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Abstract

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Keywords

trace, alpine, elements, site, zealand, sources, concentrations, implications, metal, pollution, aerosols, GeoQuest

Disciplines

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Trace elements and metal pollution in aerosols at an alpine site, New Zealand: Sources, concentrations and implications.

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Abstract

Atmospheric aerosol samples were collected at a remote site in New Zealand's Southern Alps. Collected samples were found to be a mixture of New Zealand and Australian sourced sediment, using their trace element signatures. Aerosol concentrations and the relative contribution of different sources was found to be a function of specific air-mass trajectories influencing the study site, dust entrainment rates in source areas and rainfall. Results show that Australian dust is a major source of particulate matter in New Zealand, particularly in remote alpine locations; however, locally derived dust is also important. Metal pollutants, including Pb, Cu and Sn, were enriched in the samples by approximately 15 times and up to >100 times expected natural concentrations, confirming that metal pollution is a ubiquitous component of the atmosphere, even in relatively remote locations. Moreover, pollutants were highly enriched in otherwise clean air, i.e. during and following rainfall. Additionally, high concentrations of elements naturally enriched in sea water, e.g. Sr, Ba and Rb, were deposited alongside mineral dust, reflecting the oceanic origin of air influencing the site and the role of sea spray in contributing aerosol to the atmosphere. These elements experienced the greatest enrichment during rainfall, implying sea spray and pollution become relatively important during otherwise clean air conditions.

Keywords: trace elements, Australia, dust, long-range.

1. Introduction:

Long-range dust transport is an important component of sedimentary and biogeochemical systems. Dust has, for example, been demonstrated to be a driver of ocean productivity through additions of principally Fe and Si (though other elements are also important) in settings, such as the Southern Ocean, that are otherwise very depleted in these elements (Boyd et al., 2004; Duce and Tindale, 1991; Martin et al., 1994). The role of dust in sedimentary systems is apparent in oceanic settings remote from continents where significant dust mantles the ocean floor (Hesse, 1994; McGee et al., 2007; Rea, 1994). Copious dust transport and deposition marked the glacial cycles of the Quaternary Period, resulting in accumulation of loess downwind of cold climate regions, most notably in China where loess deposits of up to 100 m date from this time, but also in Eurasia, North America, Northern Europe, southern South America and New Zealand (Maher et al., 2010). Dust therefore played a major role in biogeochemical processes during cold climate phases. In arid and semi-arid environments, such as in Australia, loess has been harder to recognize, but here also it appears that during cold climate phases dust inputs were significant (Hesse and McTainsh, 2003). Further from source, dust inputs have been shown to contribute to soil formation. For example Saharan dust has been found to contribute to soil formation in the Caribbean Islands and Florida (Muhs et al., 2007). Similarly, Asian dust contributes to Hawaiian soils (Kurtz et al., 2001; Rex et al., 1969), while Australian dust has been shown to contribute to soil formation in New Zealand (Marx et al., 2009).

There are few studies of contemporary dust deposition rates in the Australian region (Hesse and McTainsh, 2003) because with the exception of large events, deposits are difficult to identify and quantify (McTainsh, 1989). Despite this, dust deposition is still an important component of current biogeochemical cycles (Shao et al., 2011). Satellite monitoring can provide useful information on spatial and temporal characteristics of dust transport, in addition to atmospheric concentrations for both longer term, e.g., over multiple years (Prospero et al., 2002), and event-based studies (Bullard et al., 2008). Atmospheric and deposition monitoring also provide important data on dust and aerosol concentrations and chemistry (Prospero, 1999), often at a fine scale, which may not otherwise be determined, e.g. by modelling or remote sensing.

In addition to ‘natural’ dust transport, dust transport and deposition rates have increased in many settings as a result of anthropogenic activities (e.g. Marx et al., 2011; Neff et al., 2008). The composition of the dust aerosol itself has also changed as a result of enrichment of metals (e.g. Marx et al., 2008) and other contaminants within the environment (e.g. Lavin et al., 2012). Serving as evidence of the biogeochemical significance of dust additions, these anthropogenic constituents are now found accumulating in environments where dust is a major sedimentary input (e.g. Brännvall et al., 1999; Le Roux et al., 2004; Marx et al., 2010).

In this study, we examine contemporary concentrations, chemistry and sources of dust and other aerosols within the atmosphere in a remote alpine setting in the Southern Alps, South Island, New Zealand. We build on results presented in Lavin et al. (2012) using some of the same data; however, whereas that study focused on identifying sources of semi-volatile organic pollutants in the atmosphere, this study examines the concentrations, composition and sources of aerosol collected alongside the organic pollutants.

2. Methods:

2.1 Aerosol collection

Aerosol samples were collected at Temple Basin Ski Club (42.91°S, 171.57°E, 1320 m asl), in Arthur’s Pass National Park, Southern Alps, New Zealand (Fig. 1) using a total suspended particulate sampler (Flow-Set high-volume sampler TSP, Lear Siegler, Australia) on 20 cm × 25 cm, 2-µm pore size polycarbonate membrane filters (Sterlitech Corporation, Kent WA, USA) between 16-Jan and 16-Feb 2009 as described in Lavin et al. (2012). No sampling occurred on 4-Feb due to a power failure. The sampler was run for 23.5 hr/day with ~353 m³ of air sampled daily. Filters were changed daily and stored in chemically inert plastic bags prior to and following collection. Temple Basin is a westward draining basin in the central Southern Alps surrounded by peaks of >1700 m asl. The air sampler was positioned within an alpine tussock grassland and herb field on the southern side of the basin facing a north-westerly aspect.

