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A landscape-scale approach to examining the fate of atmospherically derived industrial metals in the surficial environment

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Abstract

Industrial metals are now ubiquitous within the atmosphere and their deposition represents a potential source of contamination to surficial environments. Few studies, however, have examined the environmental fate of atmospheric industrial metals within different surface environments. In this study, patterns of accumulation of atmospherically transported industrial metals were investigated within the surface environments of the Snowy Mountains, Australia. Metals, including Pb, Sb, Cr and Mo, were enriched in aerosols collected in the Snowy Mountains by 3.5-50 times pre-industrial concentrations. In sedimentary environments (soils, lakes and reservoirs) metals showed varying degrees of enrichment. Differences were attributed to the relative degree of atmospheric input, metal sensitivity to enrichment, catchment area and metal behaviour following deposition. In settings where atmospheric deposition dominated (ombrotrophic peat mires in the upper parts of catchments), metal enrichment patterns most closely resembled those in collected aerosols. However, even in these environments significant dilution (by 5-7 times) occurred. The most sensitive industrial metals (those with the lowest natural concentration; Cd, Ag, Sb and Mo) were enriched throughout the studied environments. However, in alpine tarn-lakes no other metals were enriched, due to the dilution of pollutant-metals by catchment derived sediment. In reservoirs, which were located lower within catchments, industrial metals exhibited more complex patterns. Particle reactive metals (e.g. Pb) displayed little enrichment, implying that they were retained up catchment, whereas more soluble metals (e.g., Cu and Zn) showed evidence of concentration. These same metals (Cu and Zn) were depleted in soils, implying that they are preferentially transported through catchments. Enrichment of other metals (e.g. Cd) varied between reservoirs as a function of contributing catchment area. Overall this study showed that the fate of atmospherically derived metals is complex, and depends upon metal behaviour and geomorphic processes operating at landscape scales.

Disciplines
Medicine and Health Sciences | Social and Behavioral Sciences

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Abstract

Industrial metals are now ubiquitous within the atmosphere and their deposition represents a potential source of contamination to surficial environments. Few studies, however, have examined the environmental fate of atmospheric industrial metals within different surface environments. In this study, patterns of accumulation of atmospherically transported industrial metals were investigated within the surface environments of the Snowy Mountains, Australia. Metals, including Pb, Sb, Cr and Mo, were enriched in aerosols collected in the Snowy Mountains by 3.5-50 times pre-industrial concentrations. In sedimentary environments (soils, lakes and reservoirs) they showed varying degrees of enrichment. Differences were attributed to

the *relative* degree of atmospheric input, metal sensitivity to enrichment, catchment area and metal behaviour following deposition. In settings where atmospheric deposition dominated (ombrotrophic peat mires in the upper parts of catchments), metal enrichment patterns most closely resembled those in collected aerosols. However, even in these environments significant dilution (by 5-7 times) occurred. The most sensitive industrial metals (those with the lowest natural concentration; Cd, Ag, Sb and Mo) were enriched throughout the studied environments. However, in alpine tarn-lakes no other metals were enriched, due to the dilution of pollutant-metals by catchment derived sediment. In reservoirs, which were located lower within catchments, industrial metals exhibited more complex patterns. Particle reactive metals (e.g. Pb) displayed little enrichment, implying they were retained up catchment, whereas more soluble metals (e.g., Cu and Zn) showed evidence of concentration. These same metals (Cu and Zn) were depleted in soils, implying they are preferentially transported through catchments. Enrichment of other metals (e.g. Cd) varied between reservoirs as a function of contributing catchment area. Overall this study showed that the fate of atmospherically derived metals is complex, and depends upon metal behaviour and geomorphic processes at landscape scales.

1. Introduction

Industrial metals, which include Pb, Cu, Ni, Cd, Cr, Zn, Ag, Sb and Mo, can now generally be considered a ubiquitous part of the Earth's atmospheric environment. Even in remote locations such as Enewetak Atoll in the central western Pacific (Arimoto et al., 1985) and southern New Zealand (Marx et al., 2014b), enrichment of industrial metals occurs persistently within collected aerosol samples. These metals are typically released to the atmosphere during industrial processes including metal production and mining, combustion of fossil fuels, cement production and waste incineration (Pacyna and Pacyna, 2001). They are thereafter, transported by the wind to be deposited to terrestrial and aquatic environments (Pacyna and Pacyna, 2001).

As a consequence, industrial metals have been found accumulating in the remote-from-source locations such as Antarctica (Vallelonga et al., 2002) and Greenland (Hong et al., 1996). Typically, however, these studies have focussed on those parts of the landscape which receive

high relative rates of atmospheric input such as peat mires (Marx et al., 2010; Shotyk et al., 2002) and snow and ice (Hong et al., 2004; McConnell and Edwards, 2008). Enrichment has also been demonstrated in soil (Brännvall et al., 2001; Klaminder et al., 2006) and lake sediments (Brännvall et al., 1999; Stromsoe et al., 2013; Wong et al., 1984; Yang et al., 2007) although these records maybe more complex due to the influence of catchment and *in situ* soil processes (e.g. Augustsson et al., 2010; Shotyk and Krachler, 2010). Over the last 20 years, an increasing body of literature has documented metal enrichment in such settings (peat mires and ice) where, in many cases, temporal patterns in metal enrichment directly reflect regional industrial histories (e.g. Brännvall et al., 1999; Cooke et al., 2007; Le Roux et al., 2004; Lee et al., 2008; Marx et al., 2010). These studies demonstrate the pronounced perturbation of these metals that has occurred globally since the Industrial Revolution, while also recording pre-industrial metal pollution dating from the Bronze Age in Europe and Asia (Brännvall et al., 1999; Hong et al., 1996; Lee et al., 2008).

These, atmospherically dominated archives, however, tend to record the state of the atmosphere and do not necessarily reflect the general extent of industrial metal pollution throughout the wider landscape. The significance of atmospheric industrial metals across the wider landscape is likely to be more complex, reflecting rates of atmospheric deposition relative to sediment generation (by physical, biological and chemical weathering) and sediment transport rates (by aeolian, fluvial and colluvial processes). A substantial body of literature has focussed on quantifying the inputs, flows and retention of atmospherically derived industrial metals through watersheds using a mass balance approach, often in areas experiencing relatively high rates of industrial metal enrichment (Landre et al., 2010; Lindberg and Turner, 1988; Watmough and Dillon, 2007). However, despite collected aerosol samples universally recording industrial metal enrichment (e.g. Arimoto et al., 1995; Huang et al., 2001; Marx et al., 2014b; Witt et al., 2006) there are few studies which examine the relative significance of the deposition of industrial metals across a variety of environmental archives (e.g. Landre et al., 2010; Rose et al., 2012; Starr et al., 2003; Watmough and Dillon, 2007), where they may potentially concentrate or dilute depending on the behaviour of individual metals (e.g. their particle reactivity) and hydrological and geomorphic processes.

This paper adopts a landscape-scale approach to examine patterns of industrial metal enrichment in the surface environments of the Snowy Mountains Australia. It aims to investigate the significance of atmospherically derived industrial metals in different parts of the landscape, using enrichment factors to assess the degree of contamination. This study builds on the results of two previous studies which examined metal accumulation in peat mires (Marx et al., 2010) and tarn-lakes (Stromsoe et al., 2013). However, whereas those studies focused on the chronology (historical variability) and source appointment of industrial metals, this study compares atmospheric enrichment of metals and their accumulation in various environmental archives (peats, lakes, reservoirs and soils) to investigate patterns of dilution and concentration across the landscape. Together these provide a perspective on the environmental significance of atmospheric pollutants in this region and on the fate of atmospheric pollutants in the surficial environment more broadly.

2. Physical setting

The Snowy Mountains are located in southeast Australia (Fig. 1) and, rising to 2228 m (Australian Height Datum - AHD), are the highest region in Australia. They form part of the Palaeozoic Lachlan Fold Belt, consisting primarily of granitic and sedimentary rocks with minor metamorphics and volcanics also present. The Lachlan Fold Belt forms part of the eastern boundary of the Murray-Darling Basin (MDB), a large sedimentary basin (~1 million km^2) covering approximately 1/7 of the Australian continent. Much of the MDB is classified as semi-arid, with rainfall decreasing westward. The basin is Australia's most important agricultural region, with extensive livestock grazing and cropping, and contains significant mineral resources; including the globally important Pb-Zn-Ag mines at Broken Hill (Fig. 1).

The Snowy Mountains experience a cool montane climate. Annual temperatures vary from 18° C (summer) to -7° C (winter), with annual precipitation ~2000 mm and prevailing westerly quarter winds (BOM, 2014a). Snow is generally present on the peaks for between 3-6 months of the year. Despite their alpine setting, the Snowy Mountains can be considered relatively stable in a geomorphic context, a result of the intraplate setting of the Australian continent combined with a relative lack of recent glacial activity (Barrows et al., 2001). The Snowy Mountains therefore

experience low denudation rates (Bishop and Goldrick, 2000; Young and McDougall, 1993) and sediment yields that are approximately 1-2 orders of magnitude lower than European alpine areas (Stromsoe et al., 2013; Yu and Neil, 1994).

Alpine soils of the Snowy Mountains are classed as Chernic Tenosols characterised by a high organic content and consisting of an A horizon overlying a BC horizon (McKenzie et al., 2004). The soils are also noteworthy in that they contain a high proportion of dust transported from the MDB (Costin et al., 1952; Johnston, 2001; Marx et al., 2011). This is of significance in the context of this study because industrial metals are enriched in dusts (Marx et al., 2008; Marx et al., 2014b), implying that high concentrations of industrial metals may be present in the soils of the Snowy Mountains. Vegetation above the tree line consists of alpine herb fields and heath, with ombrotrophic *Sphagmun* peat mires blanketing extensive areas (Costin, 1972; Martin, 1999). Below the treeline vegetation consists largely of Snowgum (*Eucalyptus pauciflora)* woodland with peat mires common as valley fills.
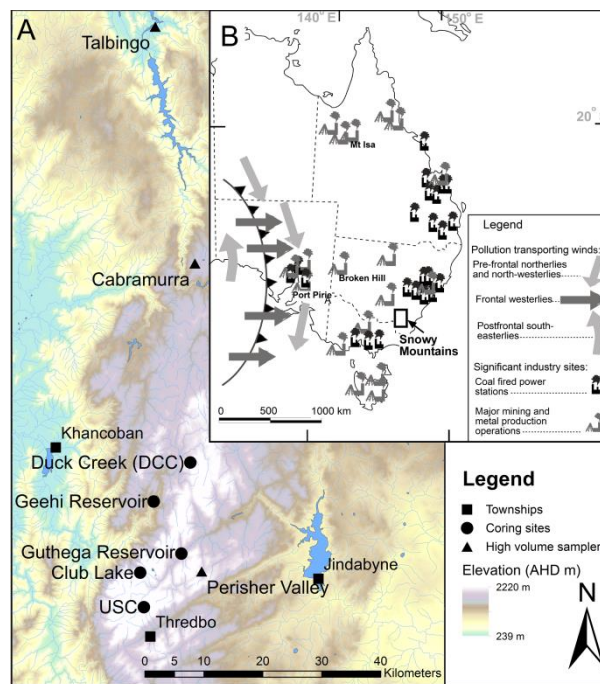
Figure 1. Locations of sampling sites in the Snowy Mountains. Aerosol samples (triangles) were collected from Talbingo, Cabramurra and Perisher. Sediment cores (circles) were collected from peat mires (DCC and USC), Club Lake and Geehi and Guthega reservoirs. Soils were sampled along a catena near Guthega Reservoir (see Fig. 4.2). The inset shows the position of the Snowy Mountains in eastern Australian, major industrial sites in eastern Australia and likely pollution transporting winds (after Marx et al., 2010).

3 Anthropogenic disturbance and sources of metals

The study region is located within Kosciusko National Park from which farming and resource extraction are currently excluded; however, alpine areas were used for grazing from the 1860s until the mid-1900s. In addition, minor local mining, mainly comprising small-scale alluvial Au workings occurred during the mid to late 1800s. Sporadic Ag, Cu and Sn mining continued up until the early 1900s but quantities produced were generally too small to be commercially viable. A major hydro-electric power generation scheme (The Snowy Mountains Scheme) was constructed in the Snowy Mountains from 1949. This involved construction of a series of hydroelectric dams and associated infrastructure. A significant skiing industry also occurs within the Snowy Mountains. While it is possible that these activities may result in minor additions of metals to the environment, previous studies of metal accumulation in sedimentary archives have not overtly recorded metals from these sources (Marx et al., 2010).

Since 2004 a cloud seeding operation has been undertaken in the Snowy Mountains in which AgI is released into the atmosphere to promote the formation of snow crystals during favourable conditions. Between 2004 and 2013 the operation released on average 10.5 kg of elemental Ag annually. This represents a potential additional source of Ag to the Snowy Mountains environment. Ag is presented along with the other metals in the current study but will be examined further in a subsequent paper.

Marx et al. (2010) found that the major sources of metal pollutants to the Snowy Mountains environment were remote sources upwind (west) of the range. These include a number of significant mining and metal production operations, most notably the Broken Hill mines and the smelters at Port Pirie; coal combustion (coal fired power stations are located around major cities upwind of the Snowy Mountains including Melbourne and Adelaide) and agriculture (Fig. 4.1).

4 Methods

4.1 Conceptual approach and sampling

The sampling strategy followed a multi-archive approach in order to examine the extent of industrial metal enrichment in the Snowy Mountains. This involved collecting and dating sediment cores from a range of geomorphic and hydrologic settings in the alpine and subalpine zone. These included from atmospherically-fed (ombrogenous) peat mires, which in the Snowy Mountains are located in upper catchments of the alpine zone, alpine lakes with small catchments, which are fed by both direct atmospheric deposition, but also by significant terrestrial runoff, and subalpine reservoirs with larger catchments fed overwhelmingly from runoff (Fig. 1 and 2 and Table 1). In addition, soil pits were sampled from a range of geomorphic positions. Together, these sedimentary archives serve to demonstrate the relative significance of atmospheric industrial metals in settings influenced by a range of additional processes including weathering, pedogenic processes and alluvial and colluvial sediment transport. In addition, a snapshot of industrial metal enrichment in the atmosphere of the Snowy Mountains was provided by sampling contemporary aerosols using a network of continuously operating high volume particulate samplers (Fig. 1 and 2 and Table 1). These were used to examine the partitioning of industrial metals between the atmosphere and the surface environments sampled and to provide an estimate of metal deposition to the surface.
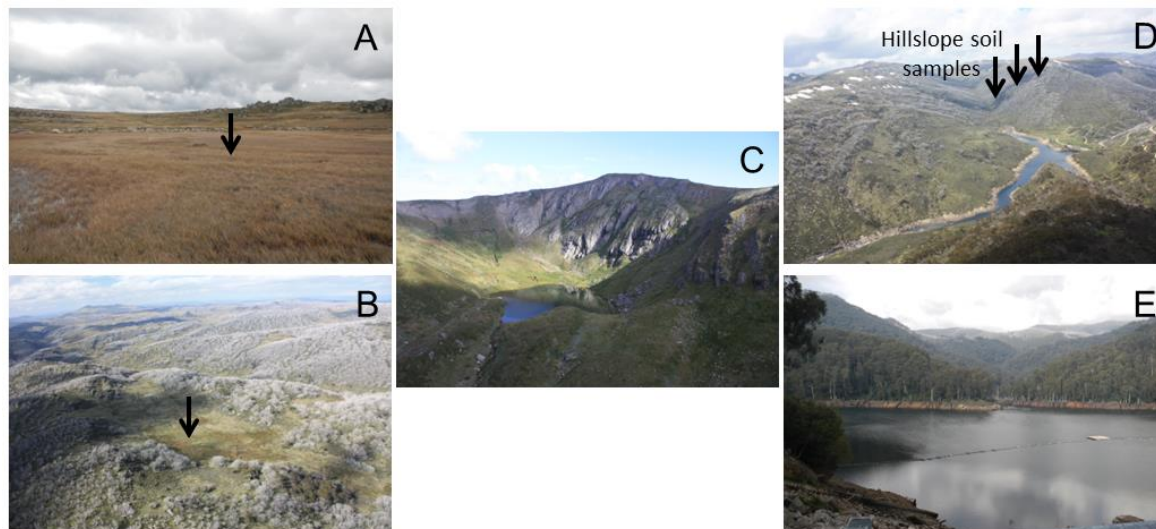

Figure 2. Surface sampling sites; A) Upper Snowy (USC) peat mire, B) Duck Creek (DCC) peat mire (arrows show location of cores), C) Club Lake, D) Guthega Reservoir (arrows show location of soil sampling sites within the catchment) and E) Geehi Reservoir.

