central Arava Valley, Israel (Oren et al., 2004); the Trans-Pecos region of West Texas (Robertson and Sharp, 2013), although in this location it is thought there are also natural sources; NW Mexico (Lechuga-Devé et al., 2013) and the Ordos Plateau (Yin et al., 2013), lower Liaohe River Plain (Sun and Yang, 2012) and Zhangye Basin (Qin et al., 2011) in China. Other studies highlight the contribution of nitrate from high concentrations of livestock waste in animal enclosures, for example in the Monte Desert, Argentina (Aranibar et al., 2011), the Kalahari (Heaton et al., 1983) and southwestern Tunisia (Kraiem et al., 2013). In addition, urban source sources of nitrate pollution to aquifers are discussed, among others, in Morocco (Boughrous et al., 2007), the Zahedan Aquifer in Iran (Khazaei et al., 2006) and the Shijiahaung region, China (Tang et al., 2004).

The unsaturated zone (USZ) is the pathway for water and contaminants from the land surface to groundwater, and in arid, and semi-arid USZs there is variability in both nitrate concentrations and the extent to which it is accumulating or being flushed through to groundwater. A landmark study across five sites in the western...
United States demonstrated an accumulation of nitrate throughout the Holocene, which therefore must involve natural production (Walvoord et al., 2003), with subsurface peaks reaching ~3000 mg NO$_3$–N/L. It also highlighted that the global subsurface nitrogen reservoir had previously been underestimated, although with caution needed in extrapolating trends from that region (Jackson et al., 2004) and a recognition that nitrogen retention in dryland ecosystems varies as a function of vegetation history and precipitation patterns (Walvoord et al., 2004). High surface nitrate concentrations (140 mg NO$_3$–N/L), decreasing towards the water table, are also observed in the Tarim River basin, China, where moisture in the USZ is understood to move upwards (Huang et al., 2012). High concentrations of naturally accumulated sub-surface nitrate are also associated with desert pavements, which limit infiltration. For example in north-eastern Badia, Jordan (Al-Taani and Al-Qudah, 2013).

In contrast, USZ profiles spanning up to 1000 years, with recharge rates of <1 mm/y, from the Badain Jaran Desert, China, contain fluctuations in nitrate (and chloride) with depth, which are suggested to be climatically controlled, via the influence of fluctuations in soil moisture on plant numbers and types (Gates et al., 2008; Ma et al., 2012). On shorter timescales, there are also sites where USZ moisture contains elevated nitrate and the interstitial water is recharging groundwater. For example, USZ profiles from the North China Plain and Loess Plateau contain both zones of subsurface nitrate elevation and high concentrations that persist down to the water table, and these are considered to owe to the surface application of N-fertiliser since the 1950s (and some natural fixation by alfalfa) (Huang et al., 2012; Yuan et al., 2012). In Senegal, where recharge rates in profiles range from 0.5 to 34 mm/y (and profiles represent 50–400 years), there are single and multiple peaks of nitrate over 10–30 m depths, which may be attributable to recent anthropogenic land-use change or correspond to climate variations (Edmunds and Gaye, 1997). Over similar USZ depths in the same region, Deans et al. (2005) demonstrated in-situ production of nitrate related to N-fixation by trees and crops. In the Australian arid-zone Barnes et al. (1992) considered nitrate to be fixed biologically near the surface by bacteria, with the largest concentrations close to termite mounds, and that the nitrate is flushed through the USZ by episodic rainfall events.

In southern Africa a compilation of ~50,000 data points from groundwater boreholes has been used to produce a first appraisal of groundwater nitrate concentrations in southern Africa (Fig. 1a) (Tredoux et al., 2001, 2009). This map shows that elevated concentrations occur in widely scattered patches and can also be traced in some linear bands, particularly along the southern fringes of the Kalahari and a northwest-southeast oriented band through the Stampriet Basin region (Fig. 1a). Recently Stadler et al. (2012) discuss three key examples across a transect in the central Kalahari (Gobabis in western Namibia, Ghanzi in western Botswana and Serowe in eastern Botswana) to argue that different management approaches are needed for nitrate on a site-to-site basis owing to the different structure and processes operating within the aquifers involved at different sites. Their comparative study highlights: (i) that the source of nitrate pollution varies between sites, from cattle waste and septic tank pollution to natural production as part of the soil nitrogen cycle, to the presence of N-fixing plants, such as Acacia, or fauna (e.g. termites) symbiotic with nitrogen fixers, and (ii) that there might be a fast through-flow and slow through-flow model for nitrate input into groundwater through the USZ.

In this paper, USZ profiles from another region of the Kalahari, further south than Stadler et al.’s (2012) Gobabis site, are presented. These are taken above the Stampriet Basin, which is often referred to as the Stampriet Artesian Basin (SAB) whether or not the artesian layers are being considered. It is a vital transboundary water resource (Christelis and Struckmeier, 2001) (Fig. 1b), and contains three main hydrogeological units (JICA, 2002) (Fig. 1c). Groundwater in this area has been found to contain high nitrate levels in the confined Auob and Nossob members (Heaton et al., 1983), as well as in the uppermost, unconfined, Kalahari aquifer (Heaton, 1984). The profiles studied here reveal initial quantification of the range of naturally-produced nitrate conditions (termed baseline conditions) in the USZ at three sites where: (i) human waste is not an issue, (ii) fertilisers have not been added to the land surface and (iii) animal kraals and watering holes are not in close proximity (although a low density of sheep graze at the two southern sites). We are targeting an estimate of the baseline conditions (which is “the range of concentrations of a given element, isotope or chemical compound in solutions, derived entirely from natural, geological, biological or atmospheric sources, under conditions not perturbed by anthropogenic activity” (Edmunds and Shand, 2008)), noting Tredoux et al.’s (2009) emphasis that “significant groundwater nitrate occurrences are found in large areas where anthropogenic influences can be excluded” (p. 2). In addition, this paper presents the first record of rainfall nitrate concentrations for the SAB region, as collected throughout the 2010–2011 rainy season, usefully indicating levels of NO$_3$–N and ratios of NO$_3$–N/Cl that enter the USZ as precipitation. We also calculate recharge rates, and nitrate-flux, through these profiles using the chloride mass balance approach.