2.2 Climate data

Rainfall data were obtained from the weather station at Arthur’s Pass Village AWS (42.94°S, 171.56°E, 738 m asl) (National Institute of Water and Atmospheric Research), 4 km south and 560 m lower than Temple Basin. Four-day air-mass back-trajectories were

generated using the HYSPLIT model (NOAA Air Resources Laboratory, Silver Spring, MD, USA). Back-trajectories were generated for each 24-hour sampling period at 1200, 1600, 2000, 2400, 0400 and 0800 hours at 2500, 2700, 2900 m asl, yielding a catalogue of trajectories/sampling day.

2.3 Australian dust activity data

Dust activity in Australia was measured using observational data from the Bureau of Meteorology held in the Dust Event Database at Griffith University (McTainsh et al., 2011). Daily dust activity was quantified as dust event frequency (DEF), representing the total number of dust storms (severe and moderate), local dust events and dust haze events (definitions in O'Loingsigh et al., 2010) occurring in the southeastern sector of the continent (bordered by Lat. 26°S and Long. 129°E).

2.4 Dust recovery and trace element analysis

To recover the collected aerosol, the filters were soaked for 72 hours at 100°C in 30 ml Teflon beakers filled with triple sub-boiling distilled 5% HNO₃ with intermittent ultrasonic agitation. Following soaking, the filters were removed with Teflon tweezers and placed in their original storage bags, while the HNO₃ solution was dried on a hotplate. The filters were rinsed over their respective beakers using ultraclean water. The solution was re-dried and the process repeated. Samples were then prepared for trace element analysis. The dried residue was digested with 0.5 ml of a 2:1 solution of concentrated HF- HNO₃. After digestion, residual fluorides were converted to nitrates with 0.24 ml of concentrated HNO₃ before being dissolved in 2% HNO₃. Enriched isotopes (⁶Li, ¹⁰³Rh, ¹⁸⁷Re ²⁰⁹Bi and ²³⁵U), covering the full mass range of analysed trace elements, were added to correct for internal drift and matrix suppression (Ulrich et al., 2010). Samples were then heated to 100 °C for 12 hours and centrifuged, after which they were inspected in clear polystyrene tubes to ensure that no residues were present.

The trace element composition of the digests was analysed on a XSeriesII Thermo Fisher Scientific Quadrupole Inductively Coupled Plasma Mass Spectrometer (Bremer, Germany) using the protocol of Kamber (2009) except no external drift monitor was used. Rock standards W-2 (two digestions) and BHVO-1, (US Geological Survey) were similarly analysed, with W-2 used as the calibration standard. The analysed trace element concentration in BHVO-1 and long term laboratory reproducibility were presented in Lavin

et al. (2012). Trace element concentrations in aerosol samples were corrected for handling and background filter contamination by subtracting concentrations in field (average of 6 filters) and laboratory blank (average of 3 filters) filters treated and analysed identically to the aerosol samples (laboratory blank was first subtracted from field blank). Field blanks were collected by installing filters into the high-volume air sampler for one minute with the power off. The only element with a significant blank concentration was Zn, for which filter in concentrations exceeded those of the smallest aerosol samples. Zn concentration could therefore not be determined in the aerosol samples.

2.5 Determining dust provenance

The provenance of collected dust aerosol was estimated by comparing the concentration of a selection of trace elements deemed stable during entrainment, transport and deposition to those of potential source sediments (PSS). Australia and the South Island of New Zealand were considered potential sources of dust to Temple Basin. Australia is a known source of dust to New Zealand (Marx et al., 2009; McGowan et al., 2005). In addition, the braided river systems of New Zealand's South Island can supply dust to the airstream (McGowan, 1996). Dust sources, which are typically associated with fluvial systems, can have unique trace element fingerprints (when analysed at ultra-high resolution) which reflect the geology of rocks in their headwater catchments and their transport history (Kamber et al., 2005; Marx and Kamber, 2010). The Temple Basin samples were compared with an existing database of >250 samples collected from the major dust producing regions in Australia, and local loess and fluvial samples from New Zealand (Marx et al., 2009). Dust provenance was determined using a mass balance model (Marx et al., 2005b) where the trace element composition each sample was compared with that of every (>250) PSS from:

$$\Sigma_D = \sum_{i=1}^n | \left((E_{d(i)} * En) / \Sigma E_D \right) - 1 | \quad 1.$$

where Σ_D is the degree of match (0 = a perfect match) between a dust and a particular PSS. En is the number of trace elements used (21). $E_{d(i)}$ is the concentration difference of a particular trace element in a dust and the PSS, defined as:

$$E_{d(i)} = ((E_{pss(i)} / E_{dust(i)}) + (E_{dust(i)} / E_{pss(i)})) / 2 \quad 2.$$

where subscripts 'pss' and 'dust' denote a PSS and dust sample, respectively. ΣE_D is the sum all the individual $E_{d(i)}$ values:

$$\Sigma E_D = \sum_{i=1}^n E_{d(i)} \quad 3.$$

As quartz hosts no trace elements, a correction for the effect of quartz dilution is included in the equation (see Marx et al., 2005b). For this study, the rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, and Lu), actinoid elements (Th and U), high field strength elements (Nb, Ta and Sc), and a Group 13 metal (Ga), were deemed to be stable during entrainment, transport and deposition (See Marx et al., 2005b). From within the database of >250 PSS, the PSS with the lowest overall Σ_D represents the most likely dust provenance.