4.2 Aerosol sampling

Aerosols were sampled continuously over one year (October 2012-October 2013) at three locations (near Talbingo and Cabramurra Townships and near Perisher) across the Snowy Mountains using Total Suspended Particulate high volume particulate samplers (Flow Set, Lear Siegler Australasia) loaded with polycarbonate membrane filters (nominal 3 µm pore size, Sterlitech) (Fig. 1). Filters were replaced at 1-4 week intervals and kept in chemically inert plastic bags prior to and following collection. Prior to use, filters were dried at 40^0 C degrees for 20 hrs and weighed on a 4 decimal place analytical balance. Following collection, filters were re-dried and weighed in order to determine dust mass. A sub-sample of dust was then gently scraped from the filter using a stainless steel spatula from where it was prepared for trace element analysis. A total of 50 aerosol samples were collected across the three sites during this study and analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Table 1. Sample details

Name	Sample type	Environment	Location	Altitude (m AHD)	Catchment	Core/pit depth (m)	Sampling date	Sampling resolution	Number of analysed samples
USC	Sediment core	Peat mire	-36.463°, 148.299°	1940	Guthega	1	2006	2-5 mm	79
DCC	Sediment core	Peat mire	-36.247°, 148.372°	1790	Geehi	0.66	2006	2-5 mm	81
Club Lake (CL3)	Sediment core	Lake	-36.414°, 148.291°	1950	Guthega	0.38	2011	2-5 mm	43
Geehi Reservoir	Sediment core	Reservoir	-36.379°, 148.371°	1578	Geehi	0.27	2012	2-5 mm	32
Guthega Reservoir	Sediment core	Reservoir	-36.305°, 148.316°	1100	Guthega	0.26	2012	2-5 mm	20
Guthega ridge	Soil pit	hill slope	-36.360°, 148.373°	1866	Guthega	0.6	2013	100 mm	6
Guthega mid-slope	Soil pit	hill slope	-36.360°, 148.370°	1804	Guthega	0.67	2013	100 mm	5
Guthega toe-slope	Soil pit	hill slope	-36.360°, 148.366°	1665	Guthega	0.46	2013	100 mm	3
Talbingo	Aerosols	Atmosphere	-35.583°, 148.293°	396	Jounama		Oct 2012-Oct 2013	1-4 wks	20
Cabramurra	Aerosols	Atmosphere	-35.939°, 148.379°	1484	Tumut		Oct 2012-Oct 2014	1-4 wks	12
Perisher	Aerosols	Atmosphere	-35.394°, 148.394°	1904	Jindabyne		Oct 2012-Oct 2015	1-4 wks	24

We note that industrial aerosols are often submicron in size, however, these are typically scavenged from the atmosphere with larger particulates with which there are transported and deposited (Han et al., 2004; Jaffe et al., 1999; Marx et al., 2008). Membrane pore filters are also known to efficiently collect particles substantially smaller than the nominal pore size with efficiency increasing substantially with increased filter loading, including over significantly shorter sampling intervals than those used here (Kemp and Kownacka, 1987; Yamamoto et al., 2004). In addition, previous field experiments obtained with using these same filters yielded largely identical results to those obtained on a cascade impactor (Marx et al., 2014a), implying use of these filters is appropriate in this context.

4.3 Estimation of aerosol/metal deposition flux

To assess the relative importance of atmospheric industrial metal fluxes to each archive, deposition rates were estimated from the atmospheric concentrations using simple models of wet and dry deposition (Jacobson, 2005; Jickells and Spokes, 2001). We note that, as with any inferential method, there are likely to be considerable uncertainties inherent in these estimates. They should therefore be considered as an estimate of the relative significance of atmospheric deposition by comparison to surface geomorphic inputs rather than an absolute measure of trace element flux.

Dry Deposition

Dry deposition was estimated from the aerosol concentration and estimated dry deposition velocities for individual aerosol particle sizes according to equation 1.

$$F_d = \sum_{i=1}^{n} V_{d,i} * C_i \tag{1}$$

where F_d is the dry deposition flux (ug m^{-2} s^{1}), V_d the particle size specific deposition velocity (m s^{-1}) and C is concentration of that size-class in the atmosphere (ug m^{-3}).

Deposition velocities were determined from particle size/mass distribution and mean atmospheric conditions during the sampling intervals using Stokes Law according to Jacobson (2005). The dry deposition flux for individual industrial metals was then estimated from the

aerosol deposition rates and the individual trace metal aerosol concentrations. A detailed description of the estimation method and equations is provided in the supplementary material.

Wet Deposition

Precipitation

Due to the lack of data with which to parameterise more complex processes-based micrometerological models, wet deposition (precipitation deposition + cloud water deposition) was estimated from simple empirical relationships relating aerosol concentration at ground level to cloud water and precipitation concentrations. Precipitation deposition was calculated by estimating the concentration of metals in precipitation from their concentration in the atmosphere using a scavenging ratio (Z), defined by the equation 4 (Duce et al., 1991):

$$Z = C_p/C_a \tag{2}$$

where C_p is the concentration of the metal in precipitation and C_a its concentration in the atmosphere . A detailed description of the process and a full set of equations is provided in the supplementary material.

We note the limitations of this approach, including in the assumption that concentrations at ground level representative of the concentration in the air from which the pollutant is being scavenged (e.g. in the precipitating cloud) (Barrie, 1985). Thus, scavenging ratios are subject to considerable uncertainty and values may vary up to ˜4-6 fold between locations and between trace elements (Arimoto et al., 1985; Gao et al., 2003). Previously measured scavenging ratio values for pollutant aerosols range most frequently from ˜ 100 – 500 (Arimoto et al., 1985; Duce et al., 1991; Kane et al., 1994; Mason, 2013), with extreme values of between 30 (Zn, Cu) (Mason, 2013) and 1500 (also Cu) (Arimoto et al., 1985). In this study the value of Z is taken as the mean of previously published values for pollutant elements, including Cu, Ni, Zn, As, Pb and Cd (Z = 380) (Arimoto et al., 1985; Kane et al., 1994; Mason, 2013). We note that there is a substantial degree of uncertainty surrounding the selection of this value. Therefore the calculation of wet deposition is repeated using upper and lower values of the mean ± the standard error of previously published values for Z (Z = 460 and 305 respectively), providing an estimated range for the flux of pollutant elements from the atmosphere to the surface. As the relative

scavenging efficiency of snow is largely unknown (Wang et al., 2014), a single Z value is applied to the total precipitation amount. Likewise, the application of a single mean value to all trace elements is necessitated by the dearth of available data for many of the pollutants considered in this study. These assumptions should be noted as a potential source of error in the deposition estimates.

Cloud water deposition

Cloud water interception is an important mechanism of trace element deposition to high-elevation ecosystems where it may account for ≥ 50% of the total wet deposition flux (Herckes et al., 2002). In this study cloud water deposition was estimated from the concentration of metals in the atmosphere, the scavenging efficiency of cloud water for aerosols, and the deposition velocity of cloud water drops according to equation 3.

$$F_{i,cw} = F_{cw} * C_{i,cw} \tag{3}$$

where $F_{i,cw}$ is the annual cloud water flux of element i (ug m^{-2} y^{-1}), F_{cw} is the annual cloud water hydrologic input (g m^{-2} y^{-1}), and $C_{i,cw}$ (ug g^{-1}) is the mean annual concentration of the element in cloud droplets. The hydrologic flux (F_{cw}) was determined from the estimated mean liquid water content of the cloud (*LWC*), the deposition velocity of cloud water droplets ($V_{c,d}$) and the time the site spends below the cloud base each year (*t*). The air equivalent concentration of each element in cloud water ($C_{i,cw}$) was estimated from the concentration in the element in interstitial aerosols (i.e. from the TSP samplers) and the scavenging efficiency of cloud water drops for aerosols (*E*). This approach is outlined in detail in the supplementary material.

The measurement of *E* (scavenging efficiency), *LWC* (liquid water content) and *t* (time below the cloud base) was beyond the scope of this study. Values are therefore estimated from previously published values for mountain environments elsewhere (*E*), from limited empirical data available for the Snowy Mountains (*LWC*) and from observation (*t*). To provide an estimate of uncertainty associated with the selection of these values the deposition flux calculations were performed using mid, low and high estimates for *E, LWC* and *t*.

4.4 Peat and lake cores

Two peat cores were collected from two mires in the Snowy Mountains in 2006. A 1 m core (named USC) was collected from the headwaters of the Snowy River (-36.463°, 148.299° 1940 m AHD) in the southern Snowy Mountains, while a 0.66 m core was collected from Duck Creek (DCC) in the central Southern Snowy Mountains (-36.247°, 148.372°, 1790 m AHD) (Fig. 1 and 2). A 0.38 m core (CL3) was collected from a Club Lake (-36.414°, 148.291°, 1950 m AHD), a tarn in the central southern Snowy Mountains (Fig. 1 and 2) in 2011. Each core was sectioned into sub-samples and dated using ^{210}Pb and ^{14}C. Metals and trace elements were then analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) on individual sub-samples through each core (n = 79, 81 and 43 for USC, DCC and the Club Lake core, respectively). Full details of the peat core collection, processing and dating was described in Marx et al., (2010), while the Club Lake core was described in Stromsoe et al. (2013).

4.5 Soil samples

Samples were collected from within three soil pits excavated along a hillslope cantena in the catchment of Guthega Reservoir in 2012 (Fig. 1 and 2). The hillslope had a westerly aspect, an average slope >20° and measured approximately 0.5 km in length. Three soil profiles were excavated at 1) the top of the hill slope close to the ridge crest (-36.360°, 148.373°, 1866 m AHD), 2), the mid-slope (-36.360°, 148.370°, 1804 m AHD) and 3) the toe slope (-36.360°, 148.366°, 1665 m AHD) respectively, in each case until the saprolite was reached (at approximately 0.6 m). Samples were collected at 100 mm depth intervals in each soil pit. They were then dried, crushed in a mortar and pestle to homogenise and their trace element composition analysed by ICP-MS.

4.6 Reservoir cores and sample processing

In 2011 cores were collected from the Guthega (-36.379°, 148.371°, 1578 m AHD) and Geehi (-36.305°, 148.316°, 1100 m AHD) reservoirs, located in the southern and central Snowy Mountains, respectively, using a gravity corer (Fig. 1 and 2). Guthega reservoir was constructed in 1955 and has a contributing catchment of 91 km^2, which is largely within the alpine zone and includes Club Lake, the mire from where the USC was collected, and the hillslope from where the soil samples were collected. The reservoir has an area of 0.26 km^2 while its depth varies as a

function of precipitation and hydro-electric power generation. Geehi reservoir was constructed in 1967 and has a contributing catchment area of 148 km^2, which includes the Duck Creek (DCC) mire. Approximately 2/3 of the catchment is within the alpine zone with the reservoir having an area of 0.66 km^2 while again its depth is variable in time. A 0.27 m core was extracted from Guthega Reservoir and a 0.26 m core from Geehi Reservoir. Cores were extracted from approximately the middle of each reservoir.

In the laboratory the cores were sliced into 2 to 5 mm samples using a stainless steel scalpel. The outermost 3 mm of each core was discarded to prevent contamination by smearing of material during core collection. Each sample was dried at 60°C for 36 hours then lightly crushed with a mortar and pestle to remove large aggregates. The metal concentration of 32 samples from Guthega and 20 samples from Geehi were analysed by ICP-MS. Subsamples from each core were dated using ^{210}Pb.

4.7 Trace element analysis

The analysis of trace elements (including industrial metals) in the aerosol samples, sediment samples extracted from the reservoirs cores, soils and samples from the Club Lake core (previously presented in Stromsoe et al., 2013) was performed by solution quadrupole ICP-MS on a Agilent 7700x instrument at the Department of Earth Sciences University of Melbourne, Australia. Sediment samples from the peat cores were analysed at Laurentian University, Ontario, Canada on a Varian 810 instrument using the same approach (Marx et al., 2010). Analytical details and presentation of rock and soil standards are provided in the supporting material and Supplementary Table 2.

4.8 Dating of sediment cores

Lake and peat cores were dated using ^{210}Pb and ^{14}C Accelerator Mass Spectrometry. Results and age model construction was previously discussed in Stromsoe (2013) and Marx et al., (2010), respectively. Sediment samples from both the Guthega and Geehi reservoirs were dated using ^{210}Pb at the Institute for Environmental Research, Australian Nuclear Science and Technology Organisation (ANSTO) by Alpha spectrometry. Dating by ^{210}Pb was performed by measuring ^{210}Po activity, the granddaughter of ^{210}Pb, with which it is assumed to be in secular equilibrium.

Supported ^{210}Pb was determined by measuring ^{226}Ra, with unsupported ^{210}Pb calculated from the difference between supported and total ^{210}Pb activity (Harrison et al., 2003).

