

Iron and nutrient content of wind-erodible sediment in the ephemeral river valleys of Namibia



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ABSTRACT

Research concerning the global distribution of aeolian dust sources has principally focussed on salt/clay pan and desiccated lacustrine emission areas. In southern Africa such sources are identified as Etosha Pan in northern Namibia and Makgadikgadi Pans in northern Botswana. Dust emitting from ephemeral river valleys, however, has been largely overlooked. Rivers are known nutrient transport pathways and the flooding regimes of ephemeral river valleys frequently replenish stores of fine sediment which, on drying, can become susceptible to aeolian erosion. Such airborne sediment may be nutrient rich and thus be significant for the fertilisation of marine waters once deposited. This study investigates the dust source sediments from three ephemeral river valleys in Namibia in terms of their particle size distribution and their concentrations of bioavailable N, P and Fe. We compare the nutrient content of these sediments from the ephemeral river valleys to those collected from Etosha and Makgadikgadi Pans and consider their relative ocean fertilising potential. Our results show that the ephemeral river valleys contain fine grained sediment similar in physical character to Etosha and Makgadikgadi Pans yet they have up to 43 times greater concentrations of bioavailable iron and enriched N and P macronutrients that are each important for ocean fertilisation. The known dust-emitting river valleys of Namibia may therefore be contributing a greater fertilisation role in the adjacent marine system than previously considered, and not-yet investigated. Given this finding a re-assessment of the potential role of ephemeral river valleys in providing nutrient-rich sediment into the aeolian and marine systems in other dryland areas is necessary.

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1. Introduction

Land-ocean and land-atmosphere-ocean sediment transport provide pathways of nutrients essential for ocean productivity (Aufdenkampe et al., 2011; Kroeze et al., 2012; Bouwman et al., 2013). Marine phytoplankton provide half of the planet's primary production (Chavez et al., 2011; Worden et al., 2015) and the biological consumption of sediment-associated nutrients plays an important role in photosynthetic marine uptake of CO₂ (Jickells et al., 2014; Hauck and Völker, 2015). Nutrient input is especially important in High Nutrient Low Chlorophyll (HNLC) regions, which includes the Southern Atlantic (Meskhidze et al., 2007), where surface water phytoplankton is limited by the absence of one or more nutrients required for photosynthetic growth (Martin et al., 1994; Quéguiner, 2013). Of the ca. 30 essential elements for life (Moore et al., 2013), the growth-limiting nutrients of primary importance are widely agreed to be the micronutrient iron (Jickells et al., 2005; Cassar et al., 2007; Quéguiner, 2013) as well as nitrogen (Falkowski, 1997; Herut et al., 2002; Bracken et al., 2015) and

phosphorus-based (Codispoti, 1989; Filippelli, 2008; Gross et al., 2015) macronutrients. It is noted that many uncertainties exist regarding the drivers that alleviate the limitation of these nutrients in surface waters, with upwelling of dissolved nutrients in deep waters and deposition of mineral aerosols being two of the main processes (see global review by Moore et al. (2013)). The complexities of atmospheric processing of aeolian sediment-bound nutrients and their deposition on the ocean surface remains poorly understood (Mahowald et al., 2009; Baker and Croot, 2010; Buck et al., 2010), with correlation between dust storms and phytoplankton blooms being made (Calil et al., 2011; Tan et al., 2017) and challenged (Boyd et al., 2009; Shaw et al., 2010). However, the overall nutrient loading of dust is widely recognised as essential to marine productivity (Mahowald et al., 2008; Zehr and Kudela, 2011; Bouwman et al., 2013). The deposition of mineral aerosols containing greater amounts of essential Fe, N and P would therefore be considered to have a higher fertilisation potential.

Globally, fluvial delivery provides the largest contributions to the oceans of sediment (Syvitski, 2003), Fe (Poulton and Raiswell, 2002), and N and P from both natural processes and human activities (Glibert et al., 2006; Howarth and Marino, 2006). Excluding glacial sediment, considered here a form of fluvial delivery over a longer timescale, the

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next largest contributor of sediment and nutrients to the ocean is aeolian transport and deposition (Jickells et al., 2005; Mahowald et al., 2008). Aeolian deposition is especially conducive for ocean productivity where sediment and adsorbed nutrients are delivered directly to the ocean surface, an environment abundant in light and oxygen which are fundamental requirements for photosynthesis (Ryther, 1956; Kroopnick, 1975). Experimental application of desert dust to HNLC ocean surfaces has been shown to trigger phytoplanktonic growth (Giovagnetti et al., 2013). However, potential ocean fertilisation pathways that encompass both modern fluvial sources and atmospheric transport have yet to be investigated.

At the global scale major sources of aeolian dust in the atmosphere are identified as dry or ephemeral lakes in arid and semi-arid regions, where deep and extensive deposits of alluvial source material have accumulated via fluvial inundation during Pleistocene lake highstand phases (Prospero et al., 2002). This includes the world's largest dust source, the Bodélé Depression formed from the remnants of palaeo Lake Chad (Washington et al., 2003; Koren et al., 2006; Washington et al., 2009). Similar sources of windblown sediment are found in southern Africa, such as the topographic lows of the Makgadikgadi Pan system in Botswana and Etosha Pan in Namibia (Prospero et al., 2002; Mahowald et al., 2005; Bryant et al., 2015).

Ephemeral rivers, on the other hand, serve as extant and replenishing sources of alluvial fines. Rivers with natural flooding and drying regimes characteristically transport large loads of sediment (Laronne, 1993) and dissolved nutrients (Skoulidakis and Amaxidis, 2009). These are deposited along flats and floodplains (Reid and Laronne, 1995) as flow events dissipate via subterranean transmission and evaporation (Seely et al., 2003; Dahan et al., 2008). This process occurs to such an extent in Namibia's ephemeral valleys that the river profiles have developed a convex shape near the coast due to the magnitude of sediment transport and deposition (Vogel, 1989). Furthermore, ephemeral rivers experience flow and flood pulses on an annual or multi-year frequency (see Tooth (2000)) providing replenishment of sediment. Increased dust emission from Australian floodplains due to the provision of alluvial fines from flooding events has been reported (McTainsh and Strong, 2007) and emission from lake beds and floodplains have been closely linked to fluvial sediment supply from flood events (Bullard et al., 2008). Such sediment has a high percentage of fines (silt-clay) and is geochemically representative of the watershed through which it has been fluvially transported (Schumm, 1960; Collins et al., 1998).

Ephemeral channel systems are known to provide nutrients that support corridors of biological productivity in otherwise nutrient-poor dryland ecosystems (e.g. Bunn et al. (2006), Zeglin et al. (2011)) and they have also been identified as notable sources of windblown dust (e.g. Schepanski et al. (2013)). Yet, to date, research focused on the chemistry of airborne sediment emitted from ephemeral river valleys has been limited to respiratory and pollution-related human health impacts (e.g. Nickling and Gillies (1993), Kuo et al. (2010), Fu et al. (2014)). There are no published studies investigating the potential for ephemeral river channels to act as ocean fertilizers. This is despite mineral aerosols making up 82% of atmospheric P (Mahowald et al., 2008) and about 95% of the global averaged Fe budget (Mahowald et al., 2009). Atmospheric processing during aeolian transport can increase the bioavailability of mineral aerosol nutrients, most notably Fe (Shi et al., 2015). This processing in the atmosphere and efficient ocean-uptake of bioavailable nutrients is partly determined by particle surface area and dust concentration (Mackie et al., 2005), thus finer particles tend to be larger potential contributors to ocean fertilisation. However, fertilisation-potential is also constrained by particle-reactivity which is determined by the terrestrial mineralogy and chemistry of the source material (Krueger et al., 2004).