The collected samples may constitute an admixture of aerosols from different sources, consequently a mixing model was used to determine the relative contribution of New Zealand and Australian particulate in each sample. An example is shown for two selected samples, collected on 28-Jan and 8-Feb, in figure 2, where the two closest matching PSS from within the two endmember groups, i.e. Australia and New Zealand (determined from equation 1), are normalised against the dust sample. Of the two PSS, the New Zealand loess best approximated the chemistry of the dust collected on 28-Jan with respect to the elements Th-Ce, Nd, Sc and Tm-Ga, and in turn returned a lower Σ_D compared to the Australian PSS (1.3 versus 1.6; Fig. 2A). For some elements, i.e. U, Sm, Gd, Tb, Sc, Ho, Er and Ga, a mixture of the two PSS yielded a better mixture than either individually, improving Σ_D . This is shown in figure 3, where a mixture of approximately 10% Australian sediment to 90% New Zealand sediment yielded the best Σ_D for the 28-Jan sample. Consequently, this analysis indicates this dust is largely sourced from New Zealand. The Australian PSS yielded the closest match with the dust collected on 8-Feb (Fig. 2B). Mixing sediment from the two respective source regions improved the Σ_D for this dust only slightly (Fig.3), implying that this sample was sourced almost exclusively from Australia (>90% Australian dust).

3. Results.

3.1 Aerosol concentrations

The mass of particulate collected on the filters was so low relative to the filter weight that it was not possible to record the weight of deposited dust from the weight difference alone. Consequently, the mass of collected particulate was estimated from the amount of solution analysed and the average concentration of conservative elements (Th, U, La, Ce, Ta, Pr, Nb, Nd, Sm, Eu, Gd, Tb, Sc, Dy, Y, Ho and Ga) relative to MUQ (MUD from

Queensland), a sediment composite of the chemistry of upper continental crust (Kamber et al., 2005). Thus, particulate mass was calculated from:

$$D_m = \frac{\sum_{i=1}^n (E_{dust(i)} * Sol(i) / E_{MUQ})}{n} \quad 4.$$

where: D_m = dust mass (g); Sol = the amount of analysed solution (g) and; E_{MUQ} = the concentration of the element in MUQ (ppb). This assumes the concentration of any element in a collected aerosol is broadly comparable to the crustal average. The suitability of these elements for this analysis was demonstrated by the low errors of aerosol concentration, estimated from the standard deviations of the 17 elements used (Fig. 4) and by their conservative behaviour relative to crustal chemistry composites, including MUQ and UCC (McLennan, 2001) (Fig. 5). This approach naturally becomes less precise for the low dust mass samples ($<0.25 \mu\text{g}/\text{m}^3$) where trace element concentrations vary more considerably in comparison to crustal chemistry proxies.

Estimated daily aerosol concentrations ranged between 3.3 and $0.05 \mu\text{g}/\text{m}^3$ (Fig. 4). Variability in atmospheric dust concentration was partially controlled by the occurrence of rainfall (Fig. 4), which was associated with low aerosol concentrations. Air mass origin and climate conditions either favouring or inhibiting dust entrainment in source area also contributed to variability in dust load.

3.2 Trace element composition of aerosol samples

Average trace element concentrations of all aerosol samples collected during the study are shown in figure 5A, normalized to MUQ. The most obvious features were enrichment of Cs, Tl, W, Rb, Ba, Pb, Li, Sr, Sn, Cu, Cr, Co and Ni, and depletion of Zr and Hf. These features were consistent across all sampling days, although the magnitude of enrichment or depletion varied. Normalisation against a different crustal average, i.e. UCC (McLennan, 2001) (Fig. 5B), showed the same patterns, as well as enrichment in Mo, Cd and Sb, which were not measured in MUQ.

The digestion approach used in this study failed to completely digest resistant minerals, such as zircon. This error has previously been shown to be systematic, i.e. the percentage of digested zircon is consistent although not complete (Marx and Kamber, 2010). Zirconium and Hf depletion could therefore be an artefact of the digestion process. However, normalisation to an identically digested sample set (109 sediments samples collected from Australia's Murray-Darling Basin; Marx and Kamber, 2010), also demonstrates Zr and Hf

depletion (not shown), implying this is a characteristic of dust, presumably due to density sorting (Marx et al., 2005b).

The overall similarity of the collected aerosols to MUQ and UCC imply that these samples are largely of crustal origin, i.e. the chemistry of the aerosol is consistent with that of mineral dust. Consequently, the fine-scale variability in the trace element composition of these samples can be used to determine dust provenance region.