Unsupported ^{210}Pb activities in both Geehi and Guthega reservoirs cores were relatively high (supplementary Table 3 and Fig. 4.3). Unfortunately, the coring equipment was not able to collect more than 0.26 m length core at Geehi and 0.27 m at Guthega, therefore unsupported ^{210}Pb activities could not be determined below these depths. Five samples between 0 and 155 mm depth were analysed from the Geehi core while seven samples between 0 and 200 mm depth were analysed from the Guthega core (^{210}Pb activities are presented in supplementary Table 3).
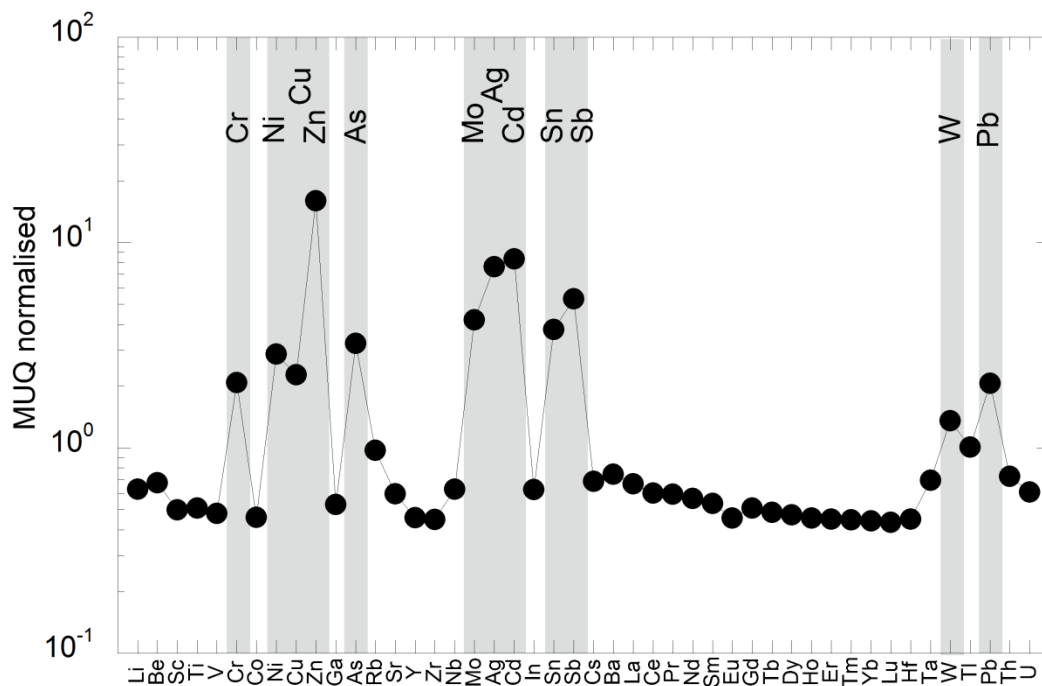
Figure 3. The average trace element composition of aerosols collected during this study normalised against MUQ (MUd from Queensland Kamber et al., 2005). Note As, Mo, Cd and Sb data are from Marx and Kamber (2010); Ag and In data from the Perisher core which predates industrial activity and is considered of local sediment chemistry (see Marx et al., 2011). The abundance of metals with concentrations significantly greater than MUQ are indicated in grey.

5. Results

5.1 Atmospheric aerosol concentrations and industrial metal enrichment

Mean aerosol concentrations over the Snowy Mountains, as measured by the three high volume particulate samplers during 2012-2013, were 7.8 ± 0.8 µg m^{-3}. Concentrations were lower during the austral winter (June-August) (4.6 ± 0.2 µg m^{-3}) relative to the rest of the year (8.9 ± 0.8 µg m^{-3}). These aerosols included industrial metals, natural dust and organics.

To identify which metals are perturbed within the atmosphere of the Snowy Mountains, i.e., have concentrations higher than would be expected naturally, the average trace element concentrations of all aerosol samples were plotted normalised against MUQ (MUd from Queensland; Kamber et al., 2005) (Fig. 3). MUQ is a compilation of alluvial sediment samples from 25 Queensland Rivers draining the major geologic units of eastern Australia. It is therefore representative of the average background (unpolluted) chemistry of rocks and sediments in eastern Australia in addition to average global composition of Upper Continental Crust. Thus it is also broadly representative of the composition of mineral dust in eastern Australia. A number of metals exhibited high concentrations with respect to continental crust, implying their concentration has been influenced by industrial activity. These were Cr, Ni, Cu, Zn, As, Mo, Ag, Cd, Sn, Sb and Pb. We note, however, the surface sediments which constitute MUQ may also be enriched in some industrial metals (see Kamber et al., 2010). Normalisation of aerosols against MUQ may therefore mask enrichment in some metals, although it still serves to show that a number of metals are enriched even with respect to the general perturbation of surface sediment geochemistry by industrial activity.

The atmospheric concentrations of individual metals were estimated from the product of the total aerosol mass per unit atmosphere and the elemental composition of sampled dust. Average atmospheric concentrations of known pollutant metals were generally < 1000 pg m^{-3} and ranged from 1 pg m^{-3} (Ag) to >3500 pg m^{-3} (Zn) (Table 2). Zinc, however, was present in high concentrations in blank analyses of the polycarbonate membrane filters (Marx et al., 2014a). Consequently, some of the total Zn concentration in this context is likely to be derived from the filter itself. Other metals present in concentrations >100 pgm^{-3} include Cr, Ni, Cu and Pb (Table 2).

Table 2. Average atmospheric industrial metal atmospheric concentrations for selected studies (pg m^{-3})

Location	This study[#]	Alpine New Zealand[*1]	West Coast New Zealand[*2]	Antarctica[#3]	Samoa[#4]
Cr	940 ±925	-	433 (300-570)	-	-
Co	77 ±74	30.7 ±23.9	-	-	0.37 ±3.0
Ni	539 ±946	371.4 ±313.9	208 (140-270)	-	-
Cu	388 ± 203	192 ±203.7	570 (400-750)	1 ±5.6	13 ±2.6
Zn	3611 ±3604	-	710 (490-940)	6.1 ±4.8	64 ±2.2
As	118 ± 80	5.6 ±7.0	-	-	-
Mo	14 ±8	14.6 ±13.2	-	-	-
Ag	1 ±1	4.2 ±6.8	-	-	11 ±3
Cd	5 ±7	17.8 ±19.9	7 (5-9)	0.06 ±0.06	-
Sn	80 ±167	-	-	-	-
Sb	17 ±10	53.2 ±23.4	4 (2-5)	-	0.19 ±1.1
W	17 ±15	-	-	-	-
Pb	226 ± 128	163 ±136.6	420 (290-560)	4.7 ±3.2	16 ±2.4

[#]Mean and standard deviation

[*]Mean and range (in parentheses)

[1]Marx et al., (2014a)

[2]Marx et al., (2008)

[3]Dick et al., (1991)

[4]Arimoto et al., (1987)

Given the potential enrichment of MUQ surface sediments, a more accurate approach for calculating metal enrichment in the aerosols is to use mineral dust sediments which were buried prior to the onset of industrial activity in Australia in the USC core, i.e. prior to ~1850 (Marx et al., 2011 and Fig. 4). The enrichment factor can then be calculated from equation 4 (Arimoto et al., 1990; Shotyk, 2002):

$$EF = (Cm/Cc_{ex})/(Cm/Cc_{natavg}) \qquad (4)$$

where EF is the enrichment factor, Cm/Cc_{ex} is the ratio of a metal whose concentration is suspected of being perturbed (Cm) in the aerosol samples to that of a conservative element (Cc),

and Cm/Cc_{natavg} is the average ratio of Cm to Cc in the pre-pollution (pre-1850) section of the USC core. To reduce the possibility that the behaviour of the conservative element may influence the metal EF, the average EF values using four conservative elements (Ta, Ga, Sc and Ti) were calculated (see Marx et al., 2014b).
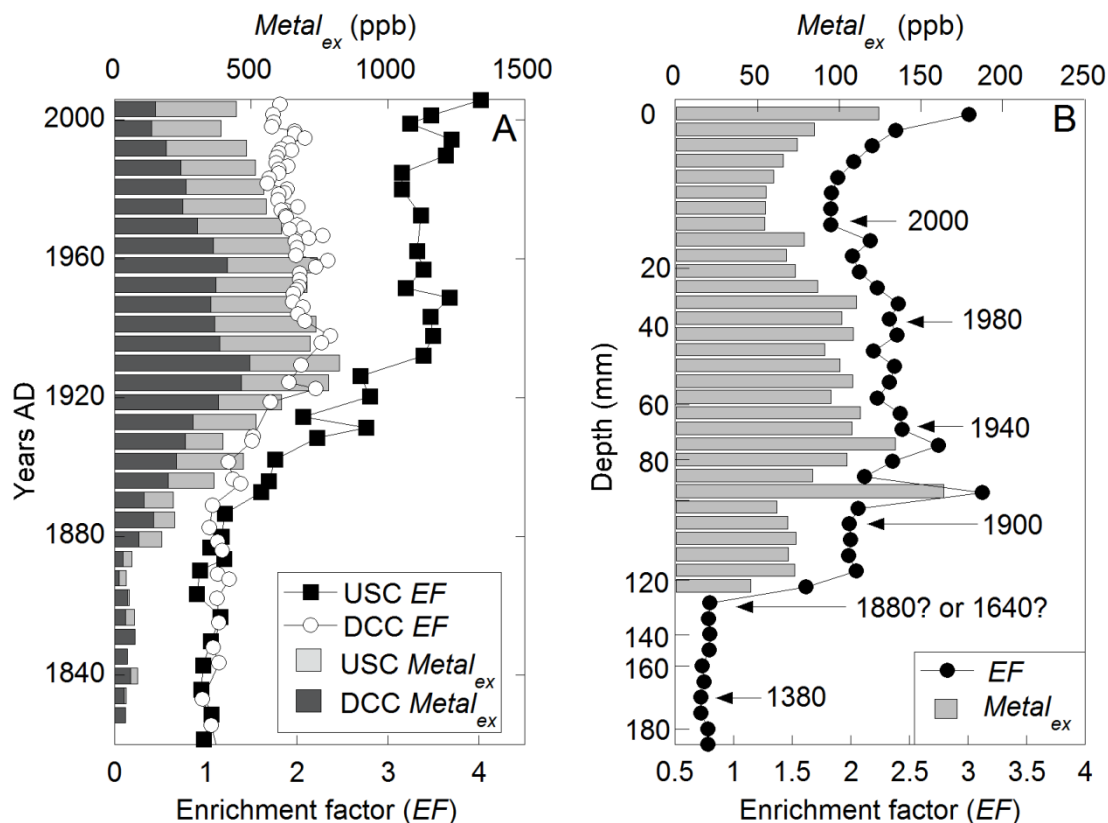

Figure 4. Antimony (Sb) enrichment (*EF*) and excess metal (*Metal_ex*) concentrations in peat mires (USC and DCC panel A) and Club Lake (panel B). Note for plotting convenience excess Sb in DCC is shown converted to the same number of data points as in USC (by averaging). In panel B, depth is plotted as a non-linear timescale and dates (AD) are indicated.

The average EF for metals in aerosols is shown in Figure 5a. Metals were enriched in aerosols in the order Ni (2.6) < Pb (3.5) < Co (3.6) < Cr (4.8) < Ag (12) < Mo (12) < Cu (13) < Sn (16) < As (24) < Cd (27) < Sb (48). EF in the aerosols varied seasonally, increasing during the austral winter and early spring (illustrated for Cr, Pb and Sb in Fig. 4.6). Wintertime EF were on average 3 times those of summer and coincided with reduced atmospheric dust concentrations. This pattern is consistent with the regional climatology (Chubb et al., 2011). During the austral winter southern Australia experiences an increase of west to south westerly winds resulting in

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increased precipitation and reduced dust entrainment (McTainsh et al., 1998). The implication of this is increased *relative* transport of industrial metals over naturally derived metals and crustal elements contained in dust occurs during the winter, i.e. there is less atmospheric dust.
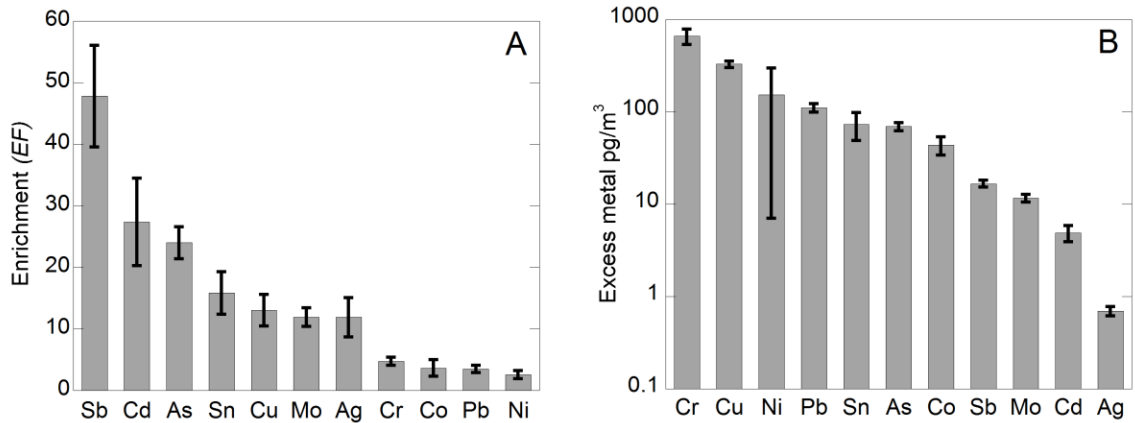

Figure 5. A) Mean enrichment factors (*EF*) for industrial metals in Snowy Mountains aerosols between 2012/2013. B) Mean excess industrial metal (*Metal_ex*) concentrations in the same aerosols. In both panels bars indicate standard errors.
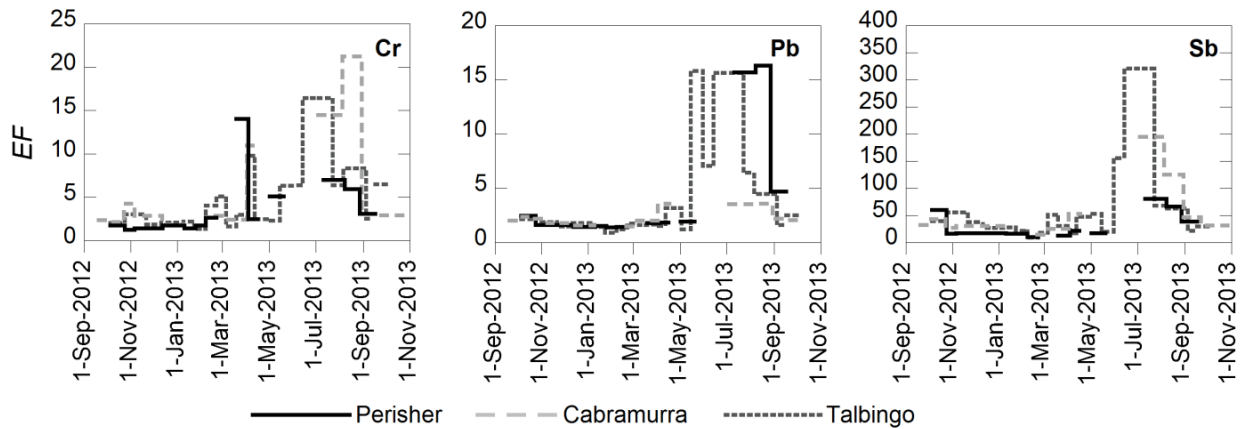

Figure 6. Time series of Cr, Pb and Sb enrichment (*EF*) in Snowy Mountains aerosols (September 2012-October 2013).

Excess atmospheric metal concentrations, i.e. the pollution derived component, were calculated from equation 5:

$$Metal_{ex} = Cm - (Cm/EF) \tag{5}$$

The $Metal_{ex}$ concentrations range from (mean ± standard error) <1 pg m^{-3} ± < 1 (Ag) to 660 ± 125 pg m^{-3} (Cr) (Fig. 4.5b). The difference between EF and $Metal_{ex}$ reflects the relative natural concentration of each metal in the atmosphere, i.e. its relative concentration in upper continental crust. Consequently, for example Sb, which was highly enriched ($EF = 48$) was present at < 20 pg m^{-3}, 7 times less than the concentration of Pb (110 pg m^{-3}) with an EF of 3.5 (Fig. 5a and b). This is an important distinction in this context because the potential for contamination of the surficial environment by atmospheric pollution may be determined not only by the degree of enrichment, but also by the mass of industrial metal deposited to the surface.