Remote sensing studies have shown that the ephemeral river valleys of Namibia are important contributors to regional dust emissions (e.g. Eckardt et al. (2001), NASA (2002), NASA (2003), Eckardt and Kuring

(2005), Vickery et al. (2013)). These analyses of dust plume frequency in southern Africa (2005–2008) noted that 34% of plumes originated from the Namibian ephemeral valleys, with 16% sourced in the Makgadikgadi Pan system and 10% in Etosha Pan. Each year strong seasonal easterly winds generate dust plumes over the Southern Atlantic. The coastal proximity of the river valley sources would be expected to increase the incidence of deposition over the ocean when compared to aeolian dust emitted from Etosha Pan which is approximately 400 km from the coast, when considering the E/E-NE winds that would transport dust, and Makgadikgadi Pan which is 1200 km from the coast.

Southern African Pan has been hypothesized as a potentially important source of minerals for ocean fertilisation (Piketh et al., 2000; Bhattachan et al., 2012, 2015) but to date there has been only limited analysis of the characteristics of either airborne dust or the emissive source sediments from Southern Africa. The long-term accumulated sediment in Makgadikgadi and Etosha Pans have been shown to have an enriched Total P and Total N in the fine fraction (sieved < 45 µm) compared with the parent sediment (Bhattachan et al., 2015). The same study also showed, conversely, that bioavailable Fe concentrations were higher in the un-sieved parent sediment in the Makgadikgadi Pan and some parts of Etosha Pan. Nutrient levels along the Namibian ephemeral river channels are known to increase downstream as the channels travel through the otherwise nutrient-poor Namib Desert (Abrams et al., 1997; Jacobson et al., 2000; Jacobson and Jacobson, 2013). However, the nutrient content and enrichment of the ephemeral river sediments in the dust emitting regions of the river have not been investigated to date.

Given the combination of factors discussed above, it can be hypothesized that the ephemeral river valley sediments of Namibia might be an important source of nutrients to the ocean through the process of atmospheric mineral dust transport. However, there has been no targeted assessment of the sedimentary characteristics of fines from the dust-emitting regions of these river systems or their susceptibility to aeolian erosion and no quantification of the potential nutrient content of such sediment. Global remote sensing and modelling assessments of dust have focused on the major single sources of emission in southern Africa (the Makgadikgadi and Etosha Pan systems), with the active dust emission sites of the ephemeral river valleys being largely overlooked, and excluded completely from any on-the-ground investigation. This paper addresses these issues for Namibian ephemeral river valleys by examining the sedimentary characteristics of valley sediments, particularly the fine fraction (susceptible to wind erosion) and the bioavailable iron and macronutrient content, which are components considered important for ocean fertilisation. Further, to put these ephemeral river sources in context we compare these properties of the valley sediments with sediments from two other major dust emitting sources in the region, Etosha and Makgadikgadi Pans.

2. Research design and methods

2.1. Regional setting

The Namib Desert runs 2000 km N-S along the coast, from Angola to South Africa (Heine and Heine, 2002) with the Namib Sand Sea lying between the coastal towns of Luderitz and Walvis Bay. North of the Sand Sea gravel plains occupy the 150–200 km wide coastal strip for 500 km until a northern dune field begins near the Huab River mouth (Grünert, 2000). Throughout the Namib, twelve ephemeral river valleys extend east-west towards the Atlantic Coast, although two, the Tsondab and the Tsauchab, presently terminate within the sand sea without reaching the ocean base level (Fig. 1a).

The coastal Namib receives almost zero precipitation with non-river channel biota reliant on frequent ocean fog as a moisture source. The river catchments themselves extend inland for over 300 km, on to the 1000 m high Great Escarpment (Morin et al., 2009) where average annual rainfall reaches 300 mm a year or more (Jacobson et al., 1995). As

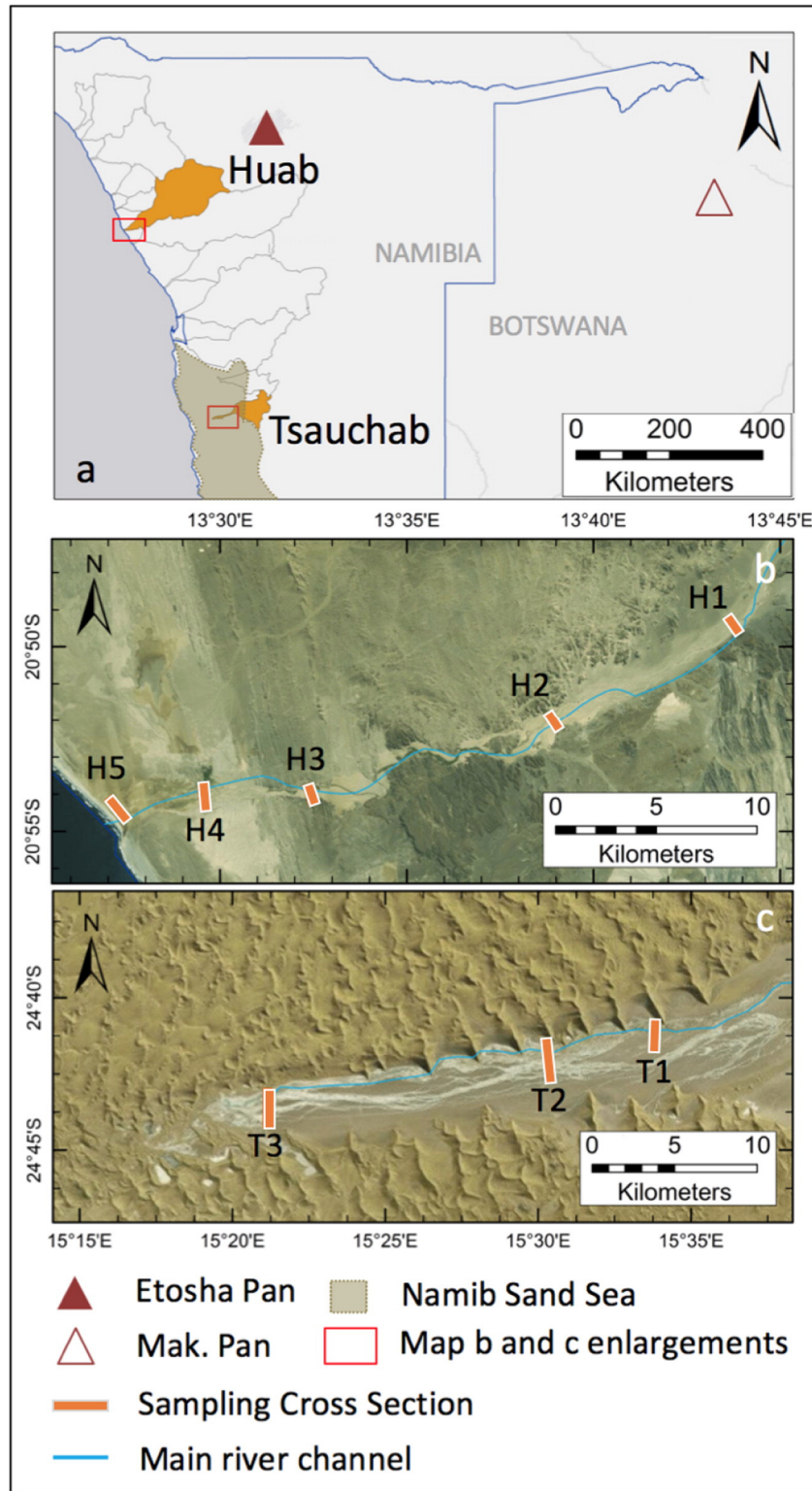


Fig. 1. a) Map of south-western Africa showing the ephemeral watersheds of western Namibia (black outline) with Huab and Tsauchab watersheds highlighted. The location of Etosha Pan and Makgadikgadi Pan in Namibia and Botswana respectively are also shown. Map enlargements b and c show the 5 cross-section sampling locations across the Huab river channel and 3 cross-section sampling locations across the Tsauchab river channel respectively.