2. Study sites and methods

The study area is in the southwest Kalahari dunefield above the Stampriet Basin (SAB) (Fig. 1b,c). Details of the hydrogeology of the basin are given by Miller (2008) and JICA (2002) and recapped briefly by Stone and Edmunds (2012). What is relevant here is that the majority of the basin (~80%) is covered by dune sands, which support a savannah type-vegetation, recorded as varying in spatial extent from 20 to 29% of the surface in the early 1990s by Bullard et al. (1995) across five representative sites, and also exhibiting temporal variability. The vegetation in the study region is typical of that of the southern Kalahari dunefield (Thomas and Shaw, 1991), including Acacia species which are known to be capable of N-fixing (such as camel thorn, Acacia erioloba), shrubs (including Rhigozum trichotomum) and grasses (including Stipagrostis amabilis, Schmidtia kalahariensis and Aristida congesta), which suggests the USZ might be conducive to natural production of nitrate (e.g. Deans et al., 2005; Dupuy and Dreyfus, 1992; Sprent, 1987). Mean annual rainfall increases from the southwest to northeast of the SAB, with long-term averages of 175 mm/y at Koess, 190 mm/y at Stampriet and 240 mm/y at Leonardville, and exhibiting high inter-annual rainfall variability (Namibian Meteorological Service records). Levels of mean annual potential evapotranspiration are high (up to 3500 mm/y).

Fig. 1a illustrates that the SAB groundwater exhibits elevated levels of nitrate, and that this occurs both in small patches and in a distinct north-west orientated linear band (of up to > 200 mg NO$_3$–N/L) (Tredoux et al., 2009). However, this map remains an imperfect picture of the nitrate distribution as (i) it is strongly influenced by the position of boreholes, which are not randomly distributed and (ii) it is not possible to determine which aquifer layers are represented by these data. Tredoux (2012, pers. comm) reports that there was often no distinction made between layers in the collation of data for this map and that the map was very much a first assessment; nonetheless, he suggests that the higher nitrate concentrations often relate to the unconfined Kalahari unit, because priority was given to the uppermost layer where multiple data points existed at a site. There are reports of significantly elevated nitrate in all three units, including confined groundwater (Heaton, 1984;
In the unconfin ed aquifer 38 boreholes measurements from the early 1980s gave a median value of 35 mg NO₃⁻N/L (converted from NO₃⁻ presented in Heaton, 1984 as meq/L), with a range of 6–209 mg NO₃⁻N/L and mean of 65 mg NO₃⁻N/L. Values for both the Auob and Nossob groundwater were corrected by Heaton et al. (1983) for denitrification using N₂/Ar ratios (see Vogel et al., 1981) where the initial nitrate in the water is represented by the nitrate presently existing in the water plus the amount of extra N₂ derived from the denitrification of dissolved nitrate. This gives a median of 13 mg NO₃⁻N/L (mean 13 mg NO₃⁻N/L and range 5–23 mg NO₃⁻N/L) for the Auob unit and 9 mg NO₃⁻N/L (mean 8 mg NO₃⁻N/L and range of 0–20 mg NO₃⁻N/L) in the Nossob unit. These are significant since they represent a high baseline (and are > WHO (2003) guidelines) in groundwaters dated to between 5700 and >40,000 radiocarbon years (Heaton et al., 1983) (unable to present calibrated value owing to absence of reported errors).

Spot measurements in March 2012 from the Terra Rouge Farm borehole (water table ~ 25 m depth, borehole 50 m deep and screened for lower 25 m) and Hoogvertoon (water table ~ 30 m depth) (10 m away from KAL11/2) (Fig. 2a) are 21 mg NO₃⁻N/L and 222 mg NO₃⁻N/L respectively. The lower concentrations for the Terra Rouge farm borehole are to be expected given its very close proximity to the ephemeral Auob River, which will contribute occasional freshwater locally via focused recharge.

The four cores of the USZ analysed here are from Kalahari dune sand sediment and were collected in March–April 2010 (Stone and Edmunds, 2012), using a hand auger. Samples were transferred from an aluminium compression head to drainpipe with tightly fitting (moisture-tight) lids for transit to the laboratory. Cores KAL11/1 and KAL11/2 lie close to the eastern Namibian border post Mata–Mata on the farm Terra Rouge (and the farm neighbouring it in the south, with a low density of sheep grazing) whilst KAL11/3 and KAL11/4 are neighbouring cores (c. 5 m apart) from Bysteek Farm, near to Stampriet (no grazing animals) (Fig. 2). Vegetation in this region is typical of that of the Kalahari dunefield described above. In particular, site KAL11/1 contains bare ground and patchy grasses at the dune crest with S. amabilis, S. ciliate, S. obtus, S.
kalihariensis and *E. lehmanniana* (Fig. 2b) whilst at KAL11/2 the grasses are less abundant on the dune crest, with trailers of the Tsamma melon plant (*C. lanatus*) at the surface (Fig. 2c). The site of KAL11/3 and KAL11/4 has a heavier cover of the same grasses as at KAL11/1 (Fig. 2d). Shrubs and *A. erioloba* are also present with the small acacia trees situated at least 15–20 m away from profile sample sites (Fig. 2d). All cores were sampled directly below areas of bare ground in-between the patchy vegetation.