In contrast to EF, $Metal_{ex}$ did not display a clear seasonal pattern (illustrated for Cr, Pb and Sb in Fig. 7) (although some wintertime enrichment is still apparent). This is explained by variability in atmospheric concentrations of industrial metals *relative* to natural dust.
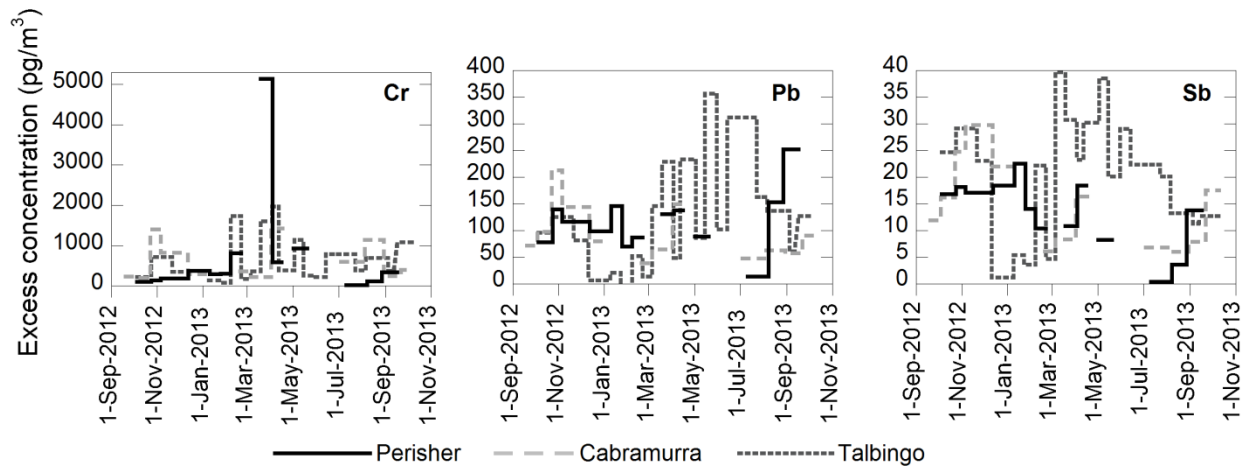

Figure 7. Time series of excess ($Metal_{ex}$) Cr, Pb and Sb concentrations in Snowy Mountains aerosols (September 2012-October 2013).

5.2 Aerosol and industrial metal deposition

The estimated average aerosol deposition rate during the sampling period (2012-2013) was ˜30 g $m^{-2} y^{-1}$. The flux for individual industrial metals, i.e. those enriched relative to MUQ (Fig. 3), varied by two orders of magnitude (Table 3), the range of enrichment being controlled by a combination of the industrial emission load for a particular metal and its natural concentration within upper continental crust. Estimated deposition flux of enriched industrial metals (mid estimate and (range)) ranged from 5 (5-10) $\mu g \, m^{-2} \, y^{-1}$ for Ag to a maximum of 3995 (3600-7910) $\mu g \, m^{-2} \, y^{-1}$ for Cr (Table 3). Notably, several potentially toxic metals are estimated to be deposited to the soils, lakes and peats of the Snowy Mountains at rates greater than 1,000 $\mu g \, m^{-2} \, y^{-1}$, including Cr, Cu, Ni and Pb (Table 3).

Table 3. Estimated total and excess metal flux from the atmosphere to the surface of the Snowy Mountains

	Total Flux ($\mu g \, m^{-2} \, y^{-1}$) mid (range)	Excess Flux ($\mu g \, m^{-2} \, y^{-1}$)
Cr	3995 (3600-7910)	2980 (2700-5730)
Co	310 (280-630)	190 (170-370)
Ni	2590 (2365-4835)	1150 (1085-1785)
Cu	2370(1885-3665)	1830 (1690-3200)
As	490 (440-985)	460 (420-930)
Mo	60 (55-120)	55 (50-105)
Ag	5 (5-10)	5 (5-10)
Cd	25 (20-45)	20 (20-40)
Sn	305 (275-640)	295 (265-605)
Sb	75 (70-145)	75 (70-145)
W	65 (60-135)	25 (25-50)
Pb	1095 (1000-2035)	670 (625-1136)

A proportion of total metal flux is derived from natural sources, i.e. from mineral dust. Therefore, a more accurate assessment of the contribution of industrial pollutants to the Snowy Mountains is provided by the $Metal_{ex}$ flux (equation 5). Estimated $Metal_{ex}$ flux to the Snowy Mountains as a proportion of the total flux (i.e. natural + industrial) ranges from 35-45% for Ni (where excess flux is 1150 (1085-1785) µg m^{-2}y^{-1}) to 98% for Sb (where excess flux 75 (70-145) µg m^{-2}y^{-1}) (Table 3). $Metal_{ex}$ fluxes were highly variable between the different industrial metals, ranging from 5 (5-10) (Ag) to 2980 (2700-5730) (Cr) µg m^{-2} y^{-1}. Excess Cr, Cu, Ni and Pb were estimated to be deposited at rates close to, or greater than, 1000 µg m^{-2} y^{-1} implying *prima facie* that these metals may have the greatest impact on the Snowy Mountains environment (Table 3).

5.3 Industrial metal accumulation in peats and lakes

The results of metal accumulation and enrichment in the peat mires and Club Lake have been described in detail elsewhere (Marx et al., 2010; Marx et al., 2014c; Stromsoe et al., 2013) and are summarised in brief here only. The peat mires and Club Lake represent different examples of natural sedimentary archives which serve to show how metals are being incorporated into the surficial environment. For both the peat cores and the lake core, *EF* were calculated by comparing the chemistry of the pre-industrial section of each core (pre-1850) with the industrial section of the cores using equation 4.

Both peat cores displayed clear temporal trends in metal enrichment that broadly reflected the history of industrial activity in southern Australia, i.e. changing *EFs* through time are primarily a function of changing industrial activity (Marx et al., 2014b). Metal enrichment commenced in the peat cores at approximately 1890, with more significant enrichment occurring after 1980 (shown for Sb by way of example in Fig. 4A). In the figure, both peat mires record a sharp rise in Sb enrichment beginning at c.1890. After 1940 the *EF* becomes stabilised at approximately 3.5 in USC and 2 in DCC. The USC mire shows a further increase in *EF* to c. 4 after 1980 which continues to the present. Excess Sb (*metal_{ex}*) in both cores generally reflect these trends, although *metal_{ex}* in DCC decreases after c. 1960 implying a reduction in industrial Sb deposition at that site.

The pre-1980 section of the core, therefore, reflected historical atmospheric industrial metal concentrations (Marx et al., 2010). By comparision, metal behaviour in the upper most section of the peat cores (post-1980) can be considered broadly comparable with the composition of the contemporary atmosphere (i.e. relatively, though not precisely, contemporaneous with the collected aerosol samples). The same suite of metals that were found enriched in the aerosols samples (Pb, Ag, Cr, Mo, Cd, Co, Cu, Ni, Sb, As, Zn and Sn) were also enriched in ombrotrophic (rainfall fed) peats (Fig. 8).

Figure 8. Industrial metal enrichment (*EF*) in peat mires post-1980 plotted beside aerosol enrichment (2012/2013) for comparison.

Average industrial (post-1850) *EF* were 2.1 and 1.7 in USC and DCC respectively, while post-1980 *EF* were 3.0 in and 2.2, respectively, meaning industrial metal concentrations have increased toward the present. Metals with average industrial *EF* > 2 in one or both cores were Mo, Cd, Sb, Cu, As, Pb, Ni, Co, Sn and Ag (*EF* are shown in Fig. 8). Metals were typically less enriched in post-1980 section of the peat cores by comparison to the collected aerosols by approximately 5 times in the USC and 7 times in the DCC (Fig. 8). However, the most highly enriched industrial metals in aerosols samples, i.e. those with *EF* > 10 (Sb, Cd, As, Sn, Cu, Mo, Ag) were generally also the most highly enriched metals in the peat cores.

EF were generally higher in the USC by comparison to the DCC by an average of 1.5 ± 0.3 times. This implies the mire from where the USC was collected receives higher atmospheric input and/or lower input of additional mineral matter (alluvial, colluvial sediment or local dust) than the Duck Creek mire, i.e. there is less dilution of the atmospheric signal. An exception to this general pattern was the behaviour of Ag and Ni where the *EF* were close to unity between the two mires, while Co was typically more enriched in DCC, displaying only minor enrichment in USC. *Metal$_{ex}$* concentrations were similarly typically higher in USC (e.g. Fig. 4), although at both sites they were more variable in comparison to *EF* through time. This difference is presumably largely a function of variability in the source(s) of mineral material deposited to the mires, including variability in the sources and relative contributions of long-range dust (e.g. see Marx et al., 2014c) and local sediment input.

By contrast with the studied peat mires, most industrial metals shown to be enriched in aerosols were not enriched within Club Lake sediments (Fig. 9). Industrial *EF* were ~1, i.e. there was no enrichment in industrial metals, for Cr, Co, Ni, Cu, Zn and Sn. Although some metals showed a more significant increase post-1980, average enrichment factors for most metals across this period were also ~1. Consequently, *EF* were on average 10 times less than observed in the aerosol samples. Relatively high rates of local unpolluted sediment generated from the sparsely vegetated cirque walls behind the tarn were concluded to be swamping input of pollutant metals resulting in comparatively low enrichment of lake sediments (Stromsoe et al., 2013).

In exception to the general behaviour of industrial metals, several industrial metals with low natural abundance, including Sb, Mo, As and Cd, displayed more substantial enrichment in Club Lake (mean post-1980 *EF* 2.1, 1.6, 1.3 and 1.4, respectively) (e.g. see Figure 4 and 9). The behaviour of Sb is shown by way of example in figure 4B. Antimony *EF* in Club Lake increases sharply after 1880. They then stabilise at c.1940 at *EF*=2, with the uppermost samples exhibiting a further increase in EF. Overall the chronology of Sb *EF* in Club Lake was comparable to that recorded in the peat mires, however *metal$_{ex}$* concentrations were significantly lower in Club Lake (Fig. 4). Arsenic and Mo displayed similar behaviour to Sb, however Cd showed enrichment in

some samples but with greater variability though time. Silver also displayed minor enrichment over this time with *EF* reaching approximately 1.2 in the uppermost samples from the core.
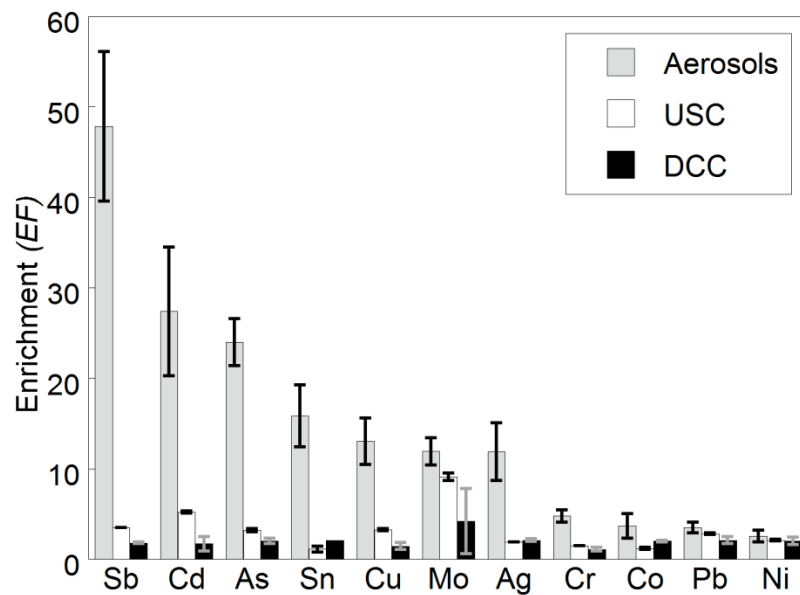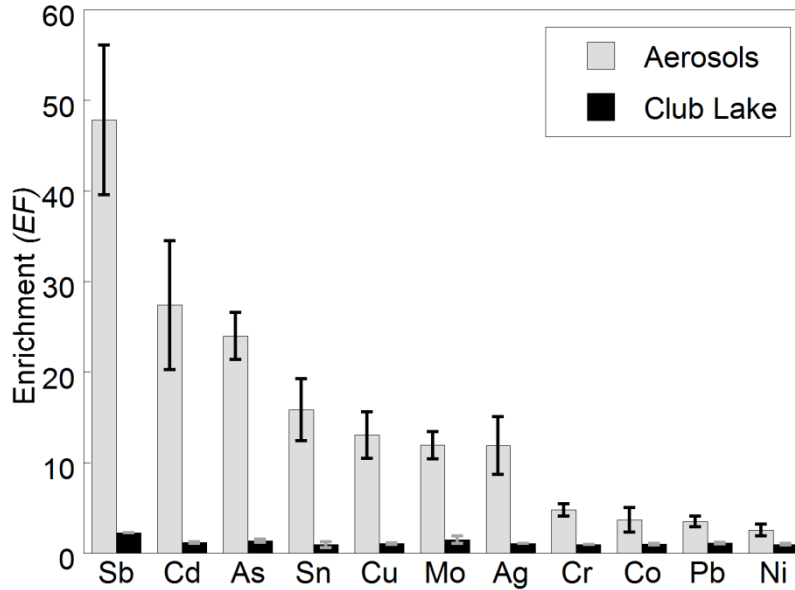

Figure 4. Industrial metal enrichment (*EF*) in Club Lake post-1980 plotted beside aerosol enrichment (2012/2013) for comparison.

4.5.4 Industrial metals in soils

Enrichment factors for the three soil profiles were calculated (using equation 4) relative to sediment samples from a core extracted in the Perisher Valley (Fig. 1). These sediments predate industrial activity and are considered representative of locally transported and eroded sediment in the Snowy Mountains (Marx et al., 2011). Three main *EF* patterns were apparent in the soil profiles. First, Pb and Zn showed apparent generalised enrichment throughout each profile, with no clear change in *EF* with depth (e.g. Pb in Fig. 10A). Second, Cu, Ni and Cr showed enrichment at the bottom of each soil profile, however *EF* decreased toward the soil surface (e.g. Cu Fig. 11A). Third, Mo, Cd, Sb and Ag showed no enrichment at the base of each soil profile, but recorded a pronounced up-profile increase in *EF* (e.g. Mo in Fig 10A). These metals also recorded the highest maximum *EF*. Arsenic patterns were inconsistent between the three soil profiles.

The age of the soil profiles is unknown, it is very unlikely, however, that the base of each soil profile, post-dates industrialisation in Australia, which accords with the onset of industrial enrichment in the peat mires (see Fig. 4 and Marx et al., 2010). Apparent enrichment of metals in the base of the profiles (Fig. 10A) is therefore an artefact of relatively low concentrations of the conservative elements used to calculate the *EF* factor (Sc, Ti, Ga, and Ta) in the soils relative to the Perisher sediments, e.g. the raw Pb concentrations in the ridge top soil are actually highest in the surface soil as opposed to the reverse pattern in *EF* shown in Fig. 10A. Calculating *EF* relative to element concentrations in the lower most soil sample for each profile therefore removes this apparent enrichment in the base of the soil profiles (e.g. Fig. 10B).

The observed low concentrations of conservative trace elements (e.g. Sc, Ti, Ga and Ta) in the base of the profiles arise from the unusual way alpine soils form in the Snowy Mountains. They are fed, at least in part, by dust deposition (Costin et al., 1952; Marx et al., 2011; McKenzie et al., 2004), the rates of input of which may exceed rates of physical and chemical weathering. Calculation of accurate *EF* relies upon the conservative behaviour of the normalising element(s) (Marx et al., 2008). In this case, however, the concentration of conservative elements varies markedly through the soil profiles, presumably as a function of relative dust input versus weathering loss. Comparing the change in relative industrial metal concentration through the profile may therefore further elucidate metal behaviour in the soils.

When the relative change in metal concentration through the soil is plotted, Mo, Cd, Sb and Ag again increase toward the top of each profile (e.g. shown for Mo Fig. 10C). Most of the other elements, however, show variability between the three soil profiles (e.g. as shown for Pb in Fig. 10D, profile locations shown in Fig. 2). Industrial metal concentrations in the uppermost (ridge-crest) soil profile increase toward the profile surface. In mid-slope profile, concentrations decline in the middle of the profile before recovering toward the top of the profile (e.g. Fig. 10D). However, whereas Cr, Pb and Sn reach unity at the surface, Co, Zn and most significantly Cu show relative concentration depletion (plot not shown). In the toe-slope profile the concentrations of most metal decline toward the surface (with the exception of Mo, Cd, Sb and Ag) (e.g. Pb in Fig. 10D).
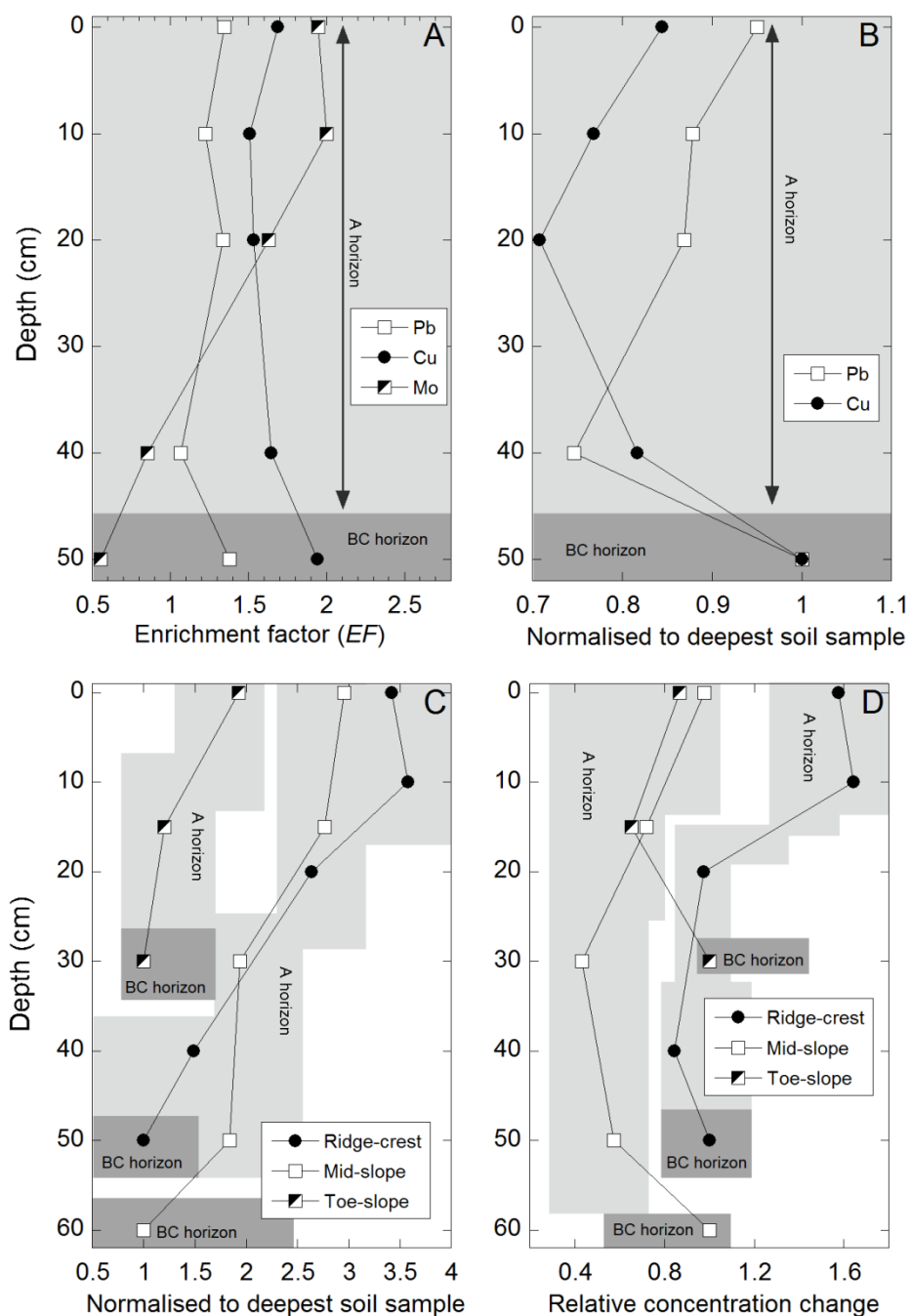
Figure 10. Industrial metal patterns in Snowy Mountains soils. A) Lead (Pb), Cu and Mo enrichment (*EF*) in the ridge-crest profile. *EF* were calculated relative to the Perisher core sediments. B) Copper (Cu) and Pb in the ridge-crest profile normalised to the deepest soil profile sample. C) Molybdenum (Mo) enrichment in each soil profile normalized to the deepest soil profile sample. D) Relative change in Pb concentration in each soil profile.

The overall impression, is, Mo, Cd, Sb and Ag show strong evidence of enrichment in the soils. Other industrial metals show some evidence of enrichment in the ridge-crest soil profile, whereas they may be depleted in the mid-slope and toe-slope profiles. Of these metals Cu shows the most significant degree of loss, implying it may be preferentially removed from the soils in this environment.

5.5 Age structure of the Reservoir cores

Unsupported ^{210}Pb activities in both Geehi and Guthega reservoirs cores were relatively high (Supplementary Table 3 and Fig. 11). In order to construct robust age models using ^{210}Pb it is necessary that ^{210}Pb activities decrease consistently down core. In the Geehi Reservoir unsupported ^{210}Pb activities did not exhibit a decreasing profile in the top 100 mm. However, ^{210}Pb activity did decrease significantly between the data points at 95 and 155 mm depth from 364 Bq kg^{-1} to 215 Bq kg^{-1} (Fig. 11A). An estimate of sediment accumulation rates (0.08 g cm^{-2} year^{-1}) was calculated from these two points using the Constant Initial Concentration (CIC) model (Robbins and Edgington, 1975). Applying this mass accumulation rate to the whole core allowed sediment ages to be calculated (Supplementary Table 3, Figure 4.11). Due to the lack of reliable ^{210}Pb data, these ages can be considered approximate only.
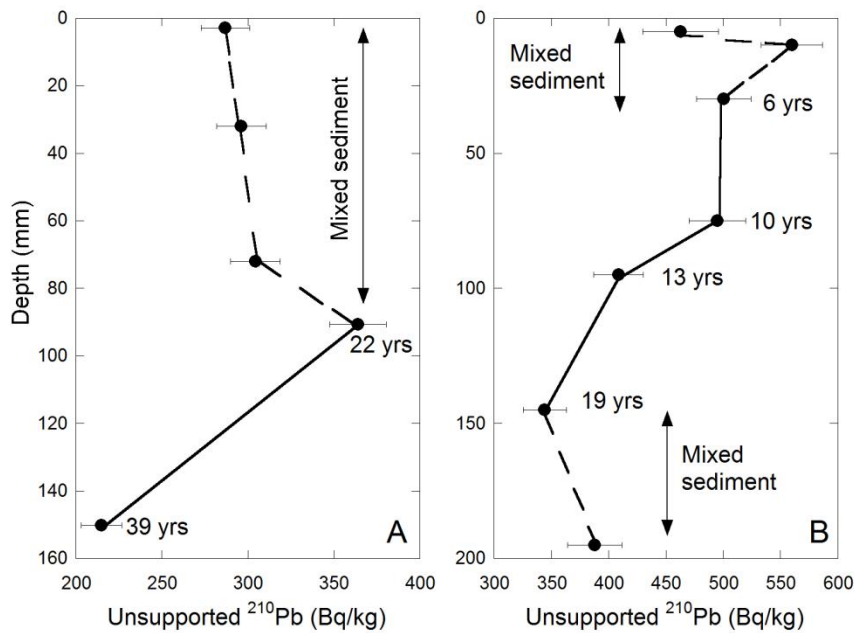
Figure 11. Unsupported ^{210}Pb activity profiles in cores collected from A) Geehi and B) Guthega reservoirs. Sediment ages (years) and regions where sediment mixing is likely are indicated on each panel.

In the Guthega Reservoir core unsupported ^{210}Pb activities exhibited a decreasing profile between 30 and 145 mm depth only (Fig. 11B). These data were used to estimate a mass accumulation rate for the whole core (0.26 g cm^{-2} year^{-1}), from which sediment ages were calculated (Supplementary Table 3, Fig. 11).

The unsupported ^{210}Pb depth typology (Fig. 11) for both reservoir cores, i.e. unsupported ^{210}Pb concentrations do not consistently decrease with depth, implies that either sediment in the reservoirs has experienced post depositional mixing, or sediment of differing age/origin (with variable ^{210}Pb activity) has been deposited in the reservoirs at different times. In Geehi Reservoir results indicate sediment mixing and/or a complex origin of sediment, at least above 100 mm depth, while in Guthega Reservoir, these effects have influenced sediment above 30 mm depth and between 145 and 190 mm depth. As a consequence, calculated ages (which are shown in figure 12) must be treated with caution. In addition, or alternatively, the ^{210}Pb results also indicate the reservoirs may not record a true temporal deposition history, i.e. based on the basal ^{210}Pb ages Guthega is missing approximately 30 years of sediment.
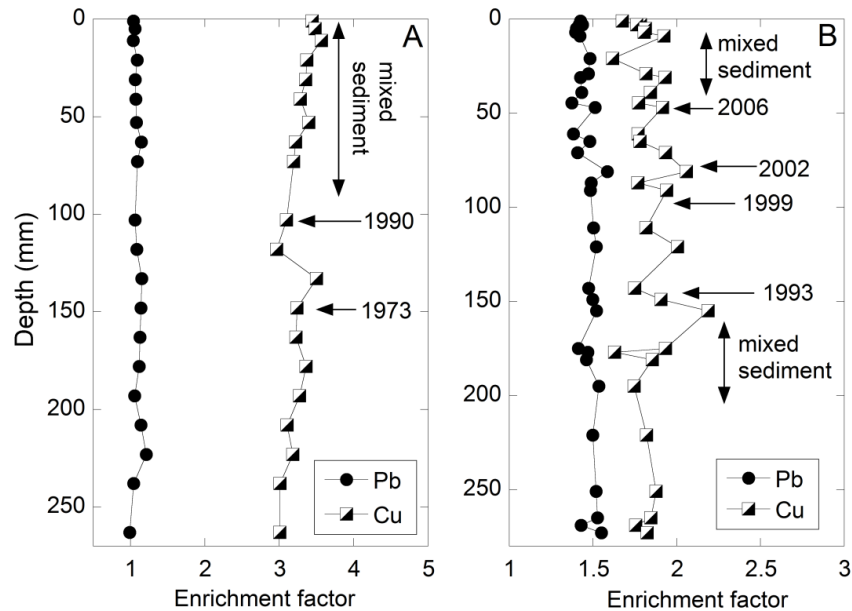
Figure 12. Lead (Pb) and Cu enrichment (*EF*); in A) Geehi and B) Guthega reservoirs cores. Ages (years AD) and regions of sediment mixing are indicated in each panel

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5.6 Industrial metal accumulation in reservoirs

In contrast to the peats mires, which receive predominately atmospheric input, and to Club Lake, which has a small contributing catchment area (0.015 km^2), the reservoirs have significantly larger catchments (91 and 141 km^2 for Guthega and Geehi, respectively). They therefore receive significant catchment input and serve to show how industrial metals are being transported through, and accumulating in the wider surficial environment.

Due to difficulties in establishing the precise age of deposited sediment, *EF* values were calculated from the average enrichment across all samples analysed in the two cores. The reservoirs do not contain pre-industrial sediment (they were constructed after 1850). Therefore metal enrichment was calculated relative to sediment from the core extracted in the Perisher Valley (Marx et al., 2011), using equation 4.

Despite uncertainty in the age of the reservoir sediments, calculated *EF* values for both reservoirs clearly demonstrate that many industrial metals found to be enriched in both the aerosol samples and the peat mire sediments (and to a lesser extent the Club Lake sediment) were not enriched in reservoir sediments. These were Pb (e.g. Fig. 12A), Ni, Cr and Sn in Geehi reservoir and Ni, Cr and Co in Guthega reservoir (Fig. 13). A number of other metals, however, showed more substantial enrichment. In Geehi reservoir As, Cd, Ag, Mo and Cu (e.g. Fig. 12A) are enriched by an average of 5.9, 6.4, 4.0, 3.6 and 3.3 times respectively, while in Guthega Reservoir they are enriched by 2.7, 3.8, 3.2, 2.5 and 1.8 times respectively (Figs. 12 and 13).
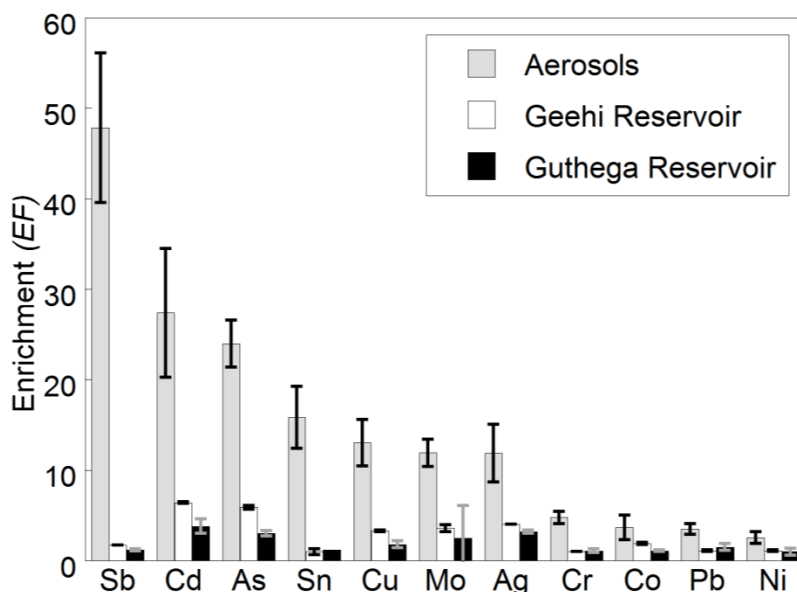
Figure 13. Industrial metal enrichment (*EF*) in reservoirs (Geehi and Guthega) plotted alongside aerosol enrichment (2012/2013) for comparison.

6 Discussion

In the following sections the results are discussed from the input of industrial metal (via enriched arosols) through the various studied landscape repositories. These include the rainfall fed peat mires and the alpine tarns and soils, located in the upper parts of catchments and soils and reservoirs located lower in the same catchments. Differences in relative enrichment between the source aerosols and each surface repository provides an opportunity to examine how industrial metals are being incorporated into and transported through the environment.

6.1 Metal enrichment in aerosols; contributing sources and comparisons

Aerosols in the Snowy Mountains were significantly enriched in pollutant metals known to be perturbed in the global atmosphere due to emissions from stationary fossil fuel combustion, (the primary source of Cr, Sb, Sn, Mo), non-ferrous metal production (the primary source of As, Cd, Cu, Pb, Ni, Zn, Ag) and fertilizer application (an additional source many metals including As, Cd, Cu, Pb, Ni and Zn) (Pacyna and Pacyna, 2001; Rauch and Pacyna, 2009). Patterns in aerosol metal enrichment evident in this study are broadly similar to that previously found within peat mires in the Snowy Mountains, where metal pollutants were shown to derive primarily from mining, metal production and coal combustion within the south-eastern Australian airshed

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(Marx et al 2010). The same suite of industrial metals present in the peat mires were enriched in the aerosols samples, although the relative order and magnitude of enrichment differed. The industrial metals most enriched in aerosols were Sb, Cu, As, Cd. These have the highest contemporary emission rates from industrial sources within Australia (NPI, 2014) relative to their natural preindustrial concentrations, again implying that aerosol enrichment in the Snowy Mountains reflects regional industrial pollution.

The concentration of pollutant metals in the atmosphere over the Snowy Mountains is generally within the same order of magnitude as that previously reported for an alpine site in New Zealand (Marx et al., 2014b) but approximately 1-2 orders of magnitude greater than concentrations recorded at more remote Southern Hemisphere sites, including Samoa (Arimoto et al., 1987) and Antarctica (Dick, 1991) (Table 2), reflecting the relative proximity of the Snowy Mountains to industrial emission sources.

6.2 The atmospheric contribution of industrial metals

In the absence of local catchment sources, deposition of aerosols enriched in industrial metals represents the most significant source of contamination to the Snowy Mountains. The estimated total aerosol flux to the Snowy Mountains during 2012-2013 was ~30 g m^{-2} y^{-1}. This value is similar, albeit slightly lower, than the 1980-2006 dust deposition rate of 49 g m^{-2} y^{-1} estimated in the USC peat using a mass-balance geochemical model (Marx et al., 2014c). . The slightly lower deposition rate reported here may reflect changing dust transport rates in response to changing climate conditions across south eastern Australia. The two years leading up to the 2012/13 sampling periods were among southern Australia's wettest (BOM 2014), implying less favourable conditions for dust entrainment, i.e. increased soil moisture and vegetation cover. In addition, average dust deposition in the peat mire was enhanced by prolonged drought in the early to mid-2000s and significant drought during strong El Niño events in 1982-83 and 1987 when large dust storms occurred (Marx et al., 2014c; McTainsh et al., 1989; Raupach et al., 1994).

Deposition flux in the Snowy Mountains is above the global range (1-25 g m^{-2} y^{-1}) shown for sites at intermediate distance (10-1000 km) from significant regional (North America, South Africa, South America and Australia) dust source areas (Lawrence and Neff, 2009). This is consistent with Australia being arguably the largest dust source in the Southern Hemisphere (Shao et al., 2011) with the lower Murray Darling Basin, upwind of the Snowy Mountains, being one of Australia's major dust producing regions (Hesse and McTainsh, 2003). Dust fluxes are, however, similar to those calculated for other relatively humid, eastern areas of the MDB (31-33 g m^{-2} y^{-1}) (Cattle et al., 2009; McTainsh and Lynch, 1996). The overall similarity between these previously published values and the results of this study (~30 g m^{-2} y^{-1}) supports the appropriateness of the deposition rate estimates. While the exact flux of individual trace elements is uncertain, the estimates appear a reasonable approximation of atmospheric deposition relative to local, surface-derived inputs.

There are few previous estimates of pollutant metal flux within the Australian region. Deposition flux reported for metropolitan areas are substantially higher than those in the Snowy Mountains. For example, the mid-range estimates of Cu and Pb deposition in the Snowy Mountains are 3-60% (Cu) and 3-25% (Pb) of rates reported for metropolitan Sydney (approximately 350 km NW of the Snowy Mountains) (Davis and Birch, 2011). By contrast, fluxes of industrial metals in this study are generally 1-2 orders of magnitude greater than in alpine and remote marine sites in New Zealand (approximately 2,000 km west of the Snowy Mountains) (Arimoto et al., 1990). Thus on one hand, low metal fluxes to the Snowy Mountains, by comparison to metropolitan areas, reflects their remote location and lack of local point sources, while on the other hand, high metal flux by comparison to other remote locations reflects the proximity of significant industrial sources on the Australian continent.

6.3 Metals concentrations in peat mires

Of the sedimentary archives examined in this study, the peat mires are generally considered to most accurately reflect rates of atmospheric industrial metal input. This is by virtue of their high *relative* atmospheric input in comparison to the other studied environmental repositories (soils, lakes and reservoirs). In addition, atmospherically deposited metals are likely to be fixed on the organic peat surface due to the availability of numerous exchange sites on which metals can be

bound (Steinnes and Friedland, 2006). For this reason, the fidelity with which peat mires record the state of the atmosphere has enabled them to be used widely to examine both the history of atmospheric pollution and natural dust transport and deposition (Le Roux et al., 2012; Marx et al., 2014c; Marx et al., 2009; Shotyk et al., 2002; Weiss et al., 2002). In the Snowy Mountains, the fidelity of peat mires has been previously demonstrated by agreement between the temporal patterns in metal enrichment recorded in the peat cores with the generalised history of industrial development across south-eastern Australia (Marx et al 2010). The high atmospheric fidelity of the peat mires is demonstrated further by the approximate equivalence in the order of trace metal enrichment between the aerosol samples and the studied peat mires. That is, those metals most enriched in aerosols (Cu, As, Mo, Ag, Cd, Sb) are also those most highly enriched in peat mires (especially in the more ombrotrophic USC).

Despite the fact that metal enrichment patterns are comparable between the aerosols and the peat mires, there are some significant differences. For example, industrial metal *EF* in the peat mires does not reflect the magnitude of atmospheric aerosol enrichment, with *EF* in peats being systematically reduced by an average of 5-7 times. Moreover, averaged across all enriched industrial metals, the measured annual accumulation rate, (that is the total volume of metals in the peat), in the USC peat mire between 1980 and 2006 was only (mid estimate and (range)) 80 (40-90) % of the estimated aerosol deposition rate. While, this suggests some possible loss of deposited metals from the peat, these differences may simply reflect the timing and temporal resolution of the peat records by comparison to those of the collected aerosols. As already noted, dust deposition flux estimated by the current study was lower than that measured in USC peat mire between 1980 and 2006. Consequently, part of the relatively low *EF* in the peat mires may arise from relatively higher natural dust loads which dilute the metal pollution concentrations. Furthermore, incorporation of metals into the peat mires over several years is likely to smooth peaks in atmospheric metal concentration observed in the weekly to monthly aerosol samples. This is supported by the relatively large reduction in *EF* factors between the aerosol samples and the peat mires for the most highly enriched industrial metals (Cu, As, Cd, Sn, and Sb). In addition, higher metal *EF* variability occurred in the aerosols, implying their higher *EF* are relatively more strongly influenced by high pollution days.

Contributing further to the difference in *EF* between the aerosols and peat mires, may be particle size fractionation of metals during deposition from the atmosphere to the peat surface (Chester et al., 1999). Atmospheric fall-out is dominated by larger particles, which are typically less enriched in industrial metals. This effect has been shown to result in relative depletion during dry deposition by comparison to bulk *in situ* (atmospheric) aerosol by a factor of between 1.8 and 9.9 (Chester et al., 1999). In this study, the *EF* difference between aerosols and peats ranges from 1.2 less times for Ni to 26 times less for Mo, with an average of 6 times less across the two peat mires.

The concentration of individual industrial metals within peat mires may also be controlled by factors specific to individual elements, such as the relative concentration of each element in aerosols compared to locally sourced sediments. For example, the difference in concentration between collected aerosol samples and non-enriched ('natural') local sediments is comparatively greater for Sb by comparison to Mo, i.e. 13 and 9 times, respectively. This implies local non-contaminated sediment delivered to the peat mires will dilute the concentration of industrial Sb more strongly than that of industrial Mo. This effect is likely to contribute to the observed differences in the relative *EF* depletion of Sb and Mo in peat mires compared to aerosols (Sb *EF* is 20 times less in peat mires relative to aerosols samples while Mo is only depleted by a factor of 2 These differences suggest other factors such as efficiency of dust scavenging of individual metal pollutants, pollutant metal phase and oxidation state, particulate size as well as conditions in the peat mires themselves, e.g. moisture content, pH and redox state, may also be important influences on how effectively atmospherically derived industrial metals are incorporated into the peat mires. Despite these differences, in this study industrial metals within peats can be considered broadly representative of atmospheric input.

6.4 Industrial metals in Club Lake

By comparison with the peat mires, Club Lake sediments respond far less sensitively to atmospheric input of industrial metals (Stromsoe et al., 2013). Consequently, only those industrial metals which have very low natural sediment concentrations (Sb, Mo, Cd and As) show significant enrichment (maximum *EF* >1.5) in Club Lake. Metals that are highly enriched in aerosols, but present in naturally high concentrations were not found to be enriched. Notably

of the elements with the highest excess atmospheric deposition flux (Cr, Ni, Cu, Pb) only Pb displayed possible minor enrichment in Club Lake sediments.

Enrichment factors for even the most highly enriched industrial metals in Club Lake were considerably lower than in the aerosol samples, i.e. 8, 18, and 21 times less for Mo, As and Sb, respectively. This highlights the subdued response of the lake even to relatively high levels of atmospheric enrichment. In addition, metal *EF* in the lake were reduced relative to the peat mires by an average of 2.4 times, suggesting this difference is unlikely to be explained by processes common to both environments such as particle size fractionation during atmospheric deposition.

As discussed in Stromsoe et al., (2013), the lack of observed industrial metal enrichment in the Club lake is explained largely by the fact that catchment derived sediment greatly exceeds atmospheric input. Overall the estimated atmospheric deposition of industrial metals (i.e. those enriched in aerosol samples) contributed and average of 35% (or 30-60% depending on the estimation method) of their concentration in the lake sediments. By comparison, atmospheric input is largely the only source of sediment in the peat mires (Marx et al., 2011). The additional 'natural' contribution of these metals is supplied by sediment derived from the lake catchment, which, considering the generally low level of enrichment must be largely free of excess industrial metal. It is therefore likely to be derived from subsurface sediment or freshly weathred material.

The exception to this is the enrichment of a number of industrial metals in Club Lake (e.g. Sb, Mo, Cd and As) which can be attributed, in part, to their enrichment sensitivity. An impression of the *relative* sensitivity of different industrial metals can be provided by comparing the increase in concentration required to produce an *EF* of 2 times background concentrations. This is achieved by dividing the background (natural) concentration of each industrial metal by their mean (background) concentration (equation 6).

$$Metal_{sens} = (C_m/C_{mean})*100 \qquad\qquad (6)$$

where *Metal_{sens}* is metal sensitivity, C_m is background concentration of a particular metal in the Perisher (pre-industrial) sediments which also displays enrichment in the aerosol samples and C_{mean} is the mean background concentration of all metals in the Perisher sediments, which are similarly enriched in the aerosol samples.

The relative sensitivity of industrial metals to contamination is shown in Table 4. The industrial metals most enriched in the lake sediments (Cd, Sb, Mo and As) are all relatively sensitive to enrichment. This means a small increase in their concentration will result in enrichment. For example, to enrich Sb two times in this context requires an anthropogenic contribution of only 121 ppb. Copper by contrast requires environmental concentrations to increase by approximately 28,000 ppb and Sn by 9,000 ppb. Silver is also relatively sensitive and showed minor enrichment in Club Lake (*EF*<1.5).

Table 4 Relative sensitivity of industrial elements to enrichment

	Relative sensitivity* (%)
Ag	0.2
Cd	0.4
Sb	1.1
Mo	1.4
As	8
Co	64
Cu	70
Ni	104
Pb	144
Cr	323
Zn	382

*Relative sensitivity is the concentration increase required to produce EF 2

6.5 Industrial metals in soils

In contrast to the other environmental archives, calculating *EF* in the soil samples is not straight forward due to variability in the behaviour of conservative elements against which enrichment is compared (Ta, Ti, Sc and Ga). This variability is presumably due to weathering/erosion loss in parts of the soil profile versus input of aeolian dust in the upper profile (Costin et al., 1952; Marx et al., 2011). Despite this difficultly, there is evidence of industrial metal enrichment in the soils. The most obviously enriched metals were Cd (*EF* ~3.4-5), Mo (*EF* ~2-3), Ag (*EF* ~0-4) and Sb (*EF* ~1-2). Enrichment factors in the upper section of the soils profiles are comparable to those of the studied peat mires for Cd and Ag, however Mo and Sb values are lower reflecting their lower relative sensitivity to enrichment (Table 4) and implying they are being diluted by additions of natural sediment.Previous studies have demonstrated that, even in areas proximal to emission sources, the identification of industrial metals in soils may be complicated by high background concentrations, or by variations in the type and amount of organic matter or clay within the soil profile (Barbieri et al., 2014). In the Snowy Mountains the obvious enrichment of Cd, Mo, Ag and Sn over other metals with significant anthropogenic sources reflects their relative sensitivity to enrichment, i.e. low background concentrations in local soils.

Metals enriched in the aerosols and peat mires, but with relatively low enrichment sensitivity (Pb, Zn, Cu, Ni, Cr), display more complex patterns in the soils. The soil profile closest to the ridge crest contains higher metal *EF* due to its landscape position. Increasing depletion (indicated by *EF* < 1) of these elements downslope is consistent with increasing dilution from 'natural' sediments due weathering, geomorphic processes and/or reduced dust input. There is some evidence of potential eluviation of industrial metals in the soils (Fig. 11), i.e. development of a rudimentary E horizon at 200-500 mm depth with an illuvated zone at 500-600 mm depth. While these soils have been previously noted for a distinctive lack of visual evidence of podzolization (Costin et al., 1952; McKenzie et al., 2004), subtle podsolization is however apparent in the ultra-high resolution trace element data presented here.

The concentration of these metals in the A0 and A1 soil horizons (0-10 cm) is approximately 1.5 to 2 times less than in the peat mires. The age of this horizon is unknown. Given the relatively

slow rate of vertical accumulation in the peat mires, i.e. 50-150 mm in 120 years, it is likely to integrate the whole history of industrial metal pollution during which metal *EF* in the peat mires has increased from approximately 1 to 5 (Marx et al., 2014c). Consequently, concentrations and *EF* in the A1 soil horizons are diluted by comparison to the post-1980 peat records as they integrate over a longer period including lower industrial metal input (1880-2006 AD; Marx et al., 2010). While it is not possible to reliably correct for this effect, a comparison of the pre and post 1980 *EF* in the peat mires, imply industrial metal input to the top of the soils may be equivalent to that of the peats mires.

There is evidence of loss of some metals from the soil, as shown by the depletion of industrial metals in the upper soil compared to the parent material, most notably for Cu, and to a lesser extent Ni and Zn and possibly Pb, Cr and As in the toe slope soil profile. This is approximately in accordance with the relative geochemical mobility of these elements in soils, which increases in the order Pb < Cr < As < Ni < Zn < Cu (Allison and Allison, 2005). Depletion of this same suite of metals was reported for Swiss forest soils (Blaser et al., 2000). Blaser et al. (2000) describe this as the net outcome of the opposing forces of depletion due to leaching and enrichment due to deposition and it is proposed this is similarly occurring in the Snowy Mountains.

6.6 Industrial metal enrichment in reservoirs

The reservoirs examined in this study are located down catchment from the other archives. Because of their relatively large catchment to lake area ratios they receive relatively little direct atmospheric input, i.e. 7 (5-10) and 15% (10-25%) of total accumulation in Guthega Reservoir and Geehi Reservoir, respectively. Total sediment accumulation rates are relatively high at 700 and 2600 g $m^{-2} y^{-1}$ for Geehi and Guthega Reservoirs, respectively. By comparison, total accumulation in Club Lake is 330 g $m^{-2} y^{-1}$ and < 50 g $m^{-2} y^{-1}$ in the peat mires. As a result, direct atmospheric deposition is only a minor source of industrial metals to the reservoirs, explaining the lack of fidelity between aerosols and reservoir *EF*.

Industrial metals found in the reservoirs are unlikely to be contemporaneous with the aerosol samples collected in this study. This is because industrial metals were accumulating in the surface soils during the preceding 70 years before reservoir construction. These older metals, which have been stored within the catchment, may be transported to the reservoirs at any point following their deposition. This implies the metal history of even the youngest sediments in the reservoirs could represent a mixture of historical metal deposition patterns (see Marx et al., 2010) in the Snowy Mountains. Hence some of the differences in metal enrichment in the reservoirs compared to, for example, the peat mires may be attributable to historical patterns in the atmospheric deposition of industrial metals.

Given that direct atmospheric deposition is only a minor source of industrial metal input in the reservoirs, it is unsurprising that metal *EF* patterns in the reservoirs mostly closely resemble those found in the soil samples. This is shown in Table 5, where the average concentration of each industrial metal in the reservoirs relative to the conservative elements (Ta, Ti, Ga and Sc) is divided by its average relative concentration to the same elements in the soils. This general agreement in *EF* between the soil samples and the reservoir sediments, , further suggests that the sediment accumulating the reservoirs is largely derived from catchment top soil. If the reservoir sediment consisted of, for example, significant subsoil (which is less contaminated by industrial metals) or freshly weathered material, relative depletion of industrial metals would be expected by comparison to the top soil samples. Thus, reservoir sediments, like the catchment soils, are generally most highly enriched in relatively enrichment sensitive metals (Mo, Cd, Sb, As and Ag). However, Table 5 also demonstrates possible additional enrichment (Co, Cu, Zn, As, Mo, Ag, Cd) or depletion (Cr, Sn, Pb) in metals in the reservoirs relative to the soils. These same groups of industrial metals are enriched or depleted in the reservoirs relative to their behaviour in the peat mires (with the exception of Mo, Co which are relatively enriched in reservoirs compared to the soil samples, but depleted relative to the peat mires).

Table 5. Industrial metal enrichment in Geehi and Guthega reservoirs relative to topsoil concentrations

	Guthega Reservoir	Geehi Reservoir
Cr	0.9	0.8
Co	1.3	1.7
Ni	1	1.1
Cu	1.2	2.1
Zn	1.2	1.3
As	1.5	2.2
Mo	1.1	1.6
Ag	1.1	1.3
Cd	1.3	1.8
Sn	0.8	0.6
Sb	0.9	1.4
Pb	0.9	0.7

The patterns in relative metal enrichment and depletion in the reservoir sediments may be attributed to differences in metal particle affinity and solubility. The partition coefficients of industrial metals in soils decrease in the order Cr >Pb >As >Ni >Sn >Zn >Cd >Ag >Cu >Sb >Co >Mo (Allison and Allison, 2005). In general, more highly particle reactive and less soluble metals, such as Pb and Cr are relatively depleted in the reservoirs, whereas less particle reactive, more mobile elements such as Zn, Cd, Ag, Cu and Mo are relatively enriched (Table 5). The behaviour of the metalloids, Sb and As, is more variable. Antimony is relatively mobile, however, it is enriched only in Geehi Reservoir, while As is relatively particle reactive but is enriched in the reservoirs over the soils. Overall, however, this implies that relatively immobile industrial metals (e.g. Pb), may be trapped within the soil matrix following deposition from the atmosphere. By contrast, more mobile metals such as Cu may be more readily transported, resulting in comparative enrichment or depletion of these elements in reservoir sediments. This assertion is supported by the soils data. Copper concentration is lower in the A1 horizon and is reduced down slope, implying it is being depleted from the soils. In addition, overall Cu is higher in the reservoirs than the catchment soils (Table 5). Zinc, Mo, Ag and Cd are also relatively enriched in the reservoirs; however, of these only Zn shows evidence of depletion in the soils

and it is significantly less pronounced than for Cu. The uptake of Cu and Zn by vegetation (Gandois, 2010) may play a part in these patterns, as organic matter may be preferentially being transported (over mineral sediment) from the highly organic alpine soils.

The differences in metal enrichment between the two reservoirs appear to be partly a function of contributing catchment area. Enrichment factors for the most enriched metals, Cd, Mo, Cu, As are higher in Geehi by 1.7, 1.4, 1.8 and 2.0 times, respectively. This is broadly equivalent to the difference in catchment area, with Geehi Reservoir 1.7 times larger than Guthega Reservoir.

6.7 Summary and implications

In this study, three factors appear to be of most importance in controlling metal enrichment patterns within different environmental archives in the Snowy Mountains. These are; 1) the relative contribution of atmospheric input; 2) the sensitivity of individual metals concentrations to perturbation from industrial contributions and; 3) the behaviour of individual metals. These factors are shown in Figure 14, where the enrichment patterns of Pb, Cu and Sb through the catchments of the Snowy Mountains are demonstrated.

Aerosols sampled in this study were enriched in industrial metals by an average of 15 times background concentrations, further confirming the widespread perturbation of industrial metals in the atmosphere. A comparison of calculated deposition flux with accumulation rates in the peat mires, the environment dominated most significantly by atmospheric deposition, implied depletion of industrial metals occurred during deposition, possibly via size fractionation, with an additional reduction in *EF* in sedimentary environments due to dilution with uncontaminated material. Despite a reduction in *EF* by 5-7 times between the aerosols and the peat mires, industrial metal enrichment was found throughout the Snowy Mountains catchments. All else being equal, the degree of metal enrichment in the various sedimentary environments sampled (peat mires, soils, lakes and reservoirs) was a function of the *relative* contribution of atmospheric aerosol input versus that of terrestrially derived sediment. Consequently, ombrogenous peat mires and soils (particularly those closer to ridge crests), which in the Snowy Mountains are partially fed by dust, tended to record the highest enrichment in industrial metals (Fig. 14). A reduction in metal *EF* therefore generally occurs down catchment (Fig. 14). However,

geomorphically active environments (with higher sediment yields) which produce uncontaminated sediment (e.g. cirques) have reduced metal enrichment due to dilution.
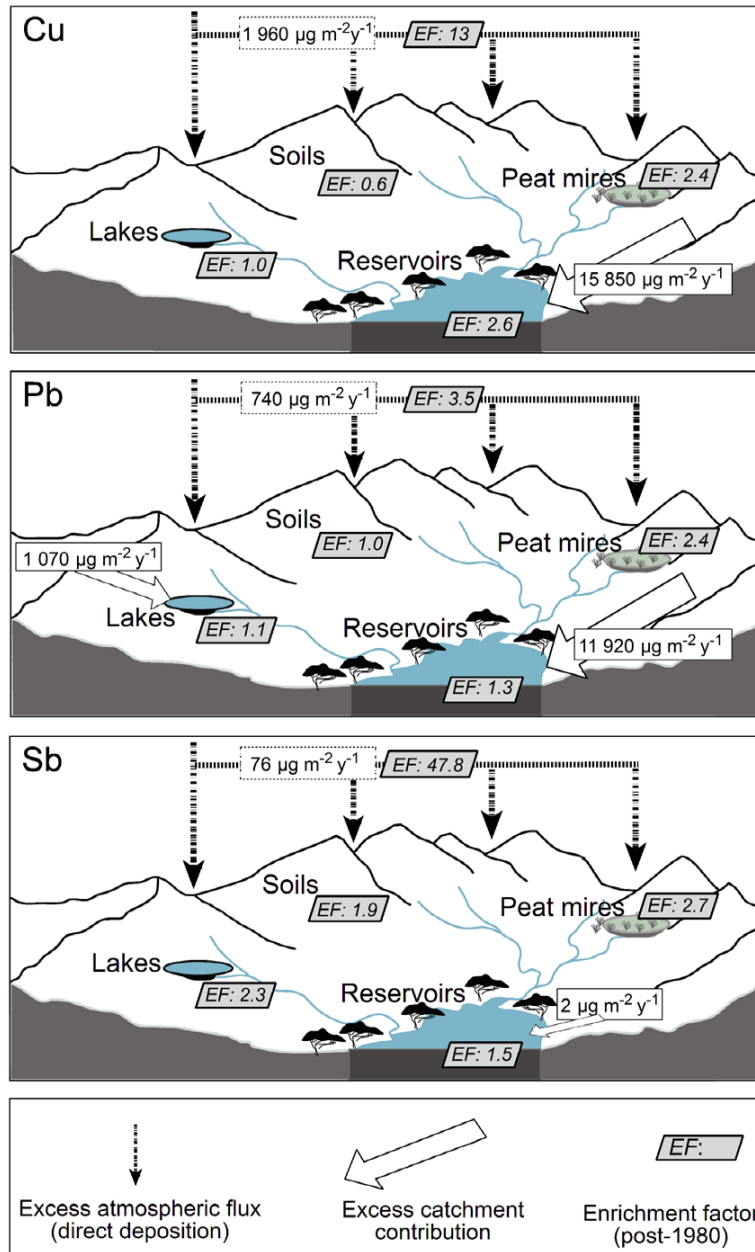

Figure 14. Industrial metal mass flux and metal enrichment (*EF*) patterns in the Snowy Mountains; shown for Pb (top panel), Cu (middle panel) and Sb (lower panel).

The sensitivity of metals to enrichment was found to be a key influence on the *EF* patterns between industrial metals. Metal sensitivity in this context was controlled by the background concentration of the metal versus its relative degree of perturbation by industrial processes. Metals with low natural abundance (Cd, Ag, Sb and Mo) were found to be consistently enriched within all the sedimentary environments examined (for example Sb in Fig. 14), because relatively lower industrial input by weight is required to raise their excess contribution over their natural concentration.

The behaviour of individual metals also influences patterns of enrichment within the surficial environment. In contrast with the general behaviour of most industrial metals, which showed reduced enrichment down catchment, was the behaviour of Cu and Cd (and to a lesser degree Zn) (Fig. 14) which were more enriched in the reservoirs than in catchment soils. Combined with evidence of Cu loss from the soils, this implies preferential transport of the most mobile industrial metals down catchment and their subsequent accumulation (and therefore concentration) in aquatic sedimentary systems. This stands in contrast to the most particle reactive metals such as Pb, which appear to be more strongly held within the soil matrix. Metals including Pb and Cr therefore experience lower relative transport rates, at least in the alpine setting of the Snowy Mountains. They are most enriched in the atmospherically dominated environments and therefore display down catchment dilution.

The presence of enriched industrial metal in all the sampled environments demonstrates that they are widespread in this otherwise relatively pristine alpine environment and that, in the case of some metals, are mobile in the environment. Examining the implications of these metals in the Snowy Mountains is beyond the scope of this paper, however, comparing them to critical pollutant loads, i.e. the Interim Sediment Quality Guidelines (ISQG) for Australia and New Zealand (ANZECC and ARMCANZ 2000), provides an assessment of their likely impact. These guidelines provide trigger values above which metal concentrations are considered deleterious.

Excess industrial metal concentrations in the Snowy Mountains were generally below the ISQG trigger values (Table 6) in all the studied environments implying no significant ecotoxicity effect

is occurring. However, Cr and Ni concentrations in Club Lake did exceed trigger values. These metals were not however found to be enriched Club Lake. Therefore their high concentration in sediments is derived from their naturally high concentration in catchment source rocks. In other environments Ni is close to trigger values as is Pb (Table 6). Industrial metals are known to be increasing in the Snowy Mountains (Fig. 4 and 12), consequently, calculating the increase in industrial metal input required to reach the threshold of the ISQG trigger values provides a perspective on the sensitivity of the environment to be impacted by metal pollutants. The required increase is calculated for each archive (peat mires, lake and reservoirs) according to equation 7.

$$RI= ((C_T-C_{TS})+C_{ES})/C_{ES} \qquad\qquad (7)$$

where RI is the required concentration increase in metal pollutant, C_T is the trigger value, C_{TS} is current concentration of the element in the sediment and C_{ES} is the excess concentration of that element in the sediment.

Table 6 shows the estimated additional atmospheric flux required to raise sediment metal concentrations to the trigger value levels. The required increase is variable both between different environments and for different metals. It ranges from 2-4 times current rates for Ni to 13-74 times for Ag. Overall, metals with higher background concentrations relative to trigger values (Cu, Cr, Pb, Ni) require the lowest proportional increase in anthropogenic metal flux to reach trigger values. Considering the relatively high pre-existing flux of these elements (Table 3), however, this equates to a considerable additional atmospheric flux (e.g. at least 2190 ug m^2 yr^{-1} in the case of Pb). Metals which are highly sensitive to enrichment (Ag, Cd and Sb) are present in low concentrations relative to trigger values. They therefore require a relatively large increase (between 6 and 74 times current rates) in deposition flux to result in concentrations reaching deleterious levels.

Overall, atmospheric industrial metal inputs demonstrated for the Snowy Mountains can be considered broadly similar to those found outside major industrial and urban centres across the eastern seaboard of Australia and in areas similarly impacted by regional pollution sources.

However, while these metals represent a significant potential source of contamination across large areas, their surface enrichment is a function of a complex set of processes which vary across the landscape. As a result monitoring of environmental contamination by atmospheric metals and determining the threat they may pose necessitates a thorough understanding of atmospheric and surficial geochemistry and its relationship to local earth surface processes.

Table 6. Sensitivity of archives to enrichment (increase in industrial flux required to produce sediment concentrations equal to trigger values)

	Trigger value[*] (mg kg^{-1})	Upper Snowy Peat Mire			Club Lake			Guthega Reservoir			Geehi Reservoir		
		Current concentration[a] (mg kg^{-1})	Excess concentration (mg kg^{-1})	Required increase[b] (x)	Current concentration (mg kg^{-1})	Excess concentration (mg kg^{-1})	Required increase[b] (x)	Current concentration (mg kg^{-1})	Excess concentration (mg kg^{-1})	Required increase[b] (x)	Current concentration (mg kg^{-1})	Excess concentration (mg kg^{-1})	Required increase[b] (x)
Cr	80	25	8	8	99	C	C	48	4	10	44	2	24
Ni	21	13	6	4	35	C	C	19	0.9	5	20	2	2
Cu	65	14	9	8	25	C	C	18	0.4	7	30	20	3
Ag	1	<0.1	<0.1	74	0.1	<0.1	60	<0.1	<0.1	18	0.1	<0.1	13
Cd	1.5	0.1	0.1	15	0.2	<0.1	15	0.2	0.1	10	0.3	0.2	7
Sb	2	0.2	0.1	18	0.1	<0.1	27	0.2	<0.1	61	*0.3*	0.1	17
Pb	50	23	14	4	45	5	2	29	9	3	21	2	18

*Dry weight.

[a]Estimated from composition of combusted peat using organic matter content of 60% and assuming bulk density of 1 g cm^{-3}.

[b]Required increase is the proportional increase in anthropogenic flux to produce sediment concentrations equivalent to trigger value.

[c]Metal was not enriched meaning that required flux increase cannot be calculated.

Note required Zn flux is not calculated due to presence of Zn in filter material used to collect aerosol samples.

Supplementary material

Estimation of aerosol/metal deposition flux

Dry deposition

Size dependent deposition velocities were estimated using Stokes terminal fall speed according the procedure of Jacobson (2005). This four step process begins by estimating the deposition velocities ($V_{d,}{}^{iest}$ cm s^{-1}) of each particle size class according to equation (1)

$$V_{d,i}{}^{est} = (2r_i{}^2(\rho_p-p_a)g/9\eta)*G_i \qquad (1)$$

where ρ_p is the density of the particle, (taken here as the density of quartz 2.65 g cm^{-3}), r is the particle radius (cm), p_a is the density of air (g cm^{-3}) determined from the mean annual temperature and elevation of the sampling sites, η is the dynamic viscosity of air and G_i is the Cunningham slip-flow correction using the values of Kasten (1968). Aerosol particle size distributions were measured for 20 randomly selected filters on a Coulter Multisizer following (McTainsh et al., 1997).

Reynold's numbers were then estimated using the estimated deposition velocities obtained from equation 2, according to equation 3.

$$Re_i{}^{est} = 2ri \ V_{d,i}{}^{est} / \upsilon_a \qquad (2)$$

where υ_a is the kinematic viscosity of air determined from mean annual temperature and elevation of the sampling sites.

Following this, the Reynolds numbers were corrected according to Beard's (1976) parameterisation for either slip flow (Re <0.01) or continuum flow (0.01 < Re < 300). The final fall velocities were then recalculated according to equation 3.

$$V_{d,i} = (Re_i \ v_a)/2r_i \tag{3}$$

where $Vd_{,i}$ is final deposition velocity for particle size class i and Re the corresponding (corrected) Reynolds number.

Dry deposition rates were then calculated for 60 aerosol size classes using equation 4.

$$F_d = \sum_{i=1}^{n} V_{d,i} * C_i \tag{4}$$

where F_d is the dry deposition flux (g m^{-2} yr^{-1}), V_d the particle size specific deposition velocity and C_i is aerosol concentration (g m^{-3}). Finally, the dry deposition flux for individual industrial metals was calculated from the total aerosol deposition rates and the individual trace metal aerosol concentrations.

Wet deposition

Precipitation deposition

Precipitation deposition was calculated by estimating the concentration of metals in precipitation from their concentration in the atmosphere using a scavenging ratio (Z), defined by the equation 5 (Duce et al., 1991):

$$Z = C_p/C_a \tag{5}$$

where C_p is the concentration of the metal in precipitation and C_a its concentration in the atmosphere .

Trace element flux (F_p) (ug m^{-2} y^{-1}) was estimated according to equation (6)

$$Fp = P*Z*C_a*p^{-1} \tag{6}$$

Where P is the annual precipitation amount (mm), Z is the scavenging ratio (which is dimensionless), C_a is the mean annual concentration of the element in the atmosphere (ug m^{-3}) and p is the density of air (taken as 1200 g m^{-3}). Precipitation depth is converted to mass of water per unit area using standard temperature and pressure.

Precipitation amount is taken as 2000 mm yr^{-1} (the estimated mean annual rate for elevations above 1700 m in the Snowy Mountains)

Cloud water deposition

Cloud water deposition was estimated using equation

$$F_{i,cw} = F_{cw} * C_{i,cw} \tag{7}$$

where $F_{i,cw}$ is the annual cloud water flux of element i, F_{cw} is the annual cloud water hydrologic input, and $C_{i,cw}$ is the mean annual concentration of the element in cloud droplets.

Cloud water composition ($C_{i,cw}$ the concentration of each element in cloud water) was estimated using equation (8)

$$C_{i,cw} = -((E*C_a)/(E-1)) \tag{8}$$

where $C_{i,cw}$ is the air equivalent concentration of the element in cloud water (pg m^{-3}), E is the scavenging efficiency of cloud water drops for aerosols and C_a is the total concentration of the element in the atmosphere (cloud water + interstitial aerosols) (pg m^{-3}).

The hydrological input from cloud water was estimated using equation 9.

$$F_{cw} = LWC * V_{d,cw} * t\_ \tag{9}$$

where F_{cw} is the annual cloud water hydrological input to the catchment, LWC is the mean liquid water content of the clouds (g m^{-3}), V_d is the deposition velocity of cloud water droplets (m s^{-1}) and t is time spent below the cloud base each year.

Obtaining site-specific measurements of scavenging efficiency, liquid water content and cloud immersion time was beyond the scope of this study. Values were, therefore, estimated from previously published values for mountain environments elsewhere (*E, LWC*), from limited

empirical data (*LWC*) and from observation (*t*). To provide an estimate of uncertainty associated with the selection of these values cloud the calculation of cloud water deposition was performed using mid, low and high estimates of *E*, *LWC* and *t*. These values are presented in Supplementary Table 1. These estimates were then summed with those of F_d and F_p to provide a range estimate of total deposition.

Trace element analysis

The analysis of trace elements (including heavy metals) in the aerosol samples, sediment samples extracted from the reservoirs cores, soils and samples from the Club Lake core (previously presented in Stromsoe et al., 2013) was performed by solution quadrupole ICP-MS on a Agilent 7700x instrument at the Department of Earth Sciences, University of Melbourne, Australia. Sediment samples from the peat cores were analysed at Laurentian University, Ontario, Canada using the same approach (Marx et al., 2010).

All samples analysed for this study were dried at 60°C for 36 h to remove moisture and homogenised using an agate mortar and pestle prior to trace element analysis. Samples from the peat cores and the soil pits were additionally combusted in a high temperate oven at 450°C for 12 hours. This volatised the organic component of each subsample, while the mineral component was retained for trace element analysis. Subsamples from each aerosol filter were carefully scraped from the filter using a stainless steel spatula before their trace element composition was measured.

All samples and standards, typically about 100 mg, were digested in Teflon beakers on a hotplate at 140°C overnight using 3 ml of a 2:1 mixture of concentrated $HF-HNO_3$. Solutions were then evaporated to dryness and then 1 ml of 15N HNO_3 was added and evaporated to dryness twice. They were then dissolved overnight in 10ml of 3N HNO_3. A procedural blank was prepared with each batch of samples. Sample solutions were transferred to polycarbonate centrifuge tubes. For silver analyses, an aliquot of the solution was diluted to 2% HNO_3 and a dilution factor of 1000 and Rh added as an internal standard. For all other elements, solutions were diluted to 2% HNO_3 with a dilution factor of 2000.

Silver was analysed in dilution gas mode with 2.2 ml of He cell gas to minimize the level of oxide interferences on Ag. A single element Ag standard was used for calibration and 2 soil standards and one shale standard analysed as unknowns. Oxide interferences were less than 10% of the silver signal and corrected for.

Other elements were analysed in dilution gas mode without cell gas using procedures comprehensively described by Eggins et al (1997) and Kamber (2009). The method uses a natural rock standard for calibration, internal drift correction using multi-internal standards (Li^6, Sr^{84}, Rh, Sm^{147}, Re and U^{235}), external drift monitors for drift correction and aggressive washout procedures. Two digestions of the USGS standard W-2 were used for instrument calibration. The preferred concentrations used for W-2 were mostly derived by analysing it against synthetic standards and a literature survey of isotope dilution analyses (Kamber et al., 2003, 2005).

The instrument was tuned to give Cerium oxide levels of $< 0.5\%$. Four replicates of 100 scans per replicate were measured for each isotope. Dwell times were 10 milliseconds, except for Mo, Cd, Sb, Ta, which were 30 milliseconds. Long sample wash-out times of 6 minutes with solutions of 0.5% Triton X-100, 0.025% HF in 5% HNO_3 and 2% HNO_3 and long sample uptake times of 120 seconds were used. Drift monitors, followed by a blank were analysed every $6 - 8$ samples. Concentrations of the samples were well above minimum detection limits. Quality control was maintained by the analysis of rock and soil standards as unknowns. External precision and accuracy for soil standards (JSo-1, GSS-1), shale standard SCo-1 and basalt and andesite standards BHVO-2, JA-2 and AGV-2 are assessed in Suppl Table 3.

Table 1. Parameter values for cloud water deposition estimates

	LWC (g m^{-3})[a]	$V_{d,cw}$ (mm s^{-1})[b]	t (%)[c]	E (%)[d]
Moderate[1]	0.2	46 (grass)	20	60
		100 (forest)		
Low[2]	0.1	10 (grass)	10	60
		45 (forest)		
High[3]	0.3	46 (grass)	30	85
		100 (forest)		

[1]moderate LWC, moderate to high cloud water deposition velocity, moderate estimate for time spent below cloud base, moderate estimate for scavenging efficiency of cloud water for aerosols
[2]low LWC, low cloud water deposition velocity, moderate estimate for time spent below cloud base, low estimate for scavenging effeciency of cloud water for aerosols
[3]moderate LWC, moderate to high cloud water deposition velocity, high estimate for time spent below cloud base, high estimate for scavenging efficiency of cloud water for aerosol

[a]Reynolds et al. 1996, Kasper et al. 1998

[b]Reynolds et al 1996, Miller et al 1993

[c]Cloud immersion time is estimated from personal observation
[d]Grassbauer et ala 1994, Shumann 1991, Kasper 1998

Table 2. ^{210}Pb activities and CIC ages for reservoir cores

Lab code	Depth (mm)	Total ^{210}Pb activity (Bq kg^{-1})	Supported ^{210}Pb activity (Bq kg^{-1})	Unsupported ^{210}Pb activity (Bq kg^{-1})	Calculated CIC Ages (years)
Guthega Reservoir					
N986[3]	0-10	485 ±30	26 ±12	463 ±33	-
N987[2]	20-30	614 ±26	57 ±5	560 ±27	-
N988[2]	40-50	553 ±23	55 ±5	501 ±24	6 ±1
N989[3]	70-80	532 ±24	41 ±3	495 ±25	10 ±1
N990[2]	90-100	462 ±21	55 ±5	409 ±22	13 ±2
N991[3]	140-150	387 ±18	46 ±4	344 ±19	19 ±2
N992	190-200	420 ±19	45 4	375 ±19	-
Geehi Reservoir					
923	0-6	356 ±15	47 ±4	287 ±14	-
924	30-34	372 ±15	54 ±4	296 ±14	-
925	70-75	374 ±15	48 ±4	304 ±14	-
926	95-100	429 ±17	38 ±3	364 ±17	22 ±5
927	150-155	285 ±12	54 ±5	215 ±12	40 ±6

Table 3.Trace element data of standards (µg g^{-1})

	W-2			BHVO-2						JA-2					
				This study		Long term**		Preferred values*		This study		Long term**		Preferred Values*	
	Calibration Standard	Preferred* Values	RSD	Digestions = 3 Analyses = 3						Digestions = 3 Analyses = 6					
				Average	RSD	Average	RSD	Average	RSD	Average	RSD	Average	RSD	Average	RSD
Sc	36	35.9	2	33	1	32	0.9	32	3	19.6	2	19.6	1.4	17.4	6.9
Ti	6356			16725	0.9	16481	1	16300	12	4018	2.3	4037	2.4		
Cr	93	93	6	308	0.8	301	1.2	280	6.8	437.8	2.4	438.5	1.6	450	8.9
Co	45	45	4	46	0.3	46	0.9	45	7	30	1.6	30	1.1	27	7
Ni	70	72	6	121	1.1	119	0.8	119	6	141	1.5	139	0.9	134	11
Cu	103	105	3	125	0.9	126	0.7	127	6	27.6	2.8	27	1.1	27.9	1
Zn	77	77	8	101	2.5	102	1.3	103	6	64	1.3	63	2.1	65	8
Ga	17	18	6	21	0.8	21	0.6	22	9	16.5	0.9	16.5	0.7	16.5	7.3
As	1.4	1.1	9	0.4	27	0.6	15	0.632-0.92[a]		0.63	22	0.59	15	0.93[b]	4
Mo	0.42	0.44		4	12	3	6.7	4	5	0.54	1.2	0.54	1.6	0.59	3.4
Ag															
Cd	0.077	0.077		0.09	4.5	0.09	2.2	0.06	10	0.06	4.6	0.06	3	0.078	
Sn	2	2	5	1.9	4.9	2.0	6.5	1.7	12	1.69	4.6	1.71	7.5	1.56	1.6
Sb	0.71	0.77	5.2	0.08	2.3	0.08	5.9	0.13	31	0.12	1.4	0.12	5.4	0.14	7.1
Ta	0.45	0.47	8.5	1.15	0.8	1.14	0.5	1.14	5	0.6	0.7	0.6	0.7	0.7	14
Pb	7.5	7.7	8	1.6	6.6	1.4	5.2	1.6	19	18.3	0.6	18.5	1.5	19.3	4

Table 3 continued

	AGV-2				Jso-1			
	This study		Preferred Values***		This study		Compiled Values*	
	Digestions = 3				Digestions = 3			
	Analyses = 3				Analyses = 3			
	Average	RSD	Average	RSD	Average	RSD	Average	RSD
Sc	13	0	13	8	33	1		
Ti	6070	1.4			7014	2		
Cr	16	2.2	16	6	74	1	71	2
Co	16	1.1	16	6	35	1	32	1
Ni	18	1.4	20	5	41	1	39	2
Cu	49	1.3	53	8	167	1	169	2
Zn	89	0.8	86	9	116	6	105	2
Ga	20	0.9	20	5	20	0		
As	0.74	10.2			9.0	3.4	8.1	0.1
Mo	2	2.4			0.7	3		
Ag					0.112[c]	2		
Cd	0.069	2.800			0.275	5.689		
Sn	2.2	8.9	2.3	17	1.6	4.3		
Sb	0.40	7.00			0.31	4.24	0.38	0.02
Ta	0.83	1.1	0.87	9.2	0.19	1.76		
Pb	12.6	0.9	13.2	4	17.9	1.0	13.0	1.0

Table 3 continued

	GSS-1			Sco-1	
	This study	Compiled Values*	This study		Compiled Values*
	Digestions = 1 Analyses = 1		Digestions = 1 Analyses = 1		
	Values	Value	Values		Value
Sc	11		12		10.8-11
Ti	11	11	3430		
Cr	58		69		68
Co	13		11		10.5-11
Ni	20	20	26		27
Cu	18	21	27		28.7-29
Zn	752	680	102		100-103
Ga	18	19	16		15
As	44	34	13.3		12-12.4
Mo	1.4	1.4	1.2		
Ag	0.36[d]	0.35	0.135		0.134
Cd	5		0.156		0.14
Sn	6.7	6.4	3.4		
Sb	1.01		2.11		
Ta	1.2	1.4	0.8		
Pb	97.0	98.0	30.4		31.0

*GeoRem (preferred/compiled values) (Jochum et al 2005)

**Long term Melbourne University Isotope and trace element geochemistry laboratory average

*** Imai et al 1995

[a] GeoRem compiled values

[b] GeoRem Compiled values are 0.77-0.85

[c] Digestions = 4, Analyses = 34

[d] Digestions = 4, Analyses = 34

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