3.3 The effect of rainfall on aerosol chemistry

Samples collected on rain days exhibited enrichment in Sr, Rb, Li, Be, Ba and U and were associated with low atmospheric aerosol concentrations (Fig. 4). For example, Sr/La ratios (where La, a conservative element indicative of crustal material) tended to map rainfall occurrence (Spearman's correlation coefficient ρ p value = 0.0028 Fig. 6). Anomalies in this relationship may partly be explained by the location of the rain gauge 580 m lower than the sampling site. As rainfall is highly variable in complex mountain terrain (Whiteman, 2000), rainfall at the sampling site and climate station did not always occur concurrently. Hence in this context, Sr/La ratios may record the influence of rainfall more accurately than the rain gauge measurements themselves, with high Sr/La ratios indicating rain washing, either pre (upwind of Temple Basin), post (rain affecting filters following dust deposition), or during deposition itself. The ratios of other soluble elements against La were also positively correlated with rainfall: Li/La (ρ p = 0.0041), Be/La (ρ p = 0.03), Ba/La (ρ p = 0.0067), Rb/La (ρ p = 0.0042) and U/Th (ρ p = 0.006). An alternative explanation is that samples with low dust concentrations are largely of oceanic origin as high Sr concentrations are indicative of sea salt (Ault et al., 2013).

Aerosols collected on rain days also tended to contain crustal element ratios with relatively extreme values. For example, when plotting Nb/Ta versus Ga/Th ratios for the aerosols alongside those of Australian and New Zealand PSS (Fig. 7a), rain effected dusts plotted towards the extreme end of the distribution. This implies that the chemistry of these samples is atypical of dust derived from upper continental crust. This effect became even more apparent when samples suspected to have been influenced by rainfall (based on the Sr/La ratios) were included (Fig. 7b).

3.4 Dust provenance

Dust provenance data were previously presented in Lavin et al. (2012) and are discussed in brief here. A summary of the chemically modelled dust provenance is shown in figure 8. Modelling implied that all samples contained a component of both Australian and New Zealand derived sediment. However, aerosols with concentrations $<0.5 \mu\text{g}/\text{m}^3$ (i.e. those collected on rain days, Fig. 4) had chemistries atypical of crustal material and did not match PSS well and. their provenance must be treated with caution. The modelled contribution of Australian dust to samples collected on 19, 20, 24, 25, 27-29-Jan and 1 and 14-Feb was relatively low ($<30\%$ by weight), whereas aerosols collected on 17 and 31-Jan and 6-11-Feb comprised sediment mainly of Australian origin ($>80\%$ by weight). These two sample groups can be considered largely of New Zealand origin and Australian origin, respectively.

Dust activity was observed in Australia throughout the sampling period, with the exception of 26-Jan and 15-Feb (Fig. 9). Two periods of significant dust activity occurred on 22-Jan and 7-Feb, when widespread dust events occurred across south-eastern Australia. Cross-correlations (Pearson's R) between the frequency of observed Australian dust activity and the concentration of Australian dust at Temple Basin returned a positive correlation ($R=0.60$, $P \text{ value}=0.0003$). Cross-correlations between Australian dust activity and total concentration of aerosol measured at Temple Basin (were not significant ($R=0.24$, $P \text{ value}=0.18$).

3.5 Air-mass trajectories

Ensemble air-mass trajectories were categorized according to aerosol concentration and origin (determined by trace element provenance modelling) (Fig. 10). These included days of; high concentrations ($>1 \mu\text{g}/\text{m}^3$) of largely Australian sourced dust ($>50\%$ by wt) termed HighAus days, i.e. 16 and 23 Jan and 7-10 Feb; B low concentrations ($<1 \mu\text{g}/\text{m}^3$) of predominately Australian dust (22 and 31 Jan) (LowAus days); high concentrations dominated by New Zealand sourced dust (HighNZ days); low concentrations of largely New Zealand dust (LowNZ days). Trajectories were not computed for rain days where the atmosphere was largely dust free. It is important to note not all plotted trajectories represent dust transport events. Alternatively, none of the plotted trajectories may capture the actual aerosol transporting air-mass due to the temporal resolution of plots versus dust entrainment and transport by spatially and temporally discrete meteorological features such as cold fronts

(McGowan and Soderholm, 2012; Strong et al., 2011). Despite this, the ensemble plots provide an overall impression of the general origin of air influencing the sampling site.

HighAus days were typically associated with westerly trajectories, which often crossed the Australian continent (Fig. 10a). However, a number of trajectories of oceanic origin occurred, derived from the central Tasman Sea, or the Southern Ocean. LowAus days had similar trajectories to HighAus days (Fig. 10b), implying source area conditions, e.g. windiness and soil moisture, inhibited dust entrainment, or dust was deposited prior to air reaching the sampling site.

HighNZ days (Fig. 10c) were associated largely with air-masses originating in the Tasman Sea, or trajectories which crossed the North Island. Trajectories also occurred during disturbed westerly flow, associated with relatively long south-westerly pathways along the South Island's west coast (e.g. compare Fig. 10a and c). These conditions have previously been shown to result in dust entrainment from the braided rivers of the South Island's west coast (Marx and McGowan, 2005). LowNZ days were associated with disturbed trajectories originating in the Tasman Sea and reverse föhn conditions, where air from the Canterbury Plains was transported to the site (Fig. 10d).