The pore moisture from the sand samples was extracted via elutriation, using 30 g of sediment and 12 ml of ultrapure deionised water, placed into a shaker tray for an hour before being centrifuged and the supernatant filtered at 0.2 μm. Analysis of nitrate and other anions was undertaken using ion chromatography at the Oxford Centre for the Environment, where the limit of detection was ~ 0.1 mg/L as based on measurements of known standard solutions and analytical precision was ~ 5% based on repeat measurements of the same elutriated solutions on different days. A number of samples were subsampled and prepared (via elutriation) up to three times, to assess sample heterogeneity, and this varied from 1 to 22% (wherever multiple elutriations were undertaken, an average value was calculated).

Rain gauges (CM1016 Professional Manual Rain Gauges, manufactured by Skyview Systems Ltd) were installed at fence post level in September 2011 in order to record rainfall amounts and provide samples for rain water chemistry analysis. The rain gauges have a funnel diameter of 100 mm and are capable of capturing both rainfall (wet deposition) and some contribution from dry deposition (above 1.5 m height of the fencepost). Acid-rinsed polypropylene bottles were provided for collecting and storing the rainfall (collected on the days when rain fell), which were refrigerated and sent in batches every two months to the laboratory in Oxford for analysis.

### 3. Results

#### 3.1. Nitrate and chloride in rainwater

Fig. 3 illustrates rainfall amounts and nitrate and chloride concentrations for each day when rain fell between November 2011 and June 2012 (capturing the rainy season) and Table 1 gives the weighted mean values (concentrations per event weighted by rainfall amount per event) for each site. Gauges were mounted at fence-post level (capturing wet and dry deposition at > 1.5 m height), and samples were refrigerated after collection and sent regularly in batches to Oxford for analysis (to minimise the time available for biological changes). For the five gauges in the Stampriet Basin, the concentrations of NO$_3$–N range from trace amounts (below the 0.1 mg/L of detection of nitrate, which converts to ~0.02 mg NO$_3$–N/L) to 1.11 mg NO$_3$–N/L with an overall (across all five SAB sites) mean of 0.31 mg NO$_3$–N/L. The weighted mean
values are the best representation of rainfall nitrate concentrations to input values into the sediment, and are: 0.11 mg NO$_3^-$N/L for Terra Rouge Farmhouse, 0.22 mg NO$_3^-$N/L for Skeerhok, 0.20 mg NO$_3^-$N/L for Hoogverton, 0.22 and 0.23 mg NO$_3^-$N/L for the two Bysteek gauges, and 0.20 mg NO$_3^-$N/L across all five SAB sites (Table 1) (Fig. 2a). Data from the urban environment of Windhoek to the north east of the SAB are given for comparison (site 6 in Table 1). These fall in line with those over the SAB, which is perhaps surprising, given the potential for urban pollution, such as wastewater treatment and vehicle exhausts, in Windhoek. There is very

Fig. 3. Rainfall amounts and chemistry in the Stampriet Basin on an event-basis, showing concentrations of Cl and NO$_3^-$N and the NO$_3^-$N/Cl ratio for (a) Terra Rouge farmhouse, (b) Skeerhok, (c) Hoogverton, (d) Bysteek 1 and (e) Bysteek 2. Weighted averages are indicated for NO$_3^-$N (solid, black line), Cl (dashed grey line) and NO$_3^-$N/Cl ratio (dotted red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Table 1
Nitrate and chloride in rainwater gauges in the Stampriet Artesian Basin and Windhoek.

<table>
<thead>
<tr>
<th>Site</th>
<th>Season’s rainfall (mm)</th>
<th>Mean NO₃-N (mg/L)ᵃ</th>
<th>Mean Cl⁻ (mg/L)ᵇ</th>
<th>Mean NO₃⁻N/Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SE region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) Terra Rouge Farmhouse</td>
<td>288</td>
<td>0.11</td>
<td>0.58</td>
<td>1.16</td>
</tr>
<tr>
<td>(25° 31’09”</td>
<td>194</td>
<td>0.22</td>
<td>1.45</td>
<td>0.34</td>
</tr>
<tr>
<td>(2) Skeerhok</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(25° 28’20”</td>
<td>140</td>
<td>0.20</td>
<td>1.67</td>
<td>0.43</td>
</tr>
<tr>
<td>(3) Hoogverton</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(25° 44’23”</td>
<td>123</td>
<td>0.22</td>
<td>0.53</td>
<td>0.45</td>
</tr>
<tr>
<td><strong>Stampriet region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) Bysteek 1</td>
<td>287</td>
<td>0.22</td>
<td>0.53</td>
<td>0.45</td>
</tr>
<tr>
<td>(24° 17’07”</td>
<td>223</td>
<td>0.23</td>
<td>0.46</td>
<td>0.99</td>
</tr>
<tr>
<td>(5) Bysteek 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(24° 17’12”</td>
<td>442</td>
<td>0.15</td>
<td>0.21</td>
<td>0.96</td>
</tr>
<tr>
<td>Overall weighted mean for basin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outside Stampriet Basin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6) Olympia/UNAM, Windhoek</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(22° 36’6”</td>
<td>442</td>
<td>0.15</td>
<td>0.21</td>
<td>0.96</td>
</tr>
</tbody>
</table>

ᵃ Using concentrations per event weighted by rainfall amount per event.

little rainfall chemistry data from southern Africa with which to compare these values. Heaton (1987) reported a weighted annual mean nitrate concentration of 0.39 mg NO₃⁻N/L for rain at Pretoria (northeast South Africa), whilst Schwiede (2007) reports values for the 2002 and 2003 rainy season at Serowe in eastern Botswana of 0.22–1.23 mg NO₃⁻N/L (and a mean of 0.64, not a weighted mean as volumes of rainfall were not recorded for two of the events) and chloride of 0.3–4.76 mg/L with a mean of 2.18 mg/L.