the rainfall increases towards the eastern edges of the watersheds native vegetation biomass, agriculture and grazing increases (Jacobson et al., 1995). The Great Escarpment runs parallel to the coast, 100–150 km inland and serves as the eastern border for the Namib Desert and the expansive central plateau of southern Africa (Goudie and Eckardt, 1999). On the plateau and highlands above the escarpment,

sufficient precipitation supports vegetation and the development of at least minimal colluvium on hillslopes (Bierman and Caffee, 2001). The ephemeral river catchments occupy the 750–1000 million years old geological Damara Granites and Damara Sequence Swakop Facies and, in the north, the ancient geological features of the Khoabendus and Haib Groups (Jacobson et al., 1995). The catchments display

relatively strong slope–channel coupling and moderately abundant sediment supply, promoting a variety of confined bedrock and alluvial braided rivers (Jacobson et al. (1995) in Thomas (2011)). The dust emission sites of interest are concentrated in the lower-reaches of the rivers within the Namib Desert (Figs. 1b, c). The modern river channels cut through valley fill comprised of Late Pleistocene deposited silts, the most studied being the Homeb silts of the Kuiseb valley (Smith et al., 1993). Channel width across the valley floor varies along the interchanging stream and braided channel system, ranging from 20 to 100 m in width until the 1.8 km or 2 km wide terminal braided fan of the Huab and Tsauchab respectively. Within the modern channels are fluvial–aeolian sand deposits and fluvial silt and mud deposits (Svendsen et al., 2003; Jacobson et al., 2000). Larger flow events spread into additional, non-primary, branches and floodplains of the braided system within the low-gradient valleys.

2.2. Research design

Two contrasting dry river valleys were investigated in this study: the Huab, which reaches the ocean during periods of high flood, and the Tsauchab, which terminates in the Namib Sand Sea (Fig. 1). Both river valleys have previously been identified as significant emitters of aeolian dust by remote sensing analysis (Vickery et al., 2013). The 14,800 km² Huab watershed extends 300 km inland, the upper watershed receiving 300–350 mm of annual rainfall (Jacobson et al., 1995). The shorter Tsauchab watershed is 3950 km² in area with the upper reaches ending between the 150–200 mm isohyets (Jacobson et al., 1995).

Surface sediment sampling was undertaken across the lower valleys at 8 cross-sections (5 in the Huab and 3 in the Tsauchab) in April–May 2013. These locations had previously been identified as sources of aeolian dust emission from remote sensing analysis (Vickery et al., 2013). The cross-sections are shown in Fig. 1b and c. In total, 68 samples of surface sediment (5–11 samples per cross-section) were collected plus eight duplicate samples to serve as laboratory duplicates for quality

control purposes. Inter-sample distance along each cross-section was determined in the field by the specific channel morphology at each site. Samples were collected from the distinct geomorphological units encountered (as shown in Fig. 2):

- valley fill – above-channel deposits forming the valley-floor through which the incised river channels are located
- coarse channel deposits – in-channel sandy deposits
- fine channel deposits – either in-channel fines forming a surface crust on top of coarse channel deposits or in-channel clay material often forming a distinct, smooth depositional pad feature ranging from 10 to 100 m² in size, or the larger clay pan system in the Tsauchab terminus
- dune deposits – sandy aeolian material originating from adjacent dune forms, or samples from the dune face itself (Tsauchab only)

Further surface samples were collected from the Etosha and Makgadikgadi Pans, Fig. 1a, as part of a wider study (Haustein et al., 2015) and are used in this paper for comparative purposes. Four samples were collected from NE Sua Pan in Botswana in 2012. These consisted of two surface crust samples (c. 1–2 cm thick) and two sub-crust samples that consisted of loose, dry powdery sediment. Six samples were collected from western Etosha Pan in 2015. These were similar to the Sua samples and consisted of three crust and three sub-crust samples. The loose, powdery sub-crust sediment is a common feature of pans and playas as evaporative processes produce ‘fluffy’ sediment via water loss and efflorescent salt growth (Reynolds et al., 2007).

2.3. Methods

2.3.1. Sample collection

Surface samples were collected using a trowel to obtain approximately 200 g of loose sediment to a depth of about 10 mm. The more consolidated crust of fine channel deposits and clay pad/pan deposits

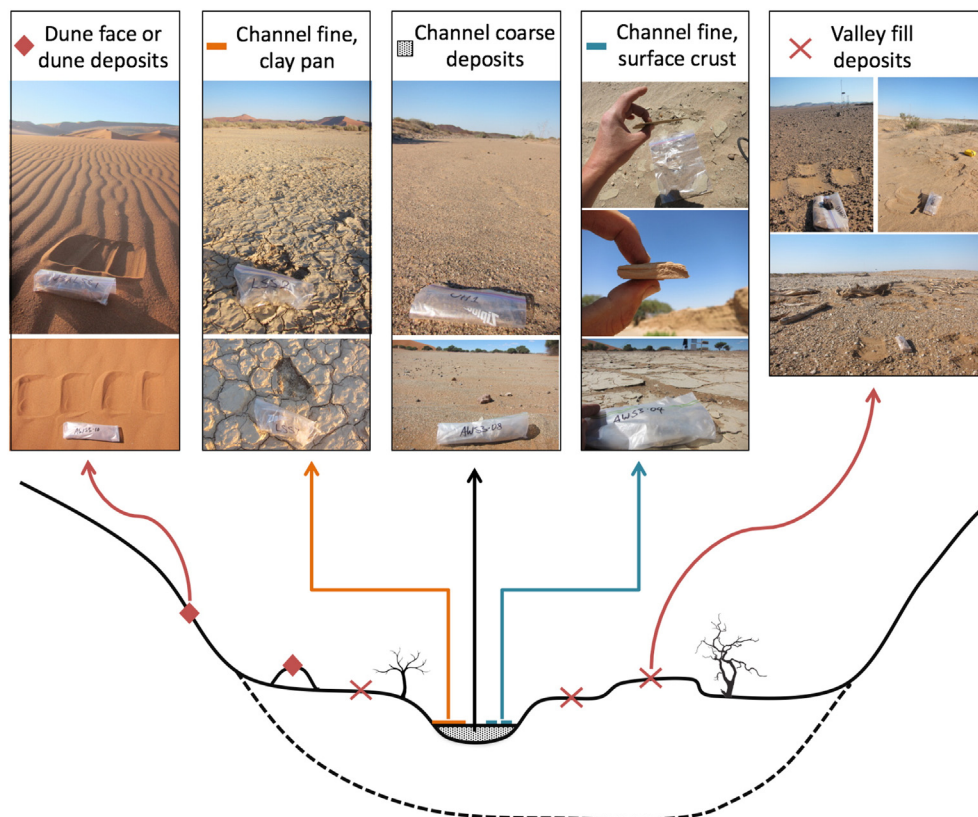


Fig. 2. Sampling points showing geomorphological units targeted along valley cross-sections.

were pried up with the crust thickness (2–20 mm) determining collection depth. Samples were stored in ziplock bags and shipped to the UK for analysis of particle size, bioavailable Fe, and P and N nutrient compounds.