4. Discussion and summary

4.1 Aerosol concentrations at Temple Basin

The average concentration of aerosol at Temple Basin ($0.9 \mu\text{g}/\text{m}^3$) was higher than concentrations at northern New Zealand during rain-free conditions ($0.2 \mu\text{g}/\text{m}^3$) (Arimoto et al., 1990). However, during that study rain days were not sampled. Comparable rain-free concentrations at Temple Basin were $\sim 1.4 \mu\text{g}/\text{m}^3$. The higher values reported here likely reflect the greater landmass surrounding Temple Basin, causing greater deposition of local dust. Prevailing westerly winds over the South Island (Sturman et al., 1984) also imply greater transport of Australian dust over the site. Concentrations in this study were lower than estimates of Australian dust transport to the South Island's West Coast, recorded over a ten year period (average $5 \mu\text{g}/\text{m}^3$; Marx et al., 2005a), where transport may have been enhanced due to high rainfall scavenging coupled with prevailing westerly winds and episodic large dust-transport events.

Values estimated here were broadly similar to dust concentrations at sites across the Pacific (Prospero et al., 1989), although were generally lower than concentrations of African

dust measured at Miami and Barbados (Prospero, 1999; Trapp et al., 2010). They were also similar to concentrations of Asian dust measured at Midway Island (average = 1.03 $\mu\text{g}/\text{m}^3$) (Prospero et al., 2003). These sites are approximately twice the distance from their respective dust source regions compared with this study. Concentrations reported here were, however, an order of magnitude higher than those measured at other remote Southern Hemisphere locations including Samoa, New Caledonia and Rarotonga (Arimoto et al., 1987; Prospero et al., 1989).

Atmospheric concentrations of individual elements were similar, although higher, than values recorded in air over northern New Zealand (Table 1; Arimoto et al., 1990), reflecting the greater aerosol mass recorded here. Conservative element concentrations were between 5.4 and 3.1 times (7 times once rain days were excluded) those of Arimoto et al. (1990), coincident with relative difference in mean mass between the two studies.

Relatively high concentrations of the soluble elements, Sr, Li, Ba, Be, Rb and U which are enriched within sea water (Bruland, 1983), occurred in all the collected aerosols. This implies that sea spray is a significant aerosol source in New Zealand reflecting the oceanic nature of air masses affecting the country. Sea spray derived salt aerosol has been demonstrated to be geochemically important over geologic timeframes. For example, high salt concentrations in Australian regolith were attributed to atmospheric deposition of marine aerosol (Chivas et al., 1991), while sea salt is similarly a significant source of aerosols to central Antarctica (Udisti et al., 2012; Wolff et al., 2010). Concentrations of these elements remained relatively high even on rain days (when they were most enriched by comparison to crustal elements) implying that sea spray accumulates in the atmosphere even when atmosphere is otherwise clean.

4.2 Metal pollutants

A marked feature of the collected samples is the enrichment of pollutant metals (Fig. 4). These are associated with industrial processes including mining and metal and cement production, fossil fuel combustion and fertiliser use (Pacyna and Pacyna, 2001). The degree of metal perturbation is commonly determined relative to a conservative non-pollution element (e.g. Al or La,) versus the average composition of continental crust, i.e.:

$$Ef = (\text{metal}/\text{La})_{\text{sample}}/(\text{metal}/\text{La})_{\text{crust}} \quad 5.$$

where Ef = enrichment factor, $(metal/La)_{sample}$ is the ratio of a pollutant metal to a conservative element (e.g. La) in a sample, and $(metal/La)_{crust}$ its ratio in a crustal average.

Samples collected on rain days recorded the highest relative EF (Table 2) simply because the atmospheric dust concentration was so low, i.e. La concentrations were low. Pollutants transported to the site during such conditions are likely to be of relatively local origin, e.g. emitted from industry located on the Canterbury Plains or West Coast, or from vehicles or aircraft travelling close to the site (Twohy and Gandrud, 1998). Despite this, total concentrations of metals were significantly higher on days when aerosol concentrations were higher, confirming the propensity of metal pollutants to attach to mineral aerosols (Marx et al., 2008).

During days where appreciable quantities of aerosol were collected ($>1 \mu\text{g}/\text{m}^3$), metal enrichment factors were approximately 15, but as high as >100 times background concentrations (Table 2). These values are ~ 2.5 times higher than those reported in Marx et al. (2008) collected from ice and in traps on the South Island's West Coast; however, deposited dusts may have experienced post depositional dilution. Thallium (Tl), W, Pb, Sn, Cu, Cr, Ni, Cd, Sb and As all had $EF > 5$, with $EF > 30$ times for Mo, Cd and Sb. Vanadium (V) and Co show lower EF of 1.4 and 2.7, respectively. Regardless, this study further confirms that the perturbation of heavy metals in the atmosphere is a globally ubiquitous result of industrial activity, even in relatively remote settings such as Temple Basin. Metal concentrations showed no discernible patterns or correlations with climate data or dust source origin, implying that at the very high temporal resolution of this study at least, anthropogenic metal concentrations reflect factors such as the specific dust plume trajectory, emissions at time of transport and dust scavenging rates.

4.3 The origin of dust at Temple Basin

Although the mass of dust collected was not useful for dust source determination (Lavin et al., 2012), a moderate positive relationship between the mass of dust collected at Temple Basin and the estimated mass of Australian dust ($r^2 = 0.48$, $P=0.035$) implying incursions of Australian air were often associated with high atmospheric dust concentrations during the sampling period. This suggests that, for the period of this study at least, Australian sourced dust was a major component of dust collected in New Zealand. This broadly agrees

with previous findings which show that at remote from source locations, including alpine environments and west coast coastal settings, Australian dust deposition provides a significant input of material to New Zealand (Arimoto et al., 1990; Marx et al., 2009). New Zealand sourced dust was, however, similarly important. Consequently, a number of patterns in the origin of dust measured at Temple Basin were apparent. These were explored further using the results of geochemical provenance modelling and air-mass trajectories.