3.2. Unsaturated zone nitrate profiles

Fig. 4 illustrates the NO₃⁻N profiles, which show clear zones of low concentration (values of ~2–8 mg NO₃⁻N/L) throughout KAL11/3 and KAL1/4, much of KAL11/2 and the uppermost metre of KAL11/1), and also elevated zones of ~100–250 mg NO₃⁻N/L (in profile KAL11/2) and 250–525 mg NO₃⁻N/L (in much of profile KAL11/1). These concentrations are between one and three orders of magnitude greater than that of weighted average rainfall for the basin (0.2 mg NO₃⁻N/L, Table 1). Addition, or enrichment, of nitrate can be considered further using NO₃⁻N/Cl⁻ ratios (e.g. Deans et al., 2005; Edmunds and Gaye, 1997). The NO₃⁻N/Cl⁻ ratio approach works because chloride behaves as a conservative tracer (not taken up or produced by plants) in the USZ, with elevated chloride concentrations (higher than input) indicating evapo-transpiration, whilst nitrate can be produced and utilised by biological processes (or added from direct, and indirect anthropogenic pollution). A constant ratio of NO₃⁻N/Cl⁻ would suggest no addition of nitrate, whilst an increase in the ratio suggests addition. The sections of the profiles containing low nitrate concentration all have NO₃⁻N/Cl⁻ ratios <1 (and often <0.5), which is in the same region as the rainfall input values (Table 1, Fig. 5). Enrichment of nitrate is seen most strongly in profile KAL11/1 and then KAL11/2, whilst the small increase in nitrate at the base of KAL11/3 is not accompanied by an increase in the NO₃⁻N/Cl⁻ ratio (it co-varies with an increase in chloride) (Fig. 4, Table 1). The enriched region in KAL11/1 is widespread through the depth of the profile, with the NO₃⁻N/Cl⁻ ratio rising, and then staying above 2 from 1.5 m depth, then rising further and fluctuating from 4 to 12 around a mean of 8 down to 7.5 m (Fig. 4a). The enriched region in KAL11/2 occurs at a greater depth (from 5.5 to 7.5 m), with a ratio of about half the magnitude of KAL11/1 and decreases to low concentrations (Fig. 4b).

Stone and Edmunds (2002) applied the chloride mass balance (CMB) method to these same profiles to provide an analogue for recharge and rates of water movement (e.g. Edmunds et al., 1988), which was based on a best-estimate of rainfall chloride extrapolated from neighbouring Botswana (1.3 ± 0.4 mg/L (from the Groundwater Recharge and Evaluation Study in Botswana, as reported in de Vries et al., 2000). If we use the 2011–2012 rainfall chloride weighted mean of 0.94 mg/L (Table 1), recharge rates fall within two standard deviation (2σ) of the initial estimates and can be revised to 5 mm/y for KAL11/1 (previously 9 ± 5 mm/y at 1σ), 4 mm/y for KAL11/2 (previously 7 ± 3 mm/y), 20 mm/y for KAL11/3 (previously 35 ± 11 mm/y) and 27 mm/y for KAL11/4 (previously 46 ± 11 mm/y) (Table 2). It is also possible to calculate the travel time (or water residence time) for any particular depth, assuming that cumulative chloride with depth is proportional to time (Cook et al., 1992). This has been used to produce the chronology for the NO₃⁻N/Cl⁻ versus cumulative chloride plots (Fig. 4), with KAL11/1 spanning 44 years, KAL11/2 spanning 58 years, KAL11/3 spanning 22 years and KAL11/4 spanning 23 years (Table 2).

4. Discussion

4.1. Potential causes of nitrate enrichment in the unsaturated zone

The enrichment zone, in KAL11/1, spans the depth from around 1 to 5 m, may most sensibly be accounted for by biological production in the USZ, given there is no history of fertiliser application, and this site has never been close to an animal enclosure/ kraal, or enclosed paddock (although there is a low density of grazing sheep across the farm). However, the precise source of nitrate is not known. The nearest Acacia was more than 15 m from the drilling site, so no large roots were encountered during hand-auguring and loss on ignition (LOI) at 550 °C reveals no significant organic content by weight in the form of fine rootlets (Fig. 4). The presence of fine roots and mycorrhizas were associated with USZ nitrate at sites with N-fixing vegetation in north-west Senegal (Deans et al., 2005). It is possible that the roots of nitrogen-fixing vegetation (or a whole plant) have oxidised and decayed, leaving the enriched nitrate signature in the pore-moisture in the profile, although the farmer has no record of removing vegetation at this site over the last ~40 years. CMB indicates a recharge rate of 5 mm/y at this site and the age model indicates downward movement of water through the zone of elevated nitrate over decadal-timescales, which would seem too short a time to accommodate die-back and removal of a tree or large shrub, instead suggesting we should still observe it. Therefore, if this is a signature of past vegetation it is most likely to be from a smaller shrub, grass and legume species that respond more quickly to the variations in rainfall and are more transient across the landscape. It is possible that the deeper enrichment zone in KAL11/2 than KAL11/1 represents vertical movement of an older nitrate front (elevated zone that accumulated closer to the surface), given the recharge rates of 4 mm/y, although it remains feasible that former vegetation had root systems reaching 7.5 m depth.