Each sample (including field duplicates) was sieved through 2 mm mesh and the <2 mm subset split with a riffle box into subsets for wet particle size analysis and chemical analyses. Solid crust and clay pad/pan material was broken into appropriately 5 g and 40 g and pieces for wet particle size and chemical analyses respectively.

2.3.2. Chemical analyses

A subset of sieved <2 mm samples, including field duplicates, were split and sent to the Kansas State University Soil Testing Laboratory where they were dried overnight in a 50 °C oven with the exception of sub-samples for iron analyses which were air dried. Samples were analysed for: Mehlich III Phosphorus; bioavailable iron through the DTPA extraction of bioavailable fractions of Fe^{2+} and Fe^{3+} (combined) followed by analyses with Flame Atomic Absorption OR ICP spectrometry (following method described by Lindsay and Norvell (1978)); inorganic Nitrogen NH_4^+ and NO_3^- extracted with 1 M of KCl and analysis in a flow analyser; total nitrogen and total phosphorus using a modified Kjeldahl digestion followed by analyses in separate colorimetric reactions using a flow analyser; and soil pH using a 1:1 mixture of soil and DI water. Methods for analysis were taken from Brown (1998) unless otherwise stated.

2.3.3. Particle size

Particle size analyses was undertaken using a Malvern Mastersizer Hydro 2000MU to determine sample particle size ranges and to identify the proportion of fine material that might be susceptible to aeolian erosion. Wet-dispersion particle size analysis was conducted in order to disaggregate peds and pellets to their parent sediment sizes. Wet-dispersion investigation provides the size of the parent constituent particles and allows comparison between unconsolidated and consolidated geomorphological units.

3–5 g of sample was processed for salt and carbonate removal as described in Soukup et al. (2008). Oven-dried (40 °C) samples were then ground using a mortar and pestle and riffled to range of weights from

0.016 g to 3.8 g and suspended in a 1:1 solution of 50 g/L sodium hexametaphosphate and DI water. Samples were placed on a linear shaker and shaken for 4 h at a rate of 250 rpm then left to stand overnight. Samples were run in the Malvern Mastersizer using standard procedures, taking 3 measurements per sample and an average calculated that was used for interpretation. Cleaning runs using DI water were undertaken between each sample.

3. Results

3.1. Particle size characteristics

Fig. 3 presents mean particle size data for the main geomorphic units in the study, and the comparison with sediments from Etosha and Makgadikgadi Pans. These data demonstrate the general characteristics of the units. Of note is the relative abundance of fine material in the channel fluvial deposits, showing similar particle size distribution to the Etosha and Makgadikgadi samples and the majority of particles <100 μm . Valley fill sediments contain a relative larger amount of coarser grains, with a peak at 200 μm . As would be expected, the dune sediments are dominated by sand-size material and contain the highest relatively coarse fraction, but do not contain material >1000 μm . Intra-sample variance of particle size is very low within geomorphic units (see Table 1) and laboratory sample repeats for each unit produced matching results.

Division of the particle size distribution into size classifications as to their transport and deposition potential is shown in Table 2. The atmospheric lifetime of particles >1 μm are not determined by gravitational settling, but by wet deposition and turbulent mixing (Tegen and Lacis, 1996; Ginoux et al., 2004). These smallest particles can be considered 'globally' transportable over 1000 km (Lawrence and Neff, 2009). Between 1 and 10 μm gravitational settling becomes the dominant removal mechanism for particle removal from the atmosphere (Tegen and Lacis, 1996), becoming increasingly so with larger particle size. Particles up to ca. 100 μm are commonly associated with dust deposition studies (e.g. Mahowald et al. (2009)) and considered suitable for local and regional aeolian transportation up to 1000 km (as defined by Lawrence and Neff (2009)). This size range is therefore the most relevant for

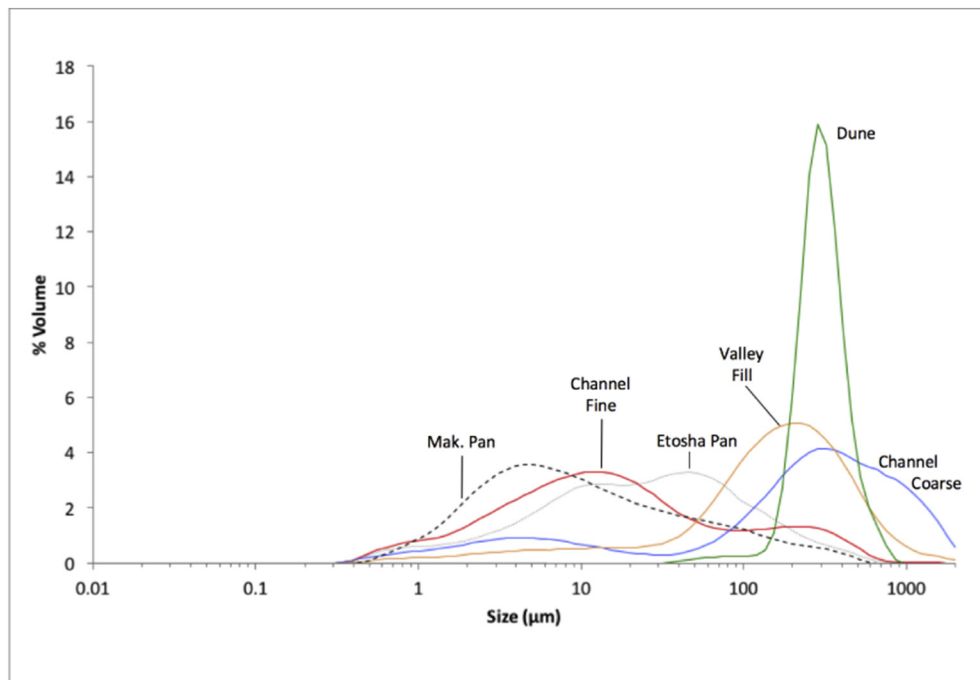


Fig. 3. Average particle size distributions of river valley geomorphological units with the combined averages of Etosha Pan and Makgadikgadi Pan crust and sub-crust samples.

Table 1Average particle size variance calculated ($\sum (x - \bar{x})^2 / (n - 1)$) and averaged according to grouped particle sizes.

	Number of samples	0–1 (μm)	1–10 (μm)	10–100 (μm)	100–1000 (μm)	1000–2000 (μm)
Channel coarse	17	0.122	1.487	0.457	8.270	3.586
Channel fine	23	0.012	0.168	0.576	0.398	0.000
Valley fill	17	0.004	0.097	1.206	4.908	0.220
Dune	3	0.000	0.000	0.046	8.123	0.000
Etosha Pan	6	0.018	0.764	2.823	1.647	0.000
Mak. Pan	4	0.007	0.112	0.350	0.071	0.000

oceanic deposition, with fine channel deposits showing 82.71% of particles <100 μm , a similar content to Etosha Pan (84.86%) and Makgadikgadi Pan (91.04%) (Table 2). Valley fill contains 39% particles <100 μm while the coarse channel sediment assemblage is predominantly 100 μm –2 mm.

Fig. 4 shows that the channel fines of both river valleys have a similar clay (<2 μm) content to Etosha and Makgadikgadi Pans with values slightly below 10%. The Tsauchab channel fines had a higher sand fraction (39%) than the Huab (16%). This is likely explained by windblown transport of sand from the surrounding Namib Sand Sea and flow events eroding slipfaces encroaching into the channel. This sand source hypothesis is supported by data in Fig. 3 where the particle size of channel fines shows a bimodal distribution with a second peak between 200 and 300 μm , aligning with the particle size distribution of the dune samples.

