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Global-scale patterns in anthropogenic Pb contamination reconstructed from natural archives

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Abstract
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contamination, reconstructed, global, natural, scale, archives, patterns, anthropogenic, pb

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Abstract

During the past two centuries metal loads in the Earth’s atmosphere and ecosystems have increased significantly over pre-industrial levels. This has been associated with deleterious effects to ecosystem processes and human health. The magnitude of this toxic metal burden, as well as the spatial and temporal patterns of metal enrichment, is recorded in sedimentary archives across the globe. This paper presents a compilation of selected Pb contamination records from lakes (n=10), peat mires (n=10) and ice fields (n=7) from Europe, North and South America, Asia, Australia and the Northern and Southern Hemisphere Polar regions. These records quantify changes in Pb enrichment in remote from source environments. The presence of anthropogenic Pb in the environment has a long history, extending as far back as the early to mid-Holocene in North America, Europe and East Asia. However, results show that Pb contamination in the Earth’s environment became globally ubiquitous at the beginning of the Second Industrial Revolution (c.1850-1890 CE), after which the magnitude of Pb contamination increased significantly. This date therefore serves as an effective global marker for the onset of the Anthropocene. Current global average Pb enrichment rates are between 6 and 35 times background, however Pb contamination loads are spatially variable. For example, they are >100 times background in Europe and North America and 5-15 times background in Antarctica. Despite a recent decline in Pb loads in some regions, most notably Europe and North America, anthropogenic Pb remains highly enriched and universally present in global ecosystems, while concentrations are increasing in some regions (Australia, Asia and parts of South America and Antarctica). There is, however, a paucity of Pb enrichment records outside of Europe, which limits assessments of global contamination.

Capsule abstract: The global surface environment became contaminated with Pb from c. 1850s CE with enrichment currently estimated at 6-35 times background. The magnitude of Pb enrichment shows high spatial variability however (>100 to 5-15), while there are no data for significant regions of the globe.

1. Introduction

Human activities have modified the flux of heavy metals in the environment as a by-product of a variety of industrial processes, e.g. coal combustion, which emit multiple metals at high concentrations (Pacyna and Pacyna, 2001). Lead is the most pervasive toxic metal and is the focus of this review. The degree of perturbation of Pb flux is such that human activity is the major component (61%) of total Pb flux, i.e., Pb emissions are >150% of natural emissions (Rauch and Pacyna, 2009). By comparison industrial fluxes of other major contaminate metals, Cu, Ni and Zn are 48, 48, 33% of natural emissions, respectively. Lead is emitted to the atmosphere primarily from fossil fuel combustion (85 Gg/yr), metal production (25 Gg/yr), fabrication/manufacturing (6.4 Gg/yr), agriculture (1.8 Gg/yr) and waste disposal (0.9 Gg/yr) (Rauch and Pacyna, 2009). As a result, anthropogenic Pb exceeds natural levels in almost every environment in which studies have
been undertaken, including in remote areas such as Greenland (Hong et al., 1994, 1996; McConnell et al., 2002), Antarctica (Dick, 1991; McConnell et al., 2014; Murozumi et al., 1969; Toscano et al., 2005; Valdelonga et al., 2002; Wolff et al., 1999) and the remote oceans (Arimoto et al., 1989; Arimoto et al., 1987). Consequently, Pb levels in modern mammals (including humans) are 100-1000 greater than in pre-industrial times (Ericson et al., 1975; Flegal and Smith, 1992; Owen and Flegal, 1998; Patterson, 1965).

Enrichment of metals in the environment has been shown to deleteriously affect ecological systems, including human populations (AMAP, 1997; Ericson et al., 1975; Mubiana et al., 2005). Toxic metals may bioaccumulate (e.g. Hg) (Castellanos et al., 2015; Grandjean et al., 1992; Madejón et al., 2002; Mubiana et al., 2005; Renzoni et al., 1998), while particular metals may inhibit biological processes or systems. For example, Ni and Cd can negatively affect photosynthetic productivity (Zolotareva, 2007), while Cu aerosols can inhibit phytoplankton growth (Jordi et al., 2012). The deleterious effects of Pb in the environment have long been recognised, for example Pb poisoning in human populations has been described since antiquity (Nriagu, 1983). Despite this, our understanding of the impact of Pb in the environment is constantly evolving. Any level of exposure to Pb is now considered harmful to human health, particularly to cognitive functioning (Smith and Flegal, 1992). For example, exposure to Pb has been linked to reduced educational performance in children (Dong et al., 2015; Schwartz, 1994), as well as reduced social skills and physical wellbeing (Dong et al., 2015).

Environmental Pb contamination has received more attention than any other toxic metal (e.g. Murozumi et al., 1969; Patterson, 1965). This is due to its long history of exploitation (De Vleeschouwer et al., 2010; Nriagu, 1983) and its widespread use, e.g. its use as an additive in gasoline between the c.1920s-1990s CE. Additionally, because the source of contaminant Pb can be determined by isotope fingerprinting, industrial Pb can be distinguished from natural (native) Pb (Bollhöfer and Rosman, 2002; Chow et al., 1975; Renberg et al., 2002) and subsequently Pb contamination is readily identifiable. Mapping changes in the magnitude of Pb enrichment in the environment therefore aids in understanding the historical and contemporary impacts of Pb pollution.

The absence of monitoring programs longer than a few decades (and then only in limited locations) (Pacyna and Pacyna, 2001) renders geological archives essential for reconstructing historical contamination trends. Since Pb is largely immobile in the environment (Weiss et al., 1999), historical patterns can be inferred from geologic archives. Consequently, a significant number of sedimentary records exist which document Pb contamination from the present into prehistory (e.g. Hong et al., 1994; Lee et al., 2008; Pompeani et al., 2013; Shotyk et al., 1998). Over the last 20 years, an increasing number of records of Pb pollution in geologic archives have been constructed from various locations around the globe, but predominantly Europe. In most instances direct comparisons between individual records have not been undertaken, due in part to a lack of consistency in methods for calculating pollution magnitude. Consequently, global variability in the timing and scale of Pb contamination has not been examined in detail. Moreover, the onset of global-scale Pb pollution, may also serve as a marker for constraining the Anthropocene (the period in
which human activity has had a global-scale effect on Earth’s systems), the onset of which
is currently under debate (Smith and Zeder, 2013; Steffen et al., 2007; Wolfe et al., 2013;
Zalasiewicz et al., 2011).