Other possibilities are micro-organisms or cyanobacteria, or excreta from grazing sheep. Cyanobacteria are largely associated with surface crusts (e.g. Barnes et al., 1992) and Thomas and Dougill (2007) find a significant increase in total nitrogen from cyanobacteria in the Kalahari sediments of western Botswana. There is no clear field evidence for a crust here, with the dunes crests composed of loose sand cover, and an initial SEM scan of sample from 5 m below the surface (A. Bogush, pers. comm.) shows that the sample has the appearance of unconsolidated sand grains, without
the filamentous cyanobacterial sheaths and exopolysaccharide secretions identified in Kalahari crusts by Thomas and Dougill (2007), but there are small particles that appear to be of organic origin. Thomas and Dougill (2007) believe crusts are not only a pervasive feature of the Kalahari but can become buried, so a potential nitrate contribution from former crusts cannot be discounted. Schwiede et al. (2005) have demonstrated a clear trend between high nitrate concentrations in the upper 3–5 m of the sediment in close proximity to termite mounds in the Orapa to Serowe region of Botswana in the eastern fringes of the Kalahari (Supplementary information, Fig. S1), as Barnes et al. (1992) have also demonstrated in Australia. However, our study site is too dry to support termites, and no termite mounds are observed in this portion of the southern Kalahari. It therefore seems most likely that any N-fixing vegetation was grass species and perhaps leguminous taxa, such as the Tsamma melon, C. lanatus that is observed at other sites in this region (including KAL11/2).

Fig. 4. Unsaturated zone profiles showing moisture content and LOI (loss on ignition) for reference (as is indicative of organic carbon content), NO$_3$–N and Cl concentrations (in mg/L), the NO$_3$–N/Cl ratio and a plot of NO$_3$–N/Cl against cumulative chloride with an age model provided by the chloride mass balance approach for (a) KAL11/1, (b) KAL11/2, (c) KAL11/3 and (d) KAL11/4.

Fig. 5. Boxplot of the NO$_3$–N/Cl ratio for measurements from individual days of precipitation received across the five rain gauges in the Stampriet Basin study region, where the median is 0.49, 1st quartile is 0.22, 3rd quartile is 0.94 and the range is 0.01–3.40 (mean is 0.80).
In the Orapa to Serowe region (Fig. 1a), detailed work was also undertaken on USZ nitrate concentrations along transects from a cattle kraal at farm Makhi (Schwiede, 2007; Schwiede et al., 2005, and reported in Stadler et al., 2012). Concentrations are high beneath the kraal, with a mean value of 1734 mg NO₃-N/L (a range of 374–3737 mg NO₃-N/L and median of 1797 mg NO₃-N/L) converted to mg/L from mg/kg of dry soil using the reported moisture contents for each sample in Schwiede, 2007 (Supplementary information, Fig. S2). This is around three times higher than the peak found at KAL11/1, although the enrichment ratio (NO₃-N/L) only reaches 3, in comparison to the elevated zone in KAL1/1, which fluctuates around 8 and reaches a maximum of 12 (Fig. 4). Schwiede (2007) also reports nitrate concentrations from three profiles at increasing distances (750 m, 1250 m and 2500 m) from the kraal, inside a closed-off paddock (Fig. S2), which are of a similar magnitude to those found in SAB profile KAL11/2 and almost as high as in KAL1/1. There are sheep grazing at Terra Rouge, and the neighbouring farm to the south, and whilst neither KAL1/1 nor KAL1/2 was taken in close proximity to a kraal, we do not discount any contribution from grazing animals. However, the sheep are not fenced into a small paddock in the same way as KAL11/1 nor KAL11/2 was taken in close proximity to a kraal, we currently unclear what the specific source of animal-excreta nitrate over the ~10 cm diameter represented by our augured borehole, over timescales of years to decades represented in our profiles. For this reason vegetation N-fixing continues to appear the most parsimonious explanation. The depths of the enriched nitrate KAL11/1 and KAL11/2 and the timescales provided by chloride mass balance implies episodic production of nitrate. It is currently unclear what the specific environmental controls on this episodic production might be. Above, we have argued that episodic growth and decay of N-fixing vegetation (or formerly deeper roots) or episodic production by micro-organisms or cyanobacteria (which feasibly could respond to changing moisture availability) appear more feasible than contribution from animal excreta. An additional tracer or control sites would be needed to conclusively discriminate between sources of nitrogen in this and similar dryland environments.

In contrast to the USZ of the western United States (described by Walvoord et al., 2003, 2004), the maximum residence time of the pore-moisture in the USZ is half a century, as opposed to 2000−16,000 years (both using the CMB approach). Recharge rates for our Kalahari profiles are between 4 and 27 mm/y, indicating that any elevated zones of nitrate represent a temporary build-up over depth and are draining, and will continue to drain, through the profiles over decadal timescales. For this reason, we cannot attribute the elevated nitrate zone in KAL11/1 to progressive accumulation over long timescales, as Walvoord et al. (2003) do for the Mojave Desert, Sonoran Desert, Chihuahuan Desert, High Plains and Los Alamos Mesa; as Huang et al. (2012) do for the a Tarim River basin profile dominated by upward moisture flux towards the surface in China, or as Al-Iaani and Al-Qudah (2013) illustrate for an USZ covered by limited-permeability desert pavements in Jordan.

### Table 2
Recharge rates and residence times using CMB for each profile also showing rainfall chemistry (Cp), mean, median and maximum values of NO₃−N and cumulative amounts of accumulated NO₃−N in the profiles.