River channel coarse deposits contained an average of 16% (Huab) and 41% (Tsauchab) fines between 2 and 16 μm . Over three quarters (77%) of fill deposits in both valleys comprise sediment coarser than 63 μm (i.e. sand). The similarity of valley fill composition between the river valleys would suggest a common long-term geomorphological process has formed the valley fill. Particle size distributions of samples from pan crust and sub-crust fluff in both Etosha and Makgadikgadi Pans show similar composition (Fig. 4).

3.2. Bioavailable Fe, N and P content

The results of the bioavailable nutrients, Mehlich P, DTPA-extractable Fe (hereafter referred to as bioavailable Fe), ammonium (NH_4^+), nitrate (NO_3^-) as well as total N (TN) and total P (TP) are given in Fig. 5. A 1-way ANOVA was performed on the results presented in Fig. 5 to assess whether statistically significant correlations were evident between sediment nutrient concentrations and the river valley geomorphological units. Further post hoc analyses was undertaken using Tukey and Bonferroni tests to identify between which geomorphological classifications the significant relationships existed. These *p* values are provided in the text. An additional 1-way ANOVA and post hoc analysis that included Etosha and Makgadikgadi Pan samples with the river samples was also performed.

The results show that, compared to the other geomorphological units sampled, the fine channel deposits have higher concentrations of all-but-one of the bioavailable nutrients, as well as TN and TP. The exception is the nitrate concentrations which did not show an elevated median (16.79 ppm) concentration (post hoc analyses *p* values between 0.235 and 0.635 against other valley sample units). The presence of a skewed distribution containing some higher sample concentrations (mean 47.35 ppm) is noted in Fig. 5d.

Table 2

Average particle size fraction (%) of ephemeral river geomorphological units, Etosha Pan and Makgadikgadi Pan samples from wet-dispersion particle size analysis.

	Course channel deposit	Fine channel deposit	Valley fill deposit	Dune	Etosha Pan	Mak. Pan
0–1 μm	1.79	3.81	1.08	0.00	3.06	2.51
1–100 μm	21.71	78.90	38.11	1.46	81.80	88.53
100–2000 μm	76.51	17.29	60.81	98.54	15.14	8.96
Total	100	100	100	100	100	100

The mean concentrations of bioavailable nutrients, TN and TP of in-channel fine deposits (Fig. 5) were used to calculate enrichment ratios against other river valley geomorphological units. The enrichment ratio was calculated for each nutrient element as:

average ppm of fine channel deposits/average ppm of geomorphological unit

(after Wan and El-Swaify (1998)).

Table 3 shows these enrichment ratios of fine channel deposits compared to other geomorphological units. The nutrient ratios are all >1, showing the fine channel deposits are enriched in nutrient content compared to other geomorphological units.

Comparison of the nutrient content of river channel fines to Etosha and Makgadikgadi Pan samples shows important differences (Fig. 5). Of particular note is that bioavailable iron concentration (14.82 ppm) is higher in the river fines than either the Etosha (0.85 ppm, *p* = 0) or Makgadikgadi Pans (0.40 ppm, *p* = 0.001) samples (Fig. 5b). No statistically significant difference was found between coarse channel deposits, valley fill or dune samples for bioavailable Fe. Further, no statistically significant difference is shown between bioavailable Fe concentrations in coarse channel/valley fill/dune samples with either Etosha or Makgadikgadi Pans. For Etosha/Makgadikgadi respectively, the *p* values demonstrating this were valley fill 0.413/0.489, coarse channel deposits 0.855/0.864, dune 0.998/0.996, with a *p* value of 1.0 for inter-pan comparison. The deposits of river channel fines in the ephemeral river valleys deposits are also significantly higher in bioavailable phosphorus, ammonium and total phosphorus than either pan (*p* < 0.05 for individual comparison of both Huab and Tsauchab with each Etosha and Makgadikgadi in all cases).

Comparison of sediment nutrients between the two river valleys shows the Tsauchab river samples have the highest concentrations of both TN (mean 1624 ppm with statistically significant difference against the Huab, *p* = 0.001, and Etosha/Makgadikgadi pans, *p* = 0.000 in both comparisons)) and NH_4^+ (mean 13.27 ppm, no statistically significant comparison with the Huab, *p* = 0.57) but significance reported for both pan comparisons, *p* = 0.000) of all clay pan/pad locations (Fig. 5). The Etosha Pan samples have statistically significantly much higher levels of nitrate (211.61 ppm) than any other site (*p* = 0.018, 0.002, 0.010 for Huab, Tsauchab and Makgadikgadi respectively). The bioavailable Fe content of Tsauchab in-channel fluvial deposits appears marginally higher than the Huab deposits but this was not significant (*p* = 0.638 Tukey, 1.0 Bonferroni). Both TP and bioavailable P concentrations are highest in the Huab channel fine deposits (TP mean 874.93 ppm, Mehlich P mean 80.33 ppm), 150% that of the Tsauchab and 400% compared to the pans, (Sua Mehlich P 13.44 ppm, TP 160.59 ppm). pH of the river clay deposits is lower (8.4 Huab, 8.1 Tsauchab average) than that of Etosha (9.6 mean) or Makgadikgadi (9.1 mean).

4. Discussion

4.1. Sediment size and suitability for aeolian transport

Surface deposits collected from the extant dry river channels in the lower catchments, which are known to emit dust (Vickery et al., 2013), showed a particle size distribution similar to samples collected

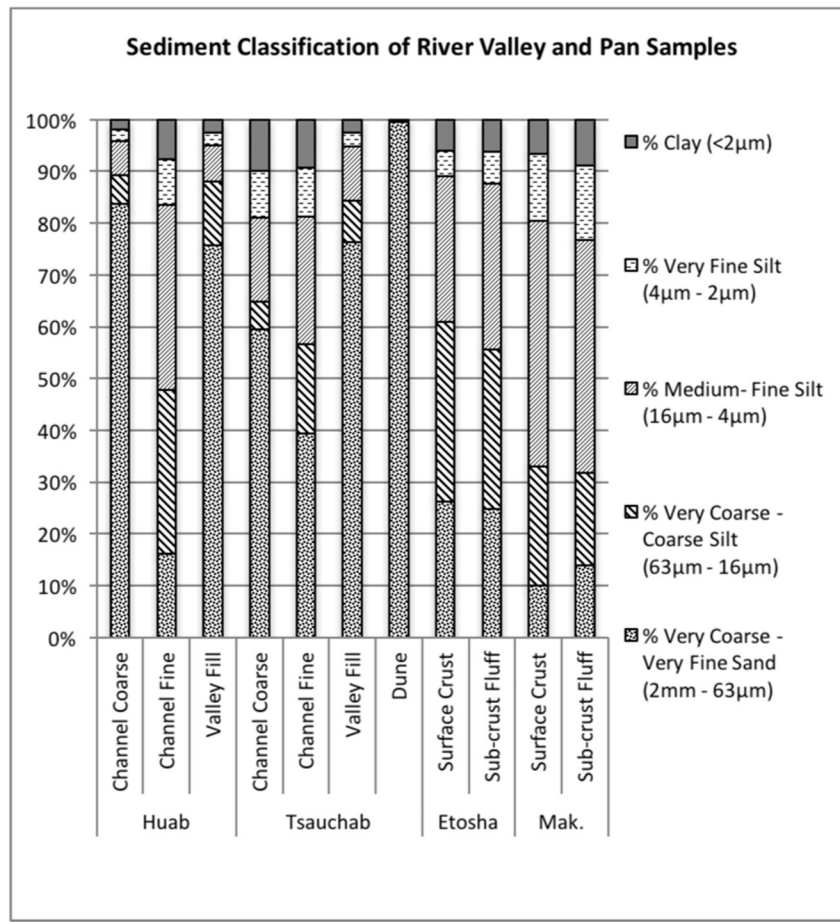


Fig. 4. Average sediment size fractions of Huab and Tsauchab River geomorphological units compared to Etosha and Makgadikgadi Pan samples.

from Etosha and Makgadikgadi Pans, the major dust emitting sources in southern Africa. In the ephemeral river valleys, over 80% of the fine channel deposits comprised particles under 100 µm (Table 2), the size range commonly found in airborne dust (Mahowald et al., 2009). These fines are derived from both the upper catchments and re-working of valley fill and constitute the suspended sediment load when the rivers are in flood. They are deposited in the lower catchments when the flood events subside and, on drying, subsequently form surface crusts and clay pads which are susceptible to wind erosive forces.