Lead is the only pollutant metal for which there are a significant number and a reasonable
spatial extent of sedimentary records. However, metallurgical and industrial processes
universally emit multiple heavy metals. For example, early Pb emissions are tied to pre-
industrial Ag mining (Cooke et al., 2008). Hg and Pb are simultaneously emitted by coal
combustion (Nriagu and Pacyna, 1988) and Pb, Zn, Ni, Cd, Cr and Hg are emitted by
ferrous metallurgy (Pacyna and Pacyna, 2001) and consequently often display linked
emission patterns (Barbante et al., 2004; Coggins et al., 2006; Martínez Cortizas et al.,
2012; Pontevedra-Pombal et al., 2013; Pratte et al., 2013). As a result, the extent and
magnitude of Pb enrichment can be considered representative of number of metal pollutants
(Marx et al., 2014b), except during the widespread use of leaded gasoline in 20th Century,
when Pb emissions are likely to have increased independently relative to other industrial
metals. This effect becomes less significant at a global scale after the 1970s CE, while, in
addition, gasoline derived Pb is less evident in settings remote from urban areas, as are the
studies presented here.

In this paper we present a synthesis of standardized data from selected sedimentary
archives to examine the extent and magnitude of atmospheric Pb contamination in the
global environment. Where possible we focus on records distal to major industrial centres,
thereby providing a measure of broad-scale, as opposed to local, metal contamination. The
presented records allow quantification Pb perturbation as well as elucidating spatial and
temporal patterns and data gaps.

2. Methods and approach

2.1 Types of environmental archives

All sedimentary archives can record a history of metal contamination, e.g. soils, marine and
fluvial sediments. However, archives that receive predominantly atmospheric input and are
geomorphically stable are considered to produce more reliable pollution records (Cooke
and Bindler, 2015; Stromsoe et al., 2013; Stromsoe et al., 2015). These include lakes, peats
and ice fields (Norton, 2007). Consequently records from these environments are
documented here.

Ice cores are ideal environments for studying atmospheric metal deposition. They are
chemically inert, with limited potential for post-depositional mobility, have high temporal
resolution and can extend beyond the onset of human metal use (Hong et al., 1994;
McConnell and Edwards, 2008; McConnell et al., 2014). They are, however, limited by
their geographic restriction to polar or high altitude environments.

Ombrotrophic (rainfall-fed) peat bogs also exclusively record atmospheric input. They can
contain high resolution chronologies and have high atmospheric fidelity. Lead is immobile
in most peat mires (Farmer et al., 2006; MacKenzie et al., 1997; Shotyk et al., 1998), although there is potential for vertical mobility under particular conditions (Novak and Pacherova, 2008; Sonke et al., 2002). Lowland ombrotrophic peats can also incorporate non-atmospheric inputs, e.g. during flood events. Ombrotrophic peat mires occur over a wider spatial area than ice fields, although are still restricted to particular geographic/geomorphic settings (Kylander et al., 2006; Mitsch and Gosselink, 1993).

Lakes are globally widespread and have been used extensively to construct contamination records (Cooke and Bindler, 2015). Autochthonous catchment inputs can, however, significantly dilute metal concentrations (Stromsoe et al., 2013). Conversely, catchment inputs can also concentrate pollution metals, especially where natural sedimentation rates are low (Camarero et al., 2009) and when metal production operations exist within the catchment. Lake records can be influenced by metal behaviour, i.e. retention of particle reactive metals within in-catchment environmental matrices and concentration of soluble metals in lake repositories (Stromsoe et al., 2015). Despite these limitations, detecting atmospheric pollution signals in lakes is possible where catchment fluxes are relatively constant and/or where they are relatively minor (Catalan, 2015; Cooke and Bindler, 2015; Meriläinen et al., 2010; Stromsoe et al., 2013).

2.2 Calculation of enrichment and metal excess

Sedimentary environments contain both natural and anthropogenic Pb. To distinguish between these, a standard approach (as employed here) is to normalize concentrations of Pb to a conservative reference element with no significant anthropogenic sources (Arimoto et al., 1990; Shotyk et al., 1998). The enrichment factor, the degree to which the metal is enriched over expected background concentrations, can then be calculated from:

\[
EF = \frac{(Pb_{ps}/Ec_{ps})}{(Pb_{nat}/Ec_{nat})}
\]

Equation 1

where \(EF\) is the enrichment factor, \(Ec\) the concentration of a conservative element not influenced by pollution (e.g., Ti or Sc), the subscript \(ps\) the section of the core affected by pollution, and the subscript \(nat\) a non-contaminated background sample(s).

\(Pb_{nat}/Ec_{nat}\) are typically derived from either the pre-pollution section of a core (as is used in this compilation), or the average \(Pb/Ec\) ratio in Upper Continental Crust (UCC). An \(EF\) of \(\leq 1\) indicates no contamination. \(EF \geq 2\) are regarded as being significant (Shotyk et al., 2000). However, values of \(EF \geq 1.2\) can be regarded as significant when: 1) \(EF\) variability in the pre-pollution section of the core is \(\leq 1\); 2) the increase in \(EF\) to this value is associated with a known metal working episode and/or; 3) the increase in \(EF \geq 1.2\) occurs within a sustained trend of rising \(EF\) in a core.

The pollution Pb concentration (Pb excess) can then be calculated from:

\[
Pb_{ex} = Pb_{con} - (P_{con}/EF)
\]

Equation 2

where \(Pb_{ex}\) is the Pb excess concentration and \(Pb_{con}\) the total Pb concentration.
EF is often calculated relative to UCC, that is, Pb/Ec is derived from UCC compilations (e.g. Ferrari et al., 2001; Hong et al., 1994; Kylander et al., 2009; Martínez Cortizas et al., 2002; Thevenon et al., 2011). This approach assumes that the natural input into the sedimentary archive is largely identical to the concentration of the Pb/Ec in UCC. This assumption is challenged by the non-uniform distribution of elements within the Earth’s crust, as demonstrated by the unique elemental signatures of aeolian dust (Marx et al., 2005; Marx et al., 2014a; Muhs et al., 2008), as well as any differences in transport behaviour between Pb and the conservative element. Where the archive Pb\textsubscript{nat}/Ec\textsubscript{nat} differs from UCC, the EF will be either overestimated or underestimated. To overcome this limitation, in this compilation, Pb\textsubscript{nat}/Ec\textsubscript{nat} was calculated from the pre-pollution section of each core. Therefore EF presented here are independent of local geochemical heterogeneity from UCC. Where EF in the original papers were calculated using a different approach they were re-calculated, allowing records to be directly compared. As a result, presented EF may vary from those in the original published records.