<table>
<thead>
<tr>
<th>Profile</th>
<th>Profile depth</th>
<th>No of samples</th>
<th>Mean rainfall (mm)</th>
<th>Cp used</th>
<th>Steady-state CI in profile</th>
<th>Mean recharge rate (mm/y)</th>
<th>Residence time (y)</th>
<th>Mean NO₃−N (mg/L)</th>
<th>Median NO₃−N (mg/L)</th>
<th>Peak NO₃−N (mg/L)</th>
<th>Mean NO₃−N: Cl ratio</th>
<th>Peak value for NO₃−N: Cl ratio in profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAL11/1</td>
<td>11.3</td>
<td>46</td>
<td>181</td>
<td>0.77</td>
<td>27.6</td>
<td>5</td>
<td>44</td>
<td>174</td>
<td>139</td>
<td>527</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>KAL11/2</td>
<td>9.2</td>
<td>23</td>
<td>181</td>
<td>0.77</td>
<td>37.4</td>
<td>4</td>
<td>58</td>
<td>54</td>
<td>14.6</td>
<td>230</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>KAL11/3</td>
<td>11.8</td>
<td>44</td>
<td>190</td>
<td>0.77</td>
<td>6.74 (above basal peak)</td>
<td>20</td>
<td>22</td>
<td>17 (2 above basal peak)</td>
<td>1.95 (1.73 above basal peak)</td>
<td>187 (8.2 above basal peak)</td>
<td>0.41</td>
<td>1</td>
</tr>
<tr>
<td>KAL11/4</td>
<td>11.6</td>
<td>22</td>
<td>190</td>
<td>0.77</td>
<td>5 (without surface 4 m)</td>
<td>27</td>
<td>23</td>
<td>2.30</td>
<td>31.3</td>
<td>0.41</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Regardless of the definitive source of the nitrate production at KAL11/1 (and KAL11/2 to a lesser extent), we can make some useful qualitative and quantitative comparisons with other USZ profiles from the Kalahari, and propose ideas about the USZ-groundwater connection. The only published USZ sites from the Kalahari are for the Orapa to Serowe region of Botswana (Fig. 1a), which is the site of the Makhi farm kraal (Schwiede, 2007; Schwiede et al., 2005, and reported in Stadler et al., 2012). A sampled transect between two termite mounds revealed a mean concentration beneath the mounds of 12,165 mg NO₃-N/L (Supplementary information, Fig. S1) which is substantially higher than beneath the kraal and 23 times higher than the peak found in our KAL11/1 profile. The NO₃−N:Cl ratios beneath the termite mounds reach 7.5 (Supplementary information, Fig. S2), indicating a similar level of nitrate enrichment as found in KAL11/1.

Stadler et al. (2012) propose two conceptual models of nitrate input to groundwater for the Kalahari (Serowe site) as a function of the depth of the USZ, the presence of calcrite, rainfall regime and source of nitrate. In the west (sites of Gobabis and Ghanzi) this is a fast through-flow scenario, where the USZ is relatively shallow (groundwater table about 10 m below the surface), there are calcrites containing dissolution breaks (sinkholes and fracture porosity) and there is an anthropogenic input of nitrate (from cattle farming). Under this scenario, nitrate builds up in the soil pool during years of regular rainfall, with water only reaching groundwater through dissolution breaks in the calcrite (focussed recharge pathway). However, during years of episodically high rainfall Stadler et al. (2012) suggest that the soil (USZ) can become saturated to a few metres depth, and that diffuse recharge flushes out the nitrate pool. We comment that this saturation could only be very localised and not widespread, perhaps in interdune regions and topographical low points above localised regions of low permeability, but is unlikely on the dunes (from which our samples are taken). The second, and contrasting, model is a slow through-flow model for the eastern Kalahari, where the USZ is around 100 m thick (Serowe site) (Stadler et al., 2012). Under this scenario there is a natural pool of nitrate that was mobilised during pluvial events of the late Quaternary (as supported by radiocarbon ages for the groundwater), whilst currently there is low recharge and low transfer of nitrate (through sands and calcrite horizons). The USZ profiles presented here provide evidence for a scenario intermediate to these two proposed by Stadler et al. (2012) in which zones of elevated nitrate are moving through the profiles over multi-decadal timescales, with recharge rates of 4–5 mm/y in the south of the SAB and up to 20–27 mm/y near Stampriet.
The concentration of nitrate in the unconfined Kalahari aquifer unit of the Stampriet Basin reported by Heaton (1984) has a mean of 65 mg NO$_3$–N/L (median 35 mg NO$_3$–N/L), if boreholes interpreted as being contaminated by livestock (on the basis of $^{15}$N) are included, and a mean of 29 mg NO$_3$–N/L (median of 38 mg NO$_3$–N/L) if those boreholes are excluded. Contamination is likely to be a localised, patchy phenomenon. These groundwater values are of a similar order of magnitude to the mean USZ concentrations in KAL11/1 (174 mg NO$_3$–N/L) and KAL11/2 (54 mg NO$_3$–N/L), but above the low-level (or background) concentrations measured in the profiles. Hydrogeologically the Kalahari aquifer is recharged from water infiltrating through the Kalahari dune sand (our sampled USZ), although at the base of the dunes this is complicated by the presence of a partly eroded (and likely discontinuous) calcite layer, with fracture porosity. In regions without Kalahari sand cover, such as between Marienj and Köes on the Weissrand (labelled on Fig. 1b), karstic sinkholes in the calcrite facilitate focussed recharge to the Auob aquifer unit where the Kalahari aquifer unit has wedged out (Tredoux et al., 2002). The enriched USZ nitrate concentrations (> 100 and up to 525 mg NO$_3$–N/L and with high NO$_3$–N ratios) are found between 2 and 8 m depth in KAL11/1 (peaking ~ 5 m) and between 5 and 8 m depth in KAL11/2, with low concentrations above and below. This region of nitrate enrichment, coupled with recharge rates of 4 or 5 mm/y (from CMB), suggests nitrate is moving down as a front toward the water table over the timescales of decades (even though the base of the profiles do not contain high concentrations). It is possible that the absence of elevated nitrate zones in KAL11/3 and KAL11/4, where recharge rates are higher (20–27 mm/y), is the product of a more complete flushing of water (and nitrate) through the USZ at those sites (as proposed by Barnes et al. (1992) for the Australian arid zone).