HighAus days i.e. 16 and 23-Jan and 7-10-Feb, were generally associated with backward air mass trajectories that crossed the Australian continent (Fig. 10a). These dates were preceded by dust activity in southeast Australia (Fig. 9) associated with the passage of cold fronts and trough lines across the Australian continent and their subsequent progression across the Tasman Sea to New Zealand. Interestingly, on the most active Australian dust days (22-Jan and 7-Feb) (Fig. 9) fronts traversed southeast Australia, whereas during the less active day (15-Jan) a front passed south of the continent. During the most active dust day in Australia (7-Feb) widespread dust storms were observed (Fig. 12b). Dust entrainment occurred during the passage of a trough line ahead of a cold front on 6-8 Feb. Trajectory modelling indicates that dust was transported to New Zealand by pre-frontal north-westerly winds (Fig. 11a) between the 6-10-Feb. Dust observations confirmed widespread dust in south central and eastern Australia, while the geochemical modelling implied the dust aerosol collected at Temple Basin was sourced from this region (Fig. 12A). Major fires ('Black Saturday') occurred in Victoria from 7-Feb while backward air-mass trajectories from Temple Basin between 6-10-Feb crossed southern Victoria. Smoke, which was observed in satellite imagery over New Zealand was likely to be a significant component of particulate in the atmosphere over at this time. There were no obvious changes in trace element composition associated with the presence of smoke in the collected samples, however, high PCB concentrations were recorded during this period (Lavin et al., 2012).

and smoke and dust were visible in satellite imagery centred east of the South Island on 9-Feb (Fig. 12c).

Back trajectories during some days, such as on the 23-Jan, did not appear to cross Australia (Fig 11b), despite geochemical modelling implying collected aerosol contained a

high proportion of Australian dust sourced from southeastern and central Australia (Fig 12B). A narrow fast moving cold front crossed eastern Australia on 22-Jan and New Zealand on the 23-Jan, with dust observed in southeastern Australia (Fig. 12A). Fast moving cold fronts can produce sudden changes in wind directions that may not be identifiable by air mass trajectory modelling (Marx, 2006; Wain et al., 2006). Consequently, air-mass trajectories can not always accurately provenance dust entrainment events.

On 16-Jan high dust concentrations ($3.35 \mu\text{g}/\text{m}^3$) derived of approximately equal contributions of Australian and New Zealand sourced dust occurred (Figs. 4 and 8). Dust was entrained in Australia during the passage of a front and trough on 14-15-Jan. As the front passed south of the continent, entrainment was limited to local dust events in south-eastern NSW. This dust was then transported to New Zealand in disturbed westerly flow (Fig. 11c). Strong westerly winds were recorded on the West Coast of the South Island associated with this disturbed flow. These appear to have entrained significant New Zealand dust which was also transported to Temple Basin (implied by geochemical modelling).

HighNz days occurred on 20, 24 and 25-Jan. On 20-Jan an anticyclone centred in the north Tasman Sea resulted in ridging and south-westerly winds over the West Coast of the South Island resulting in a terrestrial wind run of up to ~ 550 km (Fig. 11d). These conditions often result in local dust entrainment (Marx and McGowan, 2005). Despite some backward trajectories crossing southern Australia, little dust activity was observed prior to 20-Jan (Fig. 9), implying no significant transport of Australian dust to Temple Basin occurred. On 24-Jan, an anticyclone centred over northern New Zealand again resulted in relatively long terrestrial air trajectories over central and northern New Zealand (Fig. 11e). Local dust is assumed to have been entrained due to air circulation around the decaying anticyclone and strong west to southwest winds over the South Island's West Coast. Although widespread dust activity occurred across south-eastern Australia on 22 (Fig. 6 and 12a) and 23-Jan, air-mass trajectories and aerosol geochemistry implied little of this dust was transported to Temple Basin on 24-Jan.

LowNZ days occurred on the 27-Jan and 5-Feb (Fig. 8). No significant dust activity was observed in Australia from the 24-27-Jan (Fig. 9). The synoptic situation on 27-Jan resulted in anticyclonic ridging over the South Island causing south-westerly to south-easterly winds at Temple Basin, and establishment of easterly föhn conditions (Marx and McGowan, 2005) from the afternoon. Trajectories indicate that from the afternoon air affecting Temple

Basin had crossed the Canterbury Plains (Fig. 11f), where it had incorporated relatively high concentrations of the organophosphate insecticide chlorpyrifos and polychlorinated biphenyls (Lavin et al., 2012) but little dust. On 5-Feb the passage of a west-east moving anticyclone over central New Zealand resulted in low wind speeds and no significant dust entrainment (Fig. 11g). Isolated dust storms were recorded in NSW on 2-3-Feb, and although trajectories passed close to the Australian continent, geochemical modelling implied little, if any dust was transported to Temple Basin (Fig. 9). Rainfall on the east coast of the South Island on 3 and 4-Feb, is also likely to have inhibited local dust entrainment.