Valley fill was shown to have a more-varied particle size comprising both larger grains with 75% classified as very fine to very coarse sand (Fig. 4) and smaller particles with ~39% under 100 µm, a size susceptible to deflation. Valley fill consists of alluvial material within the valleys that is repeatedly reworked by ephemeral river flow. This process has been well documented, e.g. Patton and Schumm (1981), Tooth (2000), Merritt and Wohl (2003), and results in an abundance of fine sediments. In all of the river valley sampling locations and surrounds an abundance of quartz sand was observed (minimum of 16% sand in collected samples (Fig. 4) and large adjacent dune sources as shown in Fig. 2). These sand grains are likely to increase the susceptibility of the surface to deflation through both abrasion of surface crusts and clay pads (Shao et al., 1993; Wiggs, 2011) and bombardment via saltation of unconsolidated sediments, causing the ejection of fines (Gillette, 1981).

The Tsauchab coarse channel samples displayed a greater proportion of fines than those from the Huab (Fig. 4). This is expected to be a result of the Tsauchab terminus location within the Namib Sand Sea. High flood events would see river flow and suspended sediment loads reach the coast in the Huab while the Tsauchab would retain all suspended sediment load within the basin terminus. This may result in a larger long-term net accumulation of deflation material in the

terminal valleys of the Tsauchab and the Tsondab compared to the other river valleys, indicating the significance of basin characteristics for the overall dust emission potential of ephemeral rivers.

4.2. Nutrient content of sediments within southern Africa dust emission sites

Higher concentrations of TP, TN, and bioavailable P and N nutrients, excluding nitrate, were observed in fluvial channel fines when compared with other river valley geomorphological units and Etosha or Makgadikgadi Pans. In order to consider geomorphological and biogeochemical influences on nutrient content a regression analysis incorporating mean particle size was conducted (Fig. 6). Particle size is shown not to correlate with nutrient concentration independently of the sample source (river valley geomorphological units, Etosha Pan, Makgadikgadi Pan). This suggests a role for the geomorphological processes in determining nutrient content and composition within sediments. Bioavailable Fe concentrations are seen to be highest in channel fines and alluvial valley fill (Fig. 6a). This is reflective of increased levels of bioavailable Fe being characteristic of alluvium in arid environments due to lessened chemical weathering and ageing (Shi et al., 2011). Bioavailable P (Fig. 6b) and Total P (Fig. 6f) show similar relationships of concentration to particle size, likely due to active rock weathering and soil formation. Weathering of rock outcrops in the Namibian escarpment, highlands and Namib Desert has occurred throughout the Pleistocene and continues to this day (Bierman and Caffee, 2001; Viles, 2005). The bioavailable N fractions (Figs. 6c, d) and TN (Fig. 6e) also provide evidence that the sample source is a stronger determinant of N-based nutrient content than sediment particle size. Biogeochemical processes that occur due to microbial and biological

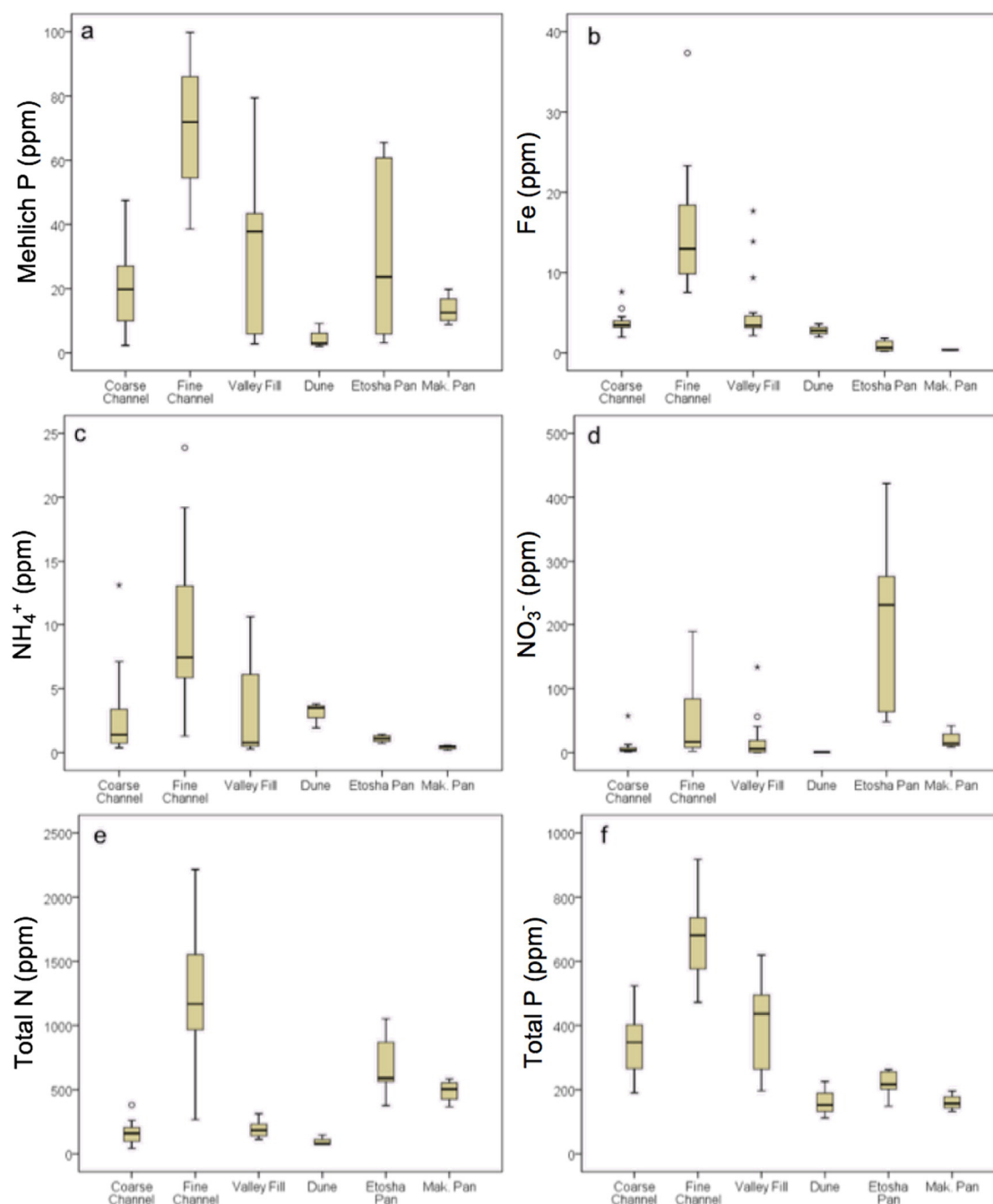


Fig. 5. Nutrient content of the Huab and Tsauchab geomorphological units and averaged crust and sub-crust samples from Etosha and Makgadikgadi Pans for (a) bioavailable P, (b) bioavailable Fe, (c) ammonium, (d) nitrate, (e) TN, and (f) TP.

activities in response to ephemeral river flows (Monger and Bestelmeyer, 2006) are expected to be a major factor influencing N concentrations. The wetting and drying effects on nutrient cycling and nitrification and denitrification processes in dryland ephemeral rivers are diverse and dependent on bacterial community composition (Scholz et al., 2002; Zeglin et al., 2011; Gómez et al., 2012; Song et al., 2012).

Table 3
Fine channel deposit enrichment ratio calculation against other geomorphological units.

Channel fines vs	pH	Mehlich P	Fe	NH_4^+	NO_3^-	TN	TP
Channel coarse	0.94	4.13	4.33	2.54	10.87	6.62	1.98
Valley fill	0.93	1.52	2.87	3.83	1.95	4.66	1.18
Dune	0.94	20.90	6.50	2.08	18.93	8.73	3.98

While the precise biogeochemical processes occurring within the geomorphological units are not known, the silts associated with hydrological flow in these valleys are known to correlate with higher levels of both N and P, resulting in increased productivity and biota abundance (Jacobson et al., 2000).

4.2.1. Bioavailable iron

The alluvial deposits in both river valleys contained higher levels of bioavailable Fe than samples of clay pan crust or sub-crust sediment from both Etosha and Makgadikgadi Pans (Fig. 5). Bioavailable Fe concentrations in the river channel fines were between 15 and 43 times greater than those found in southern Africa's major dust emitting pans (Table 4) yet the samples showed a similar particle size distribution (Fig. 3). Further, no surface area (particle size):concentration

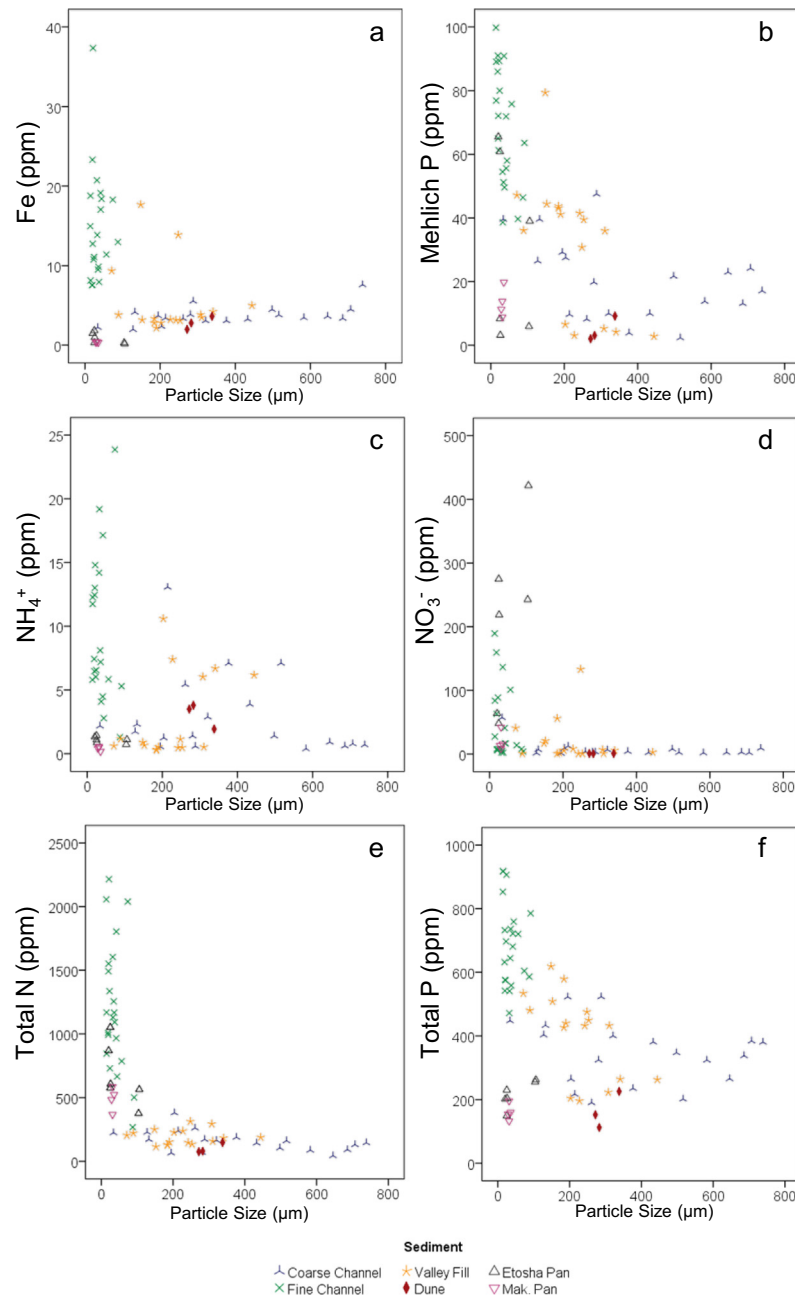


Fig. 6. Particle Size (weighted volume mean) versus nutrients concentration of river valley geomorphological units, Etosha Pan and Makgadikgadi Pan samples for (a) bioavailable Fe, (b) bioavailable P, (c) ammonium, (d) nitrate, (e) TN, and (f) TP.

relationship is observed (Fig. 6a–f). This suggests that particle size is not the primary determinant of bioavailable Fe availability, but that mineralogy and other geomorphological processes or catchment characteristics have a significant influence. This supports the findings of Journet et al. (2008), who report that the mineralogical composition of mineral aerosols, independent of particle surface area, was the primary

determinant for Fe bioavailability. Journet et al. (2008) found that the primary mineral contributor of bioavailable Fe was clay dissolution, and clay content up to 10% is seen in the ephemeral river valley sediments (Fig. 4). As shown in Table 4 the Tsauchab river terminal deposits contained slightly higher levels of bioavailable Fe than the Huab although this was not statistically significant.

Studies on iron and nutrient content of potential aeolian source sediment in Etosha and Makgadikgadi Pans are limited. In a previous study ferrous iron (Fe²⁺) had been found to be higher in the parent sediment material (63 μm – 2 mm) than in the fine fraction (<63 μm) (Bhattachan et al., 2015). The same study also showed higher bioavailable Fe in Kalahari dune sediments than either pans (170–500 ppm). The higher bioavailable Fe content of the Kalahari sediments was stated as likely being a result of iron-oxides generated from the weathering of iron rich minerals in the Kalahari sands (Thomas and Shaw (1991) in Bhattachan et al. (2015)). This same process would be expected to be

Table 4
Mean bioavailable Fe concentrations of ephemeral river channel fine deposits against Etosha and Makgadikgadi Pan deposits.

Source (mean ppm)	Etosha (0.85)	Makgadikgadi (0.40)
Huab (12.79)	15	32
Tsauchab (17.57)	20	43

occurring in the Namibian river valleys from iron-oxide coated sands (White et al., 1997). Importantly, the bioavailable Fe concentrations are not directly relatable between the two studies. The bioavailable Fe extraction methodology using 0.5 M HCl by Bhattachan et al. (2015) differs from the chelating DTPA extraction (0.005 M (Lindsay and Norvell, 1978)) used here to extract plant-available Fe. DTPA can chelate Fe^{2+} or Fe^{3+} when it is not physically occluded, this form of Fe makes up a minute fraction of total Fe, approximately 0.02% (Lindsay and Norvell, 1978). Additionally, the parent material was ground using a Pica-Mill Soil grinder for biogeochemical analyses by Bhattachan et al. (2015), which would reduce physical occlusion and expose a larger surface area for chemical digestion. Both the stronger digestive acid and the increased surface area exposed to digestion in the Bhattachan et al. (2015) study would produce higher concentrations than non-ground, DTPA-extracted samples as analysed in this study.

Noting that Fe concentrations cannot be directly compared between this study and that of Bhattachan et al. (2015), insight into the importance of the geomorphological processes occurring in the river valleys can still be cautiously made. The fine channel sediments of the river valleys showed higher levels of bioavailable Fe than the surrounding coarser sediments. This is opposite to what was found by Bhattachan et al. (2015) in the Makgadikgadi, the Kalahari interdunes and two of the four Etosha samples. This suggests that the ephemeral fluvial processes operating on the valley fill and sand deposits play an important role in biological Fe enrichment. An enriched fraction of fines, the most viable fraction for aeolian transport and ocean deposition, would further heighten the ocean fertilisation potential of the river valley sediments.

4.2.2. Phosphorus

TP and bioavailable P concentrations in valley fill and channel coarse deposits show a linear fit to particle size (Fig. 6). Bioavailable P is produced as a result of weathering of geological P sources (Holtan et al., 1988) and shows strong correlation with TP via reduced major axis regression (Fig. 7). This suggests that it is weathering of geological material and fluvial transport that is the source of enriched P in the wind-erodible sediments of the river valleys.

4.2.3. Nitrogen

Higher and lower concentrations of TN occur irrespective of particle size within the geomorphological units of the river valleys (Fig. 6). The geomorphological unit appears to be a bigger determinant for nutrient content than the mean particle size (highest concentrations of NH_4^+ and TN seen in fine channel deposits and valley fill (Figs. 6c, e) and the highest NO_3^- concentrations found in Etosha Pan and channel fine

deposits (Fig. 6d)). The large biological and ecological component of the nitrogen cycle (Coleman et al., 1983) would suggest that terrestrial and aquatic processes would need to be considered to determine N origins. The smallest watershed, the Tsauchab, has the highest levels of TN and ammonium in fluvial deposits while Etosha Pan had markedly high concentrations of nitrate (Fig. 5). Land use for grazing in the smaller Tsauchab and the highly dense fauna population of the Etosha National Park that surrounds Etosha Pan could be influencing factors.

Further, there are likely to be biological or environmental limitations upon the nitrogen cycle occurring in the Namibian Desert (Evans and Belnap, 1999) but being overcome in river channel ecosystems (Johnston et al., 2001) in association with flooding regimes. It is known that the variability and endoreic tendency of ephemeral flooding events in the Namibian catchments produces a patchwork of depositional and reworked valley fill sediment along the valleys (Svendsen et al., 2003; Morin et al., 2009) and this would also affect sediment nutrient concentrations. Large flood events leading to the deposition of datable sediments have occurred in the Kuiseb every 30–40 years during the last millennium (Grodek et al., 2013) and 66 floods have been recorded between 1963 and 2010 in the Swakop River (Greenbaum et al., 2014). Here we have shown that fluvial processes in the river valleys likely play a role in N enrichment of downstream alluvial deposits, although the processes involved appear more complex than the geomorphological accumulation of Fe and P. To understand the complexities of nitrogen fixation, ammonification and nitrification that may be occurring in the different geomorphological units (e.g. Monger and Bestelmeyer (2006)) would require further analysis. Upper catchment climate and geological gradients would also be expected to influence the nutrient content of downstream sediments and this warrants further investigation.

4.2.4. Ocean fertilisation

Ocean fertilisation is known to be influenced by nutrient inputs delivered by mineral aerosol deposition (Jickells et al., 2014). The bioavailability of these nutrients dictates the amount of nutrients available for phytoplanktonic uptake (Krishnamurthy et al., 2010) and is influenced by the added complexity of atmospheric processing before ocean deposition (Shi et al., 2011). The solubility and bioavailability of Fe in mineral aerosols remains a major uncertainty in the global biogeochemical Fe cycle (Jickells et al., 2005), with bioavailable Fe concentrations ranging from 2 to 80% of total Fe in mineral aerosol studies (Mahowald et al., 2009). Conflicting theories on the relative importance of particle size (Baker et al., 2006) mineralogy of source material (Journet et al., 2008) and iron speciation (Schroth et al., 2009) exist. Irrespective of which plays the most important role, likely a combination of processes, our results show that the Namibian river valleys are a source of bioavailable nutrient-rich sediments, which are of a particle size suitable for wind erosion and atmospheric transport, and are therefore likely to play a role in the fertilisation of the South Atlantic.

5. Conclusions

Our data show that sediment in three Namibian ephemeral river valleys that has been deposited by fluvial action but is now prone to wind erosion, comprise significant concentrations of nutrients considered important for ocean fertilisation. This is especially the case for bioavailable Fe which has been found in concentration levels that are up to 43 times greater than those found in dry pan sediments. This is significant because wind erosion of these sediments may transport the nutrients into the South Atlantic where they could have a significant fertilisation impact. Sedimentological analysis has shown that approximately 40% of valley fill and 80% of in-channel fines in the ephemeral river valleys comprise particles under 100 μm . These particles are highly susceptible to wind erosion and transport and so are likely to act as sources for the aeolian dust plumes known to emanate from these river valleys. The coastal proximity of the aeolian dust source regions in the lower

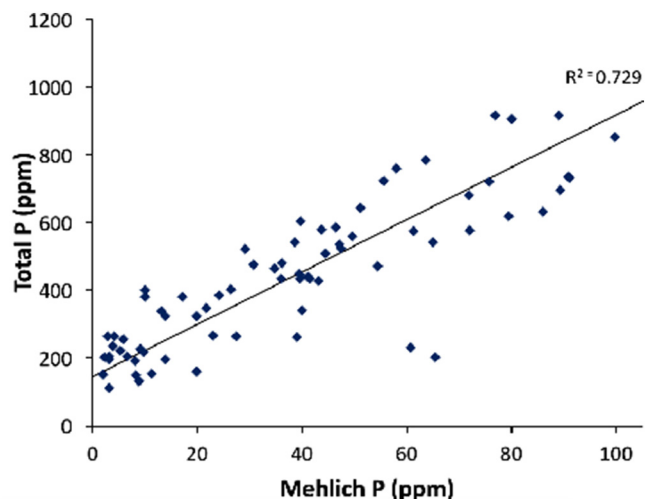


Fig. 7. Reduced Major Axis (RMA) regression analysis of TP and bioavailable P (Mehlich P) for all river valley geomorphological unit samples.

catchments of these ephemeral rivers is also likely to facilitate a high rate of deposition of nutrients into the ocean, even during relatively minor deflation events. The findings of this research suggest that the river valleys of Namibia may therefore be contributing a notable aeolian fertilisation role in the adjacent marine system and that this may have a measurable impact on the marine ecosystem. Given this, further investigation on phytoplanktonic response in the depositional waters is warranted and the regional importance of the river valley and pan dust sources considered. It seems likely that geomorphological processing acting in the ephemeral river valleys act to enrich their sediment with nutrients.

Given this, the potential role of ephemeral river valleys in providing nutrient rich sediment into the aeolian and marine systems in other dryland areas is worthy of further investigation.

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