Fig. 1a indicates that in patches groundwater nitrate concentrations are higher than recorded by Heaton (1984). Tredoux et al. (2009) suggest that across much of this area, anthropogenic sources can be discounted. If, as we argue, excreta from grazing sheep are not the main contributing source, these USZ profiles suggest significant baseline nitrate. In addition, if these patterns of nitrate production and recharge from the past four decades persisted further back in time, and are a regional feature, it is entirely plausible that the nitrate being produced naturally (and moving as a nitrate front toward the water table over multi-decadal timescales) is (and for much of the late Quaternary has been) sufficient to account for that found below the water table. This accords with the interpretation of the source of high nitrate concentrations in palaeo groundwater of northern Africa (Edmunds et al., 2004). These SAB USZ profile results suggest that elevated nitrate loadings to groundwater can occur as pulses. The nitrate profiles show that the magnitude of nitrate loadings can vary substantially across the basin, whilst the chloride-derived recharge rates suggest that the rate at which they percolate also varies. It is currently unclear what the specific controls on the concentrations and timings of produced nitrate might be, although they are likely to be related to vegetation type/density and changes in vegetation and microorganisms and/or to geomorphic position.

The palaeoclimatic record from groundwater within the Stampriet aquifer suggests that the temperature has been fairly stable during the Holocene (using a noble gas temperature proxy) (Stute and Talma, 1998), whilst records of linear dune accumulation indicate that the dunefield has been more active than present during the Holocene, with a significant depth of sediment (~4 m) accumulating in one of the profiles at the start of the Holocene, (and with some level of activity throughout much of the past 120 ka) (Stone and Thomas, 2008). Hürkamp et al. (2011) collate new and existing records from fluvial and aeolian archives in the lower Molopo River (to the south-east of the Stampriet Basin) to suggest conditions more humid that today from around 39 to 25 ka, and drying from ~20 ka. Together these records suggest that the conditions in this region during the last 20 ka, and certainly the Holocene, have not varied greatly from modern day decadal-scale fluctuations in precipitation. It is only possible to speculate about corresponding vegetation changes, owing to a lack of preserved palaeoecological material in this semi-arid environment.

4.3. Comparison with unsaturated zone nitrate concentrations in other dryland areas

The magnitude of the elevated nitrate concentrations in KAL11/1 (250–525 mg NO$_3$–N/L) and KAL11/2 (100–250 mg NO$_3$–N/L) in the SAB region are of the magnitude observed from un-vegetated and vegetated sand surfaces in the central Australian arid zone, where average concentrations throughout 3 m profiles were as high as 127 mg NO$_3$–N/L (Barnes et al., 1992), and USZ moisture fluxes are characterised as episodic recharge pulses. In central Australia noticeable subsurface bulges (elevated zones) were observed under open ground and spinifex vegetation (and not mulga), whilst the highest concentrations (2000 ppm NO$_3$–N in the soil) were measured beneath termite mounds (Barnes et al., 1992). This is also similar to baselines values from northwestern Senegal with concentrations >100 mg NO$_3$–N/L under uncultivated and rain-fed cultivated land (Edmunds and Gage, 1997) where recharge rates are 0.5–34 mm/y (from CMB). In the same region, Deans et al. (2005) related USZ nitrate to N-fixation; concentrations beneath N-fixing trees exceeded 200 mg NO$_3$–N/L and reached ~800 mg NO$_3$–N/L whilst concentrations of 150 mg NO$_3$–N/L were also found beneath a ‘control’ site (no N-fixing trees, where peanuts were planted) and a non-N-fixing species (with recharge rates of 0.13–6.55 mm/y). Radiocarbon dated palaeo groundwater across the Saharan region nearly all contain high nitrate concentrations, near or in excess of current drinking water limits (Edmunds et al., 2004). This widespread distribution across space (Libya, Mali, Niger, Sudan, Algeria and Tunisia) and through time (waters dated from 35,000 years olds to modern) lends support to a natural source from N-fixing vegetation, with a possible increase and expansion of Sudano-Guinean vegetation cover during wetter periods of the late Quaternary (Edmunds, 1999).

Greater concentrations (up to 1235 mg NO$_3$–N/L) have been measured on the Chinese Loess Plateau under N-fixing alfalfa, whilst natural grasslands, with no fertilisation, had a maximum of 43 mg NO$_3$–N/L (and recharge rates range from 33 to 68 mm/y) (Huang et al., 2012). In the Badain Jaran Desert, where stable isotopic analysis suggests anthropogenic inputs are minimal (Gates et al., 2008), nitrate concentrations reach 200 mg NO$_3$–N/L, with profile-averages of 19, 31, 59 and 50 mg NO$_3$–N/L (Ma et al., 2012). The pattern of fluctuation with depth follows that of chloride and therefore appears to record fluctuations in vegetation cover or changes in N-fixation over a thousand years (Ma et al., 2012).

In the North China Plain, where fertilisers had been applied (and recharge rates are similar to the Loess Plateau), the average nitrate concentrations in USZ profiles are higher than in our SAB cores, with values between 350 and 400 mg NO$_3$–N/L (peaking around 600 mg NO$_3$–N/L, and with one exceptional sample of 2703 mg NO$_3$–N/L) (Huang et al., 2012). This is also seen in the Luanchen aluvial plain in China, where nitrate is attributed to ammonium in fertiliser, concentrations in the root zone reach 611 mg NO$_3$–N/L, and are 70–104 mg NO$_3$–N/L beneath the root zone (Yuan et al., 2012).