On 22 and 31-Jan, a high proportion of Australian dust was modelled at Temple Basin but dust concentrations were low (LowAUS days). On 27-31 Jan minor dust activity occurred in Australia (Fig.9). An anticyclone in the Tasman Sea resulted in pre-frontal north-easterlies across central Australia, which seemingly entrained dust, albeit at low concentrations, before transporting it to New Zealand on 31-Jan (Fig. 11h). This event is climatologically similar to the April-May 1997 trans-Tasman dust transport event in which Australian dust haze was reported throughout New Zealand and high dust concentrations were measured on the South Island's West Coast (Marx et al., 2005a). In this case, despite little dust activity in Australia, relatively high Australian dust concentrations were recorded at Temple Basin.

Days on which rainfall occurred were associated with low concentrations of dust in the atmosphere due both to rainfall scavenging atmospheric dust upwind of the study site and moisture inhibiting local dust entrainment. The chemistry of these samples implied they contained little terrestrial-derived dust, but were instead dominated by sea salt emitted to the atmosphere from sea spray.

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Table 1: Average atmospheric concentrations of trace elements measured in this study (pg/m³)

	All samples		Rain free days		Northern New Zealand*	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Li	62.9	54.6	83.1	59.5		
Be	2.2	2.4	3.5	2.4		
Sc	13.1	14.1	21.1	14.1	3.9	1.8
Ti	4917.5	4797.6	7695.7	4733.1		
V	119.4	109.2	185.1	103.2	49	30.0
Cr	221.6	142.2	300.2	122.7		
Co	30.7	23.9	42.6	23.1	3.4	1.6
Ni	371.4	313.9	469.7	368.6		
Cu	192.0	203.7	250.8	239.6	120	150.0
Ga	32.3	71.4	38.6	88.1		
As	5.6	7.0	5.8	5.8		
Rb	192.9	154.6	271.6	159.8	49	40.0
Sr	1604.5	1131.2	1675.5	871.7		
Y	25.0	24.6	40.0	23.1		
Zr	87.6	88.8	137.1	89.8		
Nb	12.5	14.0	20.1	14.5		
Mo	14.6	13.2	19.0	15.7	20	20.0
Ag	4.2	6.8	5.8	8.5	26	29.0
Cd	17.8	19.9	28.6	20.7	36	3.1
In	0.1	0.1	0.1	0.1		
Sn	14.1	13.0	19.6	15.0		
Sb	53.2	23.4	61.2	24.1	4.4	3.1
Cs	8.9	8.7	13.3	9.2	1.9	0.8
Ba	1507.9	1232.7	2072.9	1369.8		
La	31.7	32.4	51.0	31.1		
Ce	67.9	67.6	109.2	63.3	13	3.7
Pr	7.9	8.0	12.7	7.6		
Nd	29.8	29.9	47.9	28.3		
Sm	6.0	6.0	9.6	5.6		
Eu	1.2	1.2	2.0	1.2	0.28	0.1
Tb	0.8	0.8	1.3	0.7	0.21	0.1
Gd	5.2	5.2	8.3	4.8		
Dy	4.6	4.6	7.4	4.2		
Ho	0.9	0.9	1.5			
Er	2.6	2.5	4.2	0.9		
Tm	0.4	0.4	0.6	0.3		

Yb	2.4	2.3	3.8	2.1		
Lu	0.3	0.3	0.6	0.3		
Hf	2.4	2.5	3.8	2.5	0.77	0.4
Ta	0.9	1.0	1.4	1.0		
W	21.9	43.7	26.0	45.0		
Tl	1.6	1.5	2.3	1.7		
Pb	163.0	136.6	223.7	151.2	210	200.0
Th	12.9	12.4	20.8	11.0	2.4	1.0
U	3.0	2.8	4.6	2.7		

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*Data from Arimoto et al., (1990)