Variability in the source area of dust/sediment transported to a site, for example during periods of increased aridity (Le Roux et al., 2012; Marx et al., 2009), or as an outcome of land-use change in upwind regions (Marx et al., 2014b), introduces a further complication to EF calculation. This effect is likely to be minor after the early 20\textsuperscript{th} Century when anthropogenic Pb emissions rose significantly (equating to ~90% of atmospheric emissions; Pacyna and Pacyna, 2001). In lakes, hydroclimate variability may change sediment fluxes, which would affect EF independent of atmospheric input. Differences in the choice of Ec between studies also have the potential to influence relative differences in EF as a result of particle fractionation and the specific physiochemical properties of the Ec used (Klaminder et al., 2003; Martínez Cortizas et al., 2002; Matschullat et al., 2000; Shotyk et al., 2000). These factors represent potential sources of inaccuracy when comparing between records.

### 2.3 Selection criteria and record characteristics

The presented records were selected based on a number of criteria: 1) the oldest part of the core predates the onset of metal use in the region. This allows quantification of metal excess and enrichment by comparison to local background concentrations. 2) Records must have geochronology which allows temporal variability in metal enrichment to be examined. 3) The concentration of a conservative element(s) (Ec) must have been measured within the archive, allowing calculation of enrichment factors (EF). 4) Geochemical data should be of a high accuracy and precision, preferentially generated by inductively coupled plasma mass spectrometry (ICP-MS), with samples having undergone full digestion using HF acid. 5) In the case of peat records, or highly organic lake records, it was deemed preferable that elemental analyses were performed on ashed samples (i.e. the mineral component only). This was to ensure that direct comparisons between different studies could be made, i.e. so that variability in Pb concentrations is not a function of variability in organic content.

Twenty seven archives (Table 1) were selected from existing literature to compare Pb contamination based on these criteria. These included 10 peat mires, 10 lake sediment records and 7 ice core records (Fig. 1). Where available, metal concentrations and
enrichment were directly calculated from tabular data, alternatively these were manually
digitized from graphics included in the published studies.

It is acknowledged there are limitations to the selection criteria. For example, full digestion
(or XRF analysis) may mask Pb contamination when the in-situ mineral Pb content is high
and/or variable. However, the criteria were selected to ensure high data quality while
allowing the greatest number of different records to be compared. In addition, where
significant spatial data gaps exist, it was necessary to include records that did not meet all
the desired criteria. As a result, records with high quality XRF data were included in some
cases (Table 1). Analysis of some of the presented peat records was undertaken on bulk
samples instead of ash (Pena De Cadela, Jura EGR, Labato Sägistalsee and Myrarnar; Table
1). Lead concentrations in these studies was estimated by multiplying the Pb/conservative
element (Ec) (e.g. Ti or Sc) ratio in the record by the Ec in UCC from McLennan (2001).
Although this introduces uncertainty in the calculation of Pb\textsubscript{ex} as a function of the
difference between Ec in the core versus that of UCC, the effect is minimal due to the low
natural variability of the Ec compared to Pb (Kamber et al., 2005; Marx and Kamber, 2010;
McLennan, 2001). In addition, the calculation of EF is independent of this effect. Other
records that did not fit the criteria include Lianghzhi Lake, where no conservative elements
were measured (EF was therefore calculated relative to basal Pb concentrations), and
Copper Falls, Lake Erhai and Ying Yun Lake where Pb was extracted by HNO\textsubscript{3} leaching.
All of these studies filled spatial gaps, however, while in addition, Copper Falls and
Lianghzhi Lake recorded the earliest onset of Pb contamination in their regions. In regions
where records of Pb accumulation in sedimentary archives were numerous, e.g. Europe or
the Great Lakes in North America, 1-2 records were selected which typified the regional
situation.

The selected records displayed varying geochronological control (Table 2). Ice cores and
varved lakes (Lake Lehliampi) display annual or sub-annual resolution (at least in the top of
cores), with layer identification often based on annual patterns in geochemistry, e.g. \delta^{18}O or
\textsuperscript{3}H or Na. Additional chronological control is provided by identification of volcanic
eruptions and \textsuperscript{14}C dating (at Sajama Glacier only). Peat and lake records are largely dated
by \textsuperscript{14}C and \textsuperscript{210}Pb, with further chronological control provided by fallout radionuclides (e.g.
\textsuperscript{137}Cs) and other chronological markers (tephra, pollen and Pb isotopes). Compared with ice
records, the resolution of the lake and peat cores is more variable. An impression of
geochronology of each peat and lake record is provided by the number of dates in different
time slices (Table 1). Records containing dates younger than 1950 and 1850 CE more
reliably map Pb contamination during the Industrial period. By comparison, records dated
solely by radiocarbon (Dumme Mosse; Pena Da Cadela, Hongyuan, Karukinka, Lianghzhi
Lake and, Laguna Taypi Chaka) rely on more poorly constrained age models to resolve
industrial changes in Pb enrichment. An overall indication of the age control in the
presented records is provided by cm/date ratio, where a ratio of <10-20 (implying 1 date
every 10-20 cm) broadly indicates a robust chronology. The effect of geochronology on
individual records is discussed further in the results.

3. Results
3.1 Lead enrichment in Europe

There are relatively numerous sedimentary Pb records from Europe. Eight were selected for inclusion here (Fig. 1), while in addition, Northern Hemisphere polar ice cores (section 3.7) provide a further measure of European Pb emissions/environmental accumulation.

European peat mire records display EF of >10 to >100 (Fig. 2B). The onset of Pb contamination ranged between c.1000-200 BCE. Earliest onset was recorded in central Europe at Etang de la Gruère (EGR), Jura Mountains, Switzerland (Shotyk, 2002; Shotyk et al., 1998), while the most recent onset occurred in northern Britain (at Flanders Moss; Cloy et al., 2008). This variability likely reflects a combination of the extent and commencement date of local metal working.

A feature of the European records is a Pb EF peak (magnitude 2-7) centred at 1 CE and attributed to Roman smelting. This peak occurs in numerous European records, including many not included in this compilation (e.g. Brännvall et al., 1999; Le Roux et al., 2004). The post-Roman record of Pb accumulation in these mires displays differing patterns by location, according to the scale of local mining and metallurgy through the Middle Ages and Renaissance. Nevertheless, the majority of European peat mires presented in this compilation (with the exception of Dumme Mosse, Scandinavia, which has poor age control; Table 2) display EF minima in the Middle Ages. From 1400 CE, following the end of the Middle Ages, enrichment generally increased.

European peat records generally display a sharp increase in Pb EF associated with the onset of the Industrial Revolution (Fig. 2B and 4) when EF increased by 1-2 orders of magnitude over natural background levels. The timing of this change varied between records from the 1890s to as early as 1750 CE. At most sites, the most significant increase occurred after c.1890 CE (Fig. 4). For some records, most notably peats from northwestern Spain, i.e. Pena De Cadela (plotted in Fig. 2B) and Penido Vello (Martinez Cortizas et al., 2002) and Roñanzas (not plotted) (Gallego et al., 2013), the Industrial Revolution did not stand out as a distinct change in EF, rather it occurred within a prolonged increase in enrichment from c.1000 CE. These records have less than ideal geochronology, however (Table 2), meaning these patterns may be a function of the limited age models.

During the 20th and 21st Centuries three clear patterns in EF were evident across multiple records. These are; 1) a rapid increase in EF; 2) a peak in EF (Average=100, range=26-183; Fig. 2B) between 1950-1980 CE (centred on 1970 CE for the high resolution records) and; 3) declining EF from c.1970 until the top of each record. The consistent increase in EF until 1970 is attributed to regional increases in industrial activity, combined with use of leaded gasoline, while the post-1970 decline reflects increasing imposition of pollution controls, the changing locus of global production, i.e. to Asia (Fig. 5), and phasing out of leaded gasoline (Harmens et al., 2007; McConnell and Edwards, 2008; Pacyna and Pacyna, 2001; Shotyk et al., 1998). The extent of post-1970s recovery from peak enrichment varies by site (Fig. 2), but on average EF decreased to levels similar to those recorded in the late
19th and early 20th Centuries. It is worth noting that none of these presented records contain data from the most recent 10-15 years.

In European lake sediments regional Pb contamination showed broadly similar spatial and temporal patterns to peat, but of a lower magnitude (Fig. 2C). For example, Lake Sägistalsee (Swiss Alps) records much lower Pb enrichment by comparison to the proximal Jura EGR peat mire, e.g., peak industrial $EF$ were 2.3 at Sägistalsee versus 183 at Jura EGR (Fig. 6) (Koinig et al., 2003). Other Swiss lakes, e.g., Lake Meidsee (not plotted), also showed subdued $EF$ and differing temporal response to both Jura EGR and to Lake Sägistalsee (Thevenon et al., 2011). In Finland, Lake Lehmilampi is geographically comparable to Dumme Mosse, however, it again showed a more subdued response ($EF < 5$ versus $EF > 100$ in the peat mires) (Augustsson et al., 2010; Meriläinen et al., 2011; Fig. 2C). These differences are assumed to be due to high and variable catchment sediment inputs affecting the fidelity of the Pb records in lakes (Koinig et al., 2003; Stromsoe et al., 2013).

### 3.2 Lead enrichment in North America

Despite its size and industrial history, there are relatively few sedimentary records of metal contamination from North America that fit the criteria of this compilation. Consequently, existing records are spatially disparate and present somewhat divergent patterns. Suitable records exist from lake sediments in Great Lakes region (Copper Falls; Pompeani et al., 2013) and two records from eastern Canada; a peat mire in eastern New Brunswick (Point d’Escuminac; Kylander et al., 2009; Weiss et al., 2002) and Lake Landry in eastern Québec (Gobeil et al., 2013) (Fig. 1). All of these records contain robust geochronology (Table 2). Copper Falls is considered a regionally representative record, with patterns in $EF$ matched by other lakes in the region (Pompeani et al., 2015; Pompeani et al., 2013).

At Copper Falls Pb contamination dates from 6500 BCE (~8500 cal. BP) (Pompeani et al., 2013). This is the earliest known onset of Pb contamination in a sedimentary record (Fig. 2). Enrichment is attributable to pre-historic Cu use, with the date of onset additionally supported by $^{14}$C dating of organic material found alongside Cu artefacts (see Pompeani et al., 2013) and a comparative record from McCargo Cove, Lake Superior (Pompeani et al., 2015). By comparison, the Point d’Escuminac peat and Lake Landry cores record the onset of enrichment much later, from the early 1800s CE, with the former attributed to regional coal-mining from ~1750 CE (Kylander et al., 2009).

Pre-Industrial Pb enrichment at Copper Falls displays transient pulses between 6500 and 3500 BCE (maximum $EF = 4.3$), after which $EF$ declined. After 1300 CE a sustained increase in $EF$ commenced, continuing into the Industrial period. Enrichment increased more rapidly from 1500 CE (i.e. $EF = 6$ at 1600 CE), presumably driven by expansions in pre-Columbian metallurgy and European settlement (Pompeani et al., 2013). Alternatively, the increased pollution at this point could be the result of bioturbation incorporating younger, more contaminated material at depth. Regardless by 1750 CE, the beginning of the Industrial Revolution, $EF$ had increased to 8 (Fig. 2C).
During the Industrial Period EF at Copper Falls rose rapidly, peaking at 57 in the early 1960s CE (Fig. 2C). Enrichment then declined to reach an early 21st Century value of 40 (2002 CE), equivalent to mid-20th Century values (Fig. 4). By comparison Industrial era EF at Point d’Escuminac and Lake Landry were an order of magnitude lower. At Point d’Escuminac, enrichment peaks in 1910 CE at 10.3. This date contrasts with Lake Landry (maximum EF = 9 in early 1970s), Copper Falls and other North American records (not included in the compilation) where peak Pb pollution occurred between the 1950s and 1980s (Norton, 2007; Pratte et al., 2013; Schindler and Kamber, 2013; Shotyk and Krachler, 2010; Vermillion et al., 2005). Both Point d’Escuminac and Lake Landry also record a less significant EF decrease in recent decades, e.g. current (c.2002 CE) EF at Copper Falls is 17 times less than peak emissions, whereas at Point d’Escuminac and Lake Landry (at c.1997, 2010, respectively) they are 1.7 times less (Fig. 4).

Copper Falls contains the highest Pb concentrations (both background Pb and Pb_{ex}) of any of the presented lakes (Fig. 2C). In the original study metals were measured on bulk (nonashed) leached samples. The Copper Falls core contained significant organics (c. 40-78%), implying metal concentrations are diluted by the presence of organics, e.g. reported background Pb and Ti concentrations were 2.3 and 115 ppm, versus UCC estimates of 17-20.4 and 4100-6910 ppm, respectively (Kamber et al., 2005; McLennan, 2001). Values were therefore corrected to average Ti values in UCC (4100 ppm) (McLennan, 2001). Study site lithology is comprised of metamorphosed basalt, which can be relatively depauperate in both Pb and Ti by comparison to UCC. Consequently, the Pb concentration data for Copper Falls presented in this paper may be an overestimate by up to 2 times. Regardless, Pb concentrations at Copper Falls are still high, reflecting significant native Pb concentrations in addition to very significant Pb_{ex} derived from local metallurgy (Pompeani et al., 2013).

3.3 Lead enrichment in South Asia

One known suitable record of Pb contamination exists from South Asia (East Rongbuk Glacier, Mt Everest; Lee et al., 2011). At East Rongbuk the onset of enrichment occurs relatively late (early 1800s CE). Enrichment is episodic (EF=1-2) during the 19th and early 20th Centuries (Fig. 2A and 4). It does not become consistently >2 until after 1920 and peaks at 6.3 in 1994 CE. The later pollution onset in this record is consistent with the regional timing of industrial development, i.e. rapid industrialisation during the later half of the 20th Century (Lee et al., 2011). In addition, the location of the East Rongbuk Glacier implies its contamination record may not reflect wider trends in South Asia. Irrespective, EF at East Rongbuk Glacier are lower than other Northern Hemisphere ice records, (Fig. 2A and 3).

3.4 Lead enrichment in East Asia

East Asian records of Pb contamination include Lake Liangzhzi, Hubei Provence, eastern central China (Lee et al., 2008), Lake Erhai (Hillman et al., 2015) and Xing Yun Lake (Hillman et al., 2014), in Yunnan Provence, southwestern China, and Hongyuan peat mire,
Tibetan Plateau (Ferrat et al., 2012) (Fig. 1). Enrichment of Pb in these archives is the lowest of any region and is comparable to that of Australia, with EF currently less than 5 in all presented archives (e.g. Fig. 2 and 3).

East Asian records show high variability in the timing of Pb contamination onset. Lead enrichment (EF >1) occurs from as early as c.2800 BCE at Lianghzhi Lake (Lee et al., 2008). In the mountainous Yunnan Provence, contamination is recorded much later at 150 BCE (Xing Yun) and 40 CE (Erhai). In Tibet enrichment occurs much later again at approximately 1700 CE. Despite an increase in EF from 1700 CE, Pb isotopes measured in the Hongyuan core did not indicate the presence of contaminate Pb, i.e. the Pb isotope composition remained similar to deeper layers in the core (Ferrat et al., 2012). In addition, as noted in the original paper, age control is poor in the top of the core (Table 2).

Prior to the Industrial Revolution, all three lakes record a minor plateau in EF (c.1.6) between c.130-450 CE, although this ended later (850 CE) at Liangzhzi (which has poorer age control; Table 2). Following this EF patterns diverge. Xing Yun Lake shows a consistent decline in EF until the 20th Century, whereas Lake Erhai, 300 km northwest, records maximum enrichment at 1300 CE (EF =6.7). This peak was attributed to Yuan (Mongol) Dynasty smelting (Hillman et al., 2014). EF at Lake Erhai then declined to 2-3 until the 1980s. Further north, Liangzhzi Lake also records a significant EF increase from 1005-1550 CE, when peak EF (2.1) occurred; however, improved geochronology in needed to further constrain the timing of this peak (Table 2).

The East Asian records do not show a significant change in EF associated with the Industrial Revolution. This is unsurprising as China remained significantly less industrialised than Europe, or the Americas, at this time. Rather, they show a minor increase in Pb enrichment within the Industrial Period. For example, Hongyuan records a linear increase in enrichment after c.1700 CE (EF=1.2), which extends to the late half of the 20th Century (EF=1.5) when the record terminates (1970 CE). As previously noted, geochronology is however limited on the upper part of this core (Table 2). The Yunnan lakes both show mid to late 20th Century increases in EF; Erhai between the 1980s (EF 2.1) and c.2000 CE (3.2) and Xing Yun between the 1920s (1.4) and c.2000 CE (EF 2.2).

Low EF values in East Asian archives reflect the location and time period covered by the records. Liangzhzi Lake (central China) predates the Great Leap Forward and has poor age control in upper part of the core (Table 2). Therefore it does not incorporate recent significant industrial growth in China. Hongyuan (Tibet) and the Yunnan lakes are remote locations and do not appear to be capturing the significant levels of contemporary air pollution experienced within East Asia. The difference between the Yunnan lake records may be attributable to variable catchment inputs and/or the effect of complex meteorology influencing atmospheric deposition in this mountainous region. It is also notable that none of these records show post 1970s CE recovery in EF, in contrast to Europe and North America.

3.5 Northern Hemisphere Polar records
Polar records of Pb contamination exist from Greenland (Candelone et al., 1995; Hong et al., 1994; McConnell et al., 2002), Devon Island (Shotyk et al., 2005b; Zheng et al., 2007) and the northern Pacific (Mt Logan, Yukon Territory, Canada; Osterberg et al., 2008) (Fig. 1). These provide some of the most reliable records of Pb pollution due to their high temporal (annual or sub-annual resolution; Table 2).

The timing of Pb contamination onset in the Arctic varies by location. At Summit (Greenland), anthropogenic Pb accumulates from c.650 BCE, similar to Europe (Fig. 2A) (Hong et al., 1994). At Devon Island (Canadian Arctic) the earliest enrichment occurs at c.1800 BCE (Zheng et al., 2007), >1000 years earlier than Summit. Devon Island therefore potentially records Greek and Phoenician metal working (Zheng et al., 2007), or possibly early metal working from North America (see Pompeani et al., 2013). At Mt. Logan the timing and magnitude of Pb enrichment is lower and later than other Polar Northern Hemisphere records, occurring at 1400 CE (EF=1.5) (Osterberg et al., 2008). Mt. Logan is thought to be largely representative of Asian emissions with only nominal Pb inputs from other regions (Osterberg et al., 2008). Despite this, enrichment onset occurred considerably later than was recorded in China (2800 BCE at Lianghzhi Lake) (Lee et al., 2008), however, it coincides with EF in Lianghzhi increasing above 2, potentially implying regional contamination from this time.

Following its onset, pre-Industrial contamination is spatially variable. At Greenland the Summit core records a history largely identical to Europe (e.g. Jura EGR), namely an EF peak corresponding to the Roman period (100 BCE to 200 CE; EF=2.1), a return to background levels in the Medieval period (c.500 CE), followed by a steady increase in EF until the onset of Industrial Revolution when EF =5 (Candelone et al., 1995; Hong et al., 1994; McConnell et al., 2002). Devon Island also records European metalworking. Episodic peaks in Pb enrichment (EF=3) occurred at 1100 BCE, 100 CE, and 1000 CE. These are ascribed to expansion of Iron-Age technology in Europe, the expansion of metalworking during the Roman period, and post-Roman economic expansion, respectively (Zheng et al., 2007). Additional Pb peaks at 1350 and 1750 CE, may track expansions in metallurgy in the central North American Mississippian cultures (Blitz, 2010) and following European settlement of North America (from the 1500s CE). At Mt Logan a steady trend of increasing EF occurs which continues into the Industrial Period.

The Industrial Revolution stands as a prolonged increase in Pb that extends until the present in the Greenland and Devon Island records, albeit displaying a decline over recent decades (Fig. 4). At Summit, Greenland, the Industrial Revolution is recorded as three phases. During the early phase (1750s-1880 CE), EF rose from preindustrial levels to an average of 48. During the Second Industrial Revolution (the period between c.1860-1914, associated with expanded production and technological change; Chandler, 1977) EF rose dramatically. Peaks of >400 occurred in 1914 and 1946, before reaching an all-time peak (EF=433) in the early 1970s CE (Candelone et al., 1995; Hong et al., 1994; McConnell et al., 2002). These trends are mirrored by the shorter (from 1750 CE) record available for the ACT2 core in Southern Greenland (not plotted), although the ACT2 records lower magnitude enrichment (McConnell and Edwards, 2008). During the third phase, after the 1970s, EF in Greenland
declined to 98 by 1995 CE, equivalent to c.1890s levels. Devon Island records a similarly
dramatic response in $EF$ during the Industrial Revolution. $EF$ increased to 5-10 after 1750
CE, >50 after 1880 CE and 440 by 1960 CE. Again similar to Summit, enrichment at
Devon Island, declines rapidly after 1960 to $EF=53$ by 2000 CE (Shotyk et al., 2005b).

Patterns of Pb enrichment at Mt Logan during the Industrial Period are different to the other
Northern Hemisphere Polar records (Fig. 2A). The Industrial Revolution is not marked by a
dramatic increase in $EF$, rather it occurs within a general trend of increasing $EF$ from 1000
CE. $EF$ increases rapidly after 1900 CE, reaching 4.4 by 1950 CE. However, the biggest
increase occurs after 1975 CE, with $EF$ reaching 14.7 at the top of the core (1997)
(Osterberg et al., 2008). Mt Logan is therefore the only Northern Hemisphere Polar archive
which shows no recovery during the late 20th or 21st Centuries (Fig. 4). Lead contamination
at Mt Logan is primarily sourced from East Asia. Therefore recent increases in Pb
enrichment likely reflect industrial expansion and increased coal-burning in East Asia
during the later 20th Century (Fig. 6).

3.6 Lead enrichment in South America

Suitable records from South America include two Bolivian lake cores (Laguna Tyapi Chaka
and Laguna Lobato; Cooke et al., 2008), a Bolivian ice core record from Sajama Glacier
(Ferrari et al., 2001; Hong et al., 2004) and a distal peat record from Tierra del Fuego
(Karuninka; De Vleeschouwer et al., 2014) (Fig. 1).

The earliest evidence of Pb contamination is recorded in Bolivia lake sediments at 400 CE
at Laguna Taypi Chaka. Onset is, however, spatially variable. For example, 500 km
southwest at the better dated (Table 2) Laguna Labato, Pb contamination commenced 600
years later (Cooke et al., 2008). Similarly, Sajama Glacier, located between the two lakes,
records Pb contamination onset later again at c.1100 CE (Ferrari et al., 2001; Hong et al.,
2004). Sajama Glacier is assumed to more accurately map the regional onset of pollution in
central South America, whereas the lake cores record catchment specific contamination,
with local metallurgical activity in each region known to be distinct (Cooke et al., 2008;
Schultze et al., 2009). In the south of continent at Tierra del Fuego (Karukinka peat mire),
Pb contamination began at c.750 CE, although there is evidence of possible Pb
contamination at 1 CE (De Vleeschouwer et al., 2014). An additional ice record from
Quelccaya ice cap, Peru (not plotted), records the onset of consistent Pb contamination
from c.1500 CE (Ugliettia et al., 2014). The Quelccaya record does, however, show earlier
spikes in Pb enrichment which the authors attribute to either changes in dust input, volcanic
input or pre-Inca metallurgy.

By contrast to most other presented records, the Bolivian Lake cores record maximum
enrichment during the pre-industrial period (Fig. 2). The Sajama Glacier and the Karukinka
peat mire record peak Pb enrichment during the Industrial period, but also record
significant pre-Industrial contamination. For example, $EF$ at the glacier reaches 2.6 by 1621
CE and 4.3 by 1795 CE, while at Karukinka $EF=6.5$ by 1700 CE (although Karukinka has
poor geochronology after 1000 CE; Table 2).
During the 20th Century South American records show contrary patterns. EF at Sajama Glacier reached 5.3 by the start of the 20th Century and a maximum EF of 5.6 at the top of the core in 1998. Laguna Lobato recorded declining EF until c. 1950 CE, followed by a marginal increase during the second half of the 20th Century (EF=3). The Bolivian ice core (Quelccaya) displayed maximum Pb enrichment in the early 1930s CE, before a decline from 1930-1955, followed by a subsequent increase between 1955 and 1989 CE. It is noteworthy, however, that other anthropogenic metals (e.g. Mo and Sb) show highest enrichment in top of this core. In contrast, in southern South America (Karukinka) Pb enrichment patterns in the Industrial Period are more similar to those of Europe. That is, EF increased dramatically during the Industrial period from 1870 CE, before reaching a maximum EF of 25 (1950s-1970s). After this, EF declined to 5.4 by 2010 CE. High EF variability in the Karukinka record during the Industrial era and was ascribed to variable soil dust fluxes (De Vleeschouwer et al., 2014), while in addition, this record suffers from poor age control during this period.

3.7 Lead enrichment in Australasia

Only two known suitable records of atmospheric contamination occur in Australasia. These are closely located (6 km apart) archives in the Snowy Mountains; the Upper Snowy (USC) peat mire (Marx et al., 2010) and Club Lake (Stromsoe et al., 2013). These are downwind of industrial emissions sources and population centres in eastern Australia and are at high elevations (c.1900 m). Therefore they record generalised regional pollution in southeastern Australia. Lead enrichment in Australia is low by comparison to the regions (Fig. 2 and 3), i.e. EF <10. This is attributed, in part, to high natural Pb concentrations in this south-eastern Australia, implying higher anthropogenic Pb concentrations are required to raise EF>1 (Stromsoe et al., 2015). In addition, the relative remoteness of the Snowy Mountains, means long airmass trajectories are required to transport pollutants to the site leading to dilution. The presented records are also downwind of a major dust-source region (the Murray-Darling Basin), which may result in further dilution of pollution Pb by natural dust aerosol (Marx et al., 2014a).

Enrichment onset in Australasia occurs at 1880 CE in USC (Fig. 2B), however Pb, isotopes suggest contaminant Pb accumulation may have begun from c.1850 CE (Marx et al., 2010; Marx et al., 2014b). EF ≥1.2 at Club Lake is recorded earlier at c.1750 CE (EF = 1.2) (Stromsoe et al., 2013). This date is before European colonisation, i.e. before regional mining/metallurgy began. The earlier onset at Club Lake is therefore attributed to the core age model, which has a step change at this point. The onset of contamination at 1750 CE is not supported by the regional metal emission history (Mudd, 2007) which accords with the onset of contamination in the mid to late 1800s as recorded in peat mires (Marx et al., 2010). Thus the onset of pollution appears concomitant with the beginning of mining and metal processing in Australia (Fig. 4).

Enrichment in the USC mire follows an increasing but irregular trend through the 20th Century, with a more rapid increase after 1980 CE attributed to increased regional mining and metal production patterns (Marx et al., 2010). EF reaches a maximum of 3.9 at the top
of the core (2006 CE). Comparatively, Club Lake records a substantially subdued pattern of
Pb enrichment typical of lake records (Fig. 2 and 6). $EF$ reaches 1.3 in the late-19th and
early 20th Century, after which it declines between 1920-1970 CE ($EF\approx1$), before again
increasing to the modern value ($EF=1.2$).

The USC peat records only a subdued response to both the onset, and phasing out, of leaded
gasoline, in the 1930s and 2000s, respectively (Marx et al., 2014b). This is despite
Australia having high per capita vehicle use. By comparison, even in a highly industrialised
east coast Australian city, gasoline was found to be the most likely source of Pb in roof dust
(Chiaradia et al., 1997). The subdued response in the USC mire may reflect the remoteness
of the study site. Excess Pb in the Snowy Mountains is derived mainly from primary
industrial sources including primarily metal production and mining, but also coal emissions
(estimated to constitute 30% of Pb deposited to the USC mire) (Marx et al., 2010).

3.8 Southern Hemisphere Polar records

Antarctic records of Pb contamination exist from Law Dome, East Antarctica (Vallelonga
et al., 2002), and Coats Land, West Antarctica (Planchon et al., 2003). These show no
significant contamination ($EF>1$) until 1890 and 1850 CE, respectively (Fig. 2A and 4).
This coincides with the onset of Pb contamination in Australia (Marx et al., 2010), although
it significantly postdates Pb enrichment in southern South America, which occurs from 750
CE (De Vleeschouwer et al., 2014). This implies Pb in Antarctica is dominantly sourced
from Australia, as also evidenced by its Pb isotope signature (McConnell et al., 2014;
Vallelonga et al., 2002). While airmasses of Australian origin influence both the West and
East Antarctic, trajectories from eastern Australia, where the majority of population and
industry, are likely to influence Coats Land more frequently (McGowan and Clark, 2008).
Coats Land recorded both earlier onset of pollution and higher $EF$ than Law Dome. $EF$ at
Coats Land are also likely to be influenced by dust and Pb transport from southern South
America (see for example McConnell et al., 2007).

At Law Dome, Pb enrichment increases after onset, reaching $EF=2$ in 1877 CE, 3.6 by
1919 CE, and 4.8 at 1989 CE at the top of the record (Vallelonga et al., 2002). Both the
magnitude and the enrichment patterns are similar to those recorded in Australian peats
(Marx et al., 2014b). At Coats Land, enrichment maxima occurs in the late 1970s
($EF=13.1$), before declining to 4.2 at the top of the record (1990 CE). The post-1970s CE
$EF$ decline at Coats Land, reflects the pattern found in southern South America, i.e. at the
Karukinka peat mire (De Vleeschouwer et al., 2014). This implies South American derived
Pb contamination may be significant at this site.

4.0 Discussion

4.1 Rates of metal enrichment

The presented records of Pb contamination confirm the ubiquitous presence of industrial
metals in the Earth’s Critical Zone (the surface/near-surface environment, including soils
and water bodies, which supports life: National Research Council, 2001) (Fig. 3). The onset
of global-scale metal contamination is coincident with the Second Industrial Revolution, in
the mid to late 19th Century, and is marked by the deposition of anthropogenic metals in the
Polar Regions of the Southern Hemisphere. The timing of global-scale Pb contamination is
a product of increased atmospheric emissions of metals (and their subsequent transport to
distal locations) and colonial expansion and development (e.g. in Australia). Many regions,
however, experienced environmental metal contamination well before this period, with the
record of Pb contamination extending into pre-history in at least, the Americas, East Asia
and Europe.

Average contemporary (most recent) rates of Pb enrichment in ecosystems, as estimated
from the presented peat mires and ice cores, are 35 and 28 times natural background levels,
respectively. The presented lake records display lower rates of contemporary enrichment
(6.1 times background) due to the dilution effect of catchment derived sediment (Catalan,
2015; Stromsoe et al., 2015). Ice and peat mire records therefore most accurately reflect the
degree of metal perturbation in the atmosphere (Hannsson et al., 2015; Stromsoe et al.,
2015). Lead enrichment across the wider environment, as implied by the presented lake
records, is therefore likely to be lower by at least a factor of 2 (Fig. 6).

The incorporation of Pb in the environment has reduced substantially across much of the
globe after 1970 CE by an average of 2.2 times (Fig. 4) (note few of the presented records
incorporate data from the last 10 years). While this reduction is ultimately beneficial to
ecosystems, the actual environmental impact of metal contaminate may not be reflected by
the most recent available data (Fig. 3). Maximum average environmental Pb enrichment
was 131 and 62 times background levels in the ice and peat records, respectively. This
historic Pb contamination is stored in the shallow surface environment and is, for the most
part, likely to be readily remobilised as the sedimentary environments in which pollutants
are stored geomorphically dynamic (e.g. Bindler et al., 2008; Bogdal et al., 2009; Rose et
al., 2012). Historical metal pollution should therefore be considered as part of the current
environmental Pb burden.

4.1 The distribution of Pb in the environment

Despite the wide distribution of Pb in the environment, there is considerable spatial
variation in the degree of the Pb enrichment (Fig. 2, 3 and 4). Some of these patterns are an
artefact of the fidelity, resolution, geochronology and the air mass trajectories and specific
local meteorology conditions influencing the presented records, while others reflect
regionally distinctive pollution patterns, i.e. emissions.

There are noteworthy hemispheric differences in Pb EF. The Northern Hemisphere is
polluted by 1-2 orders of magnitude more than the Southern Hemisphere (Fig. 3). This
largely reflects the lower population and industrial activity in the Southern Hemisphere
(Pacyna and Pacyna, 2001). This could also be in partly attributable to the spatial location
of available records, with the presented records from the southern hemisphere generally
located at greater distances from urban and population centres. In addition, two sets of the
presented records are from the two least inhabited continents, Antarctica and Australia.
The available evidence suggests Europe is significantly more polluted than the rest of the

globe (Fig. 3). Maximum industrial EF in European fed ice cores are >100 times

background (Fig. 2A). Similarly peat mires from central Europe and Scandinavia record

similar values (EF >100). By comparison, maximum EF~≤100 and <10 occur in peats and

lakes in more remote locations (northern Britain, northwest Spain and the Faroe Islands)

(Fig. 3). Europe has both a long history of Pb pollution, while the magnitude of Pb

enrichment in many of the presented European records had already exceeded maximum

enrichment across the rest of the globe before the onset of the Industrial Revolution (Fig.

2A and 2B). The magnitude of Pb enrichment in Europe therefore has a strong influence on

average global Pb pollution and removing the European data reduces global EF to 5 and 9

(from 35 and 28) for the peat and ice record data, respectively.

Outside of Europe, there are insufficient records to provide a complete picture of the extent

of environmental metal pollution. The USA overtook Europe as the largest industrial centre
during the 19th Century (e.g. see Fig. 5). However, this is not consistently demonstrated in

the presented North American records. The three exclusively fed North American records

(Copper Falls, Point d’Escuminac and Lake Landry) have EF~≥10, however, these records

show a variable picture. EF at Copper Falls (and in proximal lakes) are much higher than in

any records from northeastern North America. Copper Falls is located in the (former)

industrial heartland of the USA. Consequently, significant Pb emissions would be expected.

In the more remote Lake Landry and Point d’Escuminac, maximum industrial EF is

approximately 10, substantially lower than the presented records from Europe. The

presented records imply the extent of Pb enrichment may therefore be spatially patchy

across North America, associated with variability in sub-regional emissions (Shotyk et al.,

2014). A more complete understanding of Pb enrichment in the North American

environment is therefore impeded by the lack of records.

There are a lack of suitable Asian records that map regional contamination and which

extend to the present time, while no known Central Asian records which meet the criteria of

this compilation exist. Contemporary EF for Asia ranges from <2 to 15 in reported ice, peat

and lake studies from East Asia and South Asia (Fig. 2 and 3). Distally, the Mt. Logan ice

core records a significant increase in Pb enrichment in recent decades (Fig. 4), attributed to

increasing East Asian pollution (Osterberg et al., 2008). The other presented Asian records

do not capture this recent change, due to their age resolution or location (Table 2).

Critically, although Chinese Pb emissions are rising, they remain significantly below those

of Europe and USA at height of Pb emissions during the 1970s CE (Fig. 5). Since the late

1990s CE Chinese Pb emissions have been comparable to, or higher than, those of Europe

or North America (Fig. 5). This change is not yet recorded in the presented records, most of

which predate it. Consequently, new records would be expected to reflect this nascent

pollution load (Fig. 2 and 3).

While Pb enrichment in the Southern Hemisphere is on average lower than that of North

America and Europe, EFs are variable depending on the proximity to local pollution

sources. Industrial era EFs from South America approach the global average at 5-25 times

natural background concentrations (Fig. 2 and 3). However, records which are most
reflective of regional scale pollution, e.g. the Bolivian (Sajama) ice core, display
enrichment factors of ~5, lower than those from Europe and North America (Fig. 2A). In
Australia, regional Pb enrichment, as best recorded by the USC mire, is also low (EF=4).
The USC mire can be considered a remote location, however, significant regions of the
Australian continent are even more remote from pollution sources, implying the Pb
enrichment over much of the content could be negligible.

Overall, this compilation highlights the major data gaps which exist outside of Europe and
the Northern Hemisphere Polar Regions. Most significantly, there are no known Pb
enrichment records from the Africa. Other major data gaps exist throughout Asia where
data are patchy and do not allow a robust assessment of changing environmental Pb levels
associated with the recent increase in industrial activity.

4.2 Changing metal pollution through time

Pre-industrial Pb enrichment is recorded in both Hemispheres. However, in the Southern
Hemisphere only South America records pre-industrial contamination, while its onset is
later than recorded in Europe, Asia or North America (Fig. 2). Records of early Pb
contamination are typically local in extent and thus the date at which Pb enrichment first
becomes locally apparent differs by up to several thousand years. Globally, the earliest
record of Pb contamination from the selected archives dates from 6500 BCE in the Great
Lakes region, North America (e.g. at Copper Falls), which is near to prehistoric mines
(Pompeani et al., 2013). Liangzhi Lake, eastern central China, records Pb pollution from
2800 BCE, indicating localised metal working from the start of the Bronze Age in ancient
China (Lee et al., 2008). In other East Asian records, contamination onset is later however.
In Europe, the Jura EGR peat mire seemingly provides a more regional-scale record by
comparison to other European sites. It records the impact of Pb production on the Iberian
Peninsula at 1000 BCE (Shotyk et al., 2000; Shotyk et al., 1998). In the Southern
Hemisphere lake