These baseline and fertiliser-induced USZ concentrations are surpassed by the concentrations beneath deserts in the western United States, where values exceed 2000 mg NO$_3$–N/L (Walvoord
et al., 2003), and there is no downward moisture flux (recharge). The highest concentrations (1000–3000 mg NO$_3$–N/L) in that region are from the Mojave Desert, the High Plains and the Sonoran Desert, whilst concentrations in the Chihuahuan Desert (around 200 mg NO$_3$–N/L) are in line with that measured in our SAB cores. Reviewing groundwater with nitrate levels above the World Health Organization (WHO) guideline of 11.3 mg NO$_3$–N/L. This work adds to: (i) the handbook of studies of levels of nitrate in Kalahari groundwater (Heaton, 1984; Heaton et al., 1983; Stadler et al., 2008, 2010, 2012; Tredoux et al., 2005; Wabel, 2005), most of which focus on anthropogenic nitrate and nitrate sources from human waste (e.g. septic tanks) or animal waste from cattle and (ii) the one other USZ study, from eastern fringes of the Kalahari (Schwiede et al., 2005; Stadler et al., 2008, 2010, 2010), which shows enhanced nitrate concentrations associated with both cattle kraals (indirect anthropogenic pollution) and termite mounds (a natural source). The implication of baseline nitrate values that are 10–20 times WHO guidelines in the USZ where the downward moisture flux is between 4 and 27 mm/y, is that high nitrate water appears to be a pervasive (if patchy) natural feature in parts of the Kalahari. This makes it a difficult water quality issue to manage. Putting limits on additional anthropogenic sources is imperative in regions where natural levels of nitrate in the USZ and groundwater are already high. We concur with Stadler et al.’s (2012) assertion that a focus on both source attribution and understanding hydraulic regime is critical to understanding, and managing, nitrate and water quality issues. One challenge is to get a handle on what generalisations about nitrate production and transport to groundwater can be made, in order to understand the apparently patchy nature of high nitrate concentrations in groundwater (see Fig. 1a). Detailed site-specific studies are vital for improving our understanding. The magnitude of nitrate observed in this setting is in line with enrichment in other areas of Africa and other continents (e.g. the Sahara-Sahel, China and western U.S.A.) and this raises the issue of the fate of naturally produced nitrogen in recharge areas in relation to the underlying groundwater bodies.

5. Conclusion

The unsaturated zone (USZ) nitrate profiles presented here provide a substantial insight into naturally produced, or baseline, nitrate in the Kalahari. Zones of nitrate enrichment are found in the two cores in the south of the study region where nitrate concentrations reach 100–250 mg NO$_3$–N/L (KAL11/2) and 250–525 mg NO$_3$–N/L (KAL11/1) and high nitrate to chloride ratios demonstrate an addition of nitrate, rather than an evaporative concentration of that from rainfall input. These enriched zones compare with low background levels in the same cores, and two other cores, of ~2–8 mg NO$_3$–N/L and a weighted mean value of 0.2 mg NO$_3$–N/L received in rainfall during 2010–2011. The profiles demonstrate that there is a significant pool of nitrate in the soil, which builds up temporarily, although nitrate and moisture are moving through the profile, as shown by chloride mass balance recharge rate estimates of 4–5 mm/y (in the south) and 20–27 mm/y (near Stampriet). The results also suggest that nitrate concentrations and recharge rates are variable at the regional scale. Our samples are from dune sands that make up the uppermost USZ of the Stampriet Basin (a multi-layered aquifer, and an important transboundary groundwater resource for southern Africa), and we have chosen sites unaffected by direct human pollution and also spaced at a good distance from animal enclosures, minimising indirect pollution. We note that although sheep graze in low concentrations at Terra Rouge (sites KAL11/1 and KAL11/2), we feel it is unlikely that excreta would provide a consistent source of nitrate over years to decades over the small spatial area of an augured borehole that would be needed to account for elevated concentrations of nitrate that span 2 m and 4 m (representing between one and two decades of moisture infiltration) in those two profiles. Whilst we have tried to eliminate certain origins of nitrate, it remains difficult to obtain confirmatory evidence for natural production associated with vegetation owing to the oxidising nature of the dune sediments in this semi-arid area.

The Kalahari appears to be typical of many semi-arid, and arid settings in experiencing elevated levels of nitrate in groundwater, and there are potential concerns for human and animal health when consuming groundwater with nitrate levels above the World Health Organisation (WHO) guideline of 11.3 mg NO$_3$–N/L. This work adds to: (i) the handbook of studies of levels of nitrate in Kalahari groundwater (Heaton, 1984; Heaton et al., 1983; Stadler et al., 2008, 2010, 2012; Tredoux et al., 2005; Wabel, 2005), most of which focus on anthropogenic nitrate and nitrate sources from human waste (e.g. septic tanks) or animal waste from cattle and (ii) the one other USZ study, from eastern fringes of the Kalahari (Schwiede et al., 2005; Stadler et al., 2008, 2010, 2010), which shows enhanced nitrate concentrations associated with both cattle kraals (indirect anthropogenic pollution) and termite mounds (a natural source). The implication of baseline nitrate values that are 10–20 times WHO guidelines in the USZ where the downward moisture flux is between 4 and 27 mm/y, is that high nitrate water appears to be a pervasive (if patchy) natural feature in parts of the Kalahari. This makes it a difficult water quality issue to manage. Putting limits on additional anthropogenic sources is imperative in regions where natural levels of nitrate in the USZ and groundwater are already high. We concur with Stadler et al.’s (2012) assertion that a focus on both source attribution and understanding hydraulic regime is critical to understanding, and managing, nitrate and water quality issues. One challenge is to get a handle on what generalisations about nitrate production and transport to groundwater can be made, in order to understand the apparently patchy nature of high nitrate concentrations in groundwater (see Fig. 1a). Detailed site-specific studies are vital for improving our understanding. The magnitude of nitrate observed in this setting is in line with enrichment in other areas of Africa and other continents (e.g. the Sahara-Sahel, China and western U.S.A.) and this raises the issue of the fate of naturally produced nitrogen in recharge areas in relation to the underlying groundwater bodies.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jaridenv.2014.02.015.

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