Table 2: Metal enrichment factors

Day	V	Cr	Co	Ni	Cu	As	Mo	Cd	Sn	Sb	W	Pb
16-Jan	1.1	2.4	2.1	9.0	9.7	5.3	179.8	59.1	5.8	41.7	24.0	10.4
17-Jan	1.5	15.1	22.9	150.0	70.2	5.1	1329.2	1437.8	17.7	80.8	422.5	47.9
18-Jan	1.8	16.2	27.7	284.5	164.5	8.2	1104.7	1773.0	73.2	306.3	290.3	168.1
19-Jan	1.9	-1.3	6.9	103.3	27.5	6.8	354.2	393.6	11.9	64.2	38.9	27.8
20-Jan	1.5	1.8	2.3	8.2	3.5	7.9	11.6	29.0	2.8	8.6	5.2	5.1
21-Jan	1.4	4.2	5.2	87.3	23.0	4.3	86.0	114.9	7.1	42.2	78.4	9.2
22-Jan	1.6	4.3	2.7	23.6	6.5	5.2	58.1	29.6	4.8	39.9	11.0	6.6
23-Jan	1.2	3.5	1.2	12.8	4.6	5.4	19.5	11.0	4.1	15.9	2.3	6.9
24-Jan	1.2	4.3	2.0	12.5	3.5	5.7	16.2	10.9	3.6	39.5	2.5	8.1
25-Jan	1.6	2.2	2.0	6.2	3.0	6.4	9.3	6.3	2.6	23.0	1.8	4.4
26-Jan	1.2	3.2	2.1	9.2	3.8	5.5	9.2	10.6	2.3	13.7	2.3	5.9
27-Jan	1.2	3.2	2.8	14.2	2.9	5.7	15.5	31.4	2.1	16.7	9.1	9.3
28-Jan	1.5	1.9	3.4	13.1	4.5	6.8	15.6	55.3	2.6	21.3	3.0	7.5
29-Jan	1.6	4.1	4.6	30.8	7.9	7.3	41.5	122.3	3.6	26.2	15.4	14.3
30-Jan	1.4	5.2	1.3	23.7	7.4	5.8	63.9	83.3	13.5	26.3	12.2	9.6
31-Jan	1.9	4.9	1.3	21.5	10.2	4.7	69.8	37.2	4.6	47.3	6.6	8.1
1-Feb	2.5	7.4	5.5	62.9	10.1	5.5	92.0	167.6	7.5	38.8	16.9	13.8
2-Feb	1.8	4.5	4.0	38.1	14.8	7.2	64.6	34.7	7.5	71.3	4.2	15.5
3-Feb	2.4	4.8	6.1	69.5	9.0	5.2	117.1	132.2	5.8	76.2	9.3	9.0
5-Feb	1.7	14.6	2.6	22.9	11.1	6.3	55.2	44.8	13.9	138.4	5.9	12.2
6-Feb	3.9	13.5	5.1	37.5	7.2	6.5	53.7	147.4	7.2	71.6	8.8	11.8
7-Feb	2.1	7.7	3.5	23.8	7.0	4.9	28.2	18.0	5.5	27.6	2.7	17.8
8-Feb	1.4	3.3	2.1	6.1	2.4	4.6	10.2	6.3	2.5	19.0	1.8	3.3
9-Feb	1.5	3.3	2.9	8.7	2.2	4.2	11.1	14.9	2.4	19.3	1.9	3.3
10-Feb	1.6	10.1	3.0	16.0	7.2	4.2	12.4	74.1	5.8	49.3	2.3	19.1
11-Feb	1.5	11.0	4.3	24.5	13.0	3.5	100.3	55.4	4.8	48.1	7.8	13.2
12-Feb	2.8	107.7	16.8	189.4	111.3	6.1	584.7	1756.7	35.1	183.2	62.1	176.9
13-Feb	1.9	14.2	2.7	39.6	12.5	4.9	66.1	104.4	7.4	241.3	6.8	37.5
14-Feb	1.9	4.3	8.1	104.2	20.6	6.3	134.0	110.6	16.6	325.8	9.8	29.5
15-Feb	1.8	9.4	6.4	65.1	4.7	6.3	73.4	270.3	43.4	67.9	12.1	8.9

Figure 1. (A) The relative position of New Zealand and Australia. The arrow indicates the main dust transport pathway from eastern Australia. (B) Location of Arthur's Pass in the central South Island, New Zealand.

Figure 2. Potential source sediments (PSS) from Australia and New Zealand normalised against a collected aerosol samples from Temple Basin, for; (A) aerosol collected on 26-Jan and; (B) collected on 8-Feb).

Figure 3. A provenance mixing diagram showing the degree of match (Σ_D) in binary mixtures between collected dust samples (on the 26-Jan and 8-Feb) and PSS from Australia and New Zealand. The lowest Σ_D for the two samples indicates the best approximation of the relative contribution of New Zealand and Australian sediment to the collected dust, where 0 Australian dust equals 100% New Zealand sediment.

Figure 4. Concentrations of aerosol collected on each sampling day ($\mu\text{g}/\text{m}^3$) at Temple Basin (data modified from Lavin et al., 2012). Daily rainfall, recorded at Arthur's Pass Village is shown plotted on the figure as bars. Error bars represent the standard deviation of the 17 elements used to model the mass of dust deposition (see text for details). Note no dust sample collected on 4-Feb.

Figure 6. (A) Sr/La ratios (black diamonds) for the collected dusts plotted against daily rainfall (bars). Note no dust sample was collected on 4-Feb.

Figure 7. (A) Nb/Ta versus Ga/Th ratios for samples collected on rain days and non-rain days at Temple Basin. A comparative compilation of sediments from Australia's Murray-Darling Basin (Marx and Kamber, 2010) and New Zealand loess (Marx et al., 2005b) is plotted for comparison. (B) Nb/Ta versus Ga/Th ratios for dust samples collected on days suspected to be influenced by rainfall based on their Sr/La ratio (see Fig. 4 and main text for discussion).

Figure 8. The relative fraction of Australian and New Zealand derived sediment in the collected dusts, as modelled using trace element chemistry (modified after Lavin et al., 2012).

Figure 9. The concentration of Australian dust recorded at Temple Basin (black triangles) plotted alongside observed dust event frequency in southeast Australia. *No dust sample collected 4-Feb.

Figure 10. Ensemble 5-day backward air-mass trajectories for selected sampling days at Temple Basin, plotted at three heights 2500, 2700 and 2800 m asl at four hourly intervals. (A) HighAus days; (B) LowAUS days; (C) HighNZ days and; (D) LowNZ days (see text for details).

Figure 11. Backward air-mass trajectories as described for figure 10 for (A) trajectories influencing the site on 7-Feb; (B) 23-Jan; (C) 16-Jan; (D) 20-Jan; (E) 24-Jan; (F) 27-Jan; (G) 5-Feb and; (H) 31-Jan.

Figure 12. (A) Dust event observations in Australia on 22-Jan and; (B) 7-Feb. The modelled provenance of dust collected at Temple Basin is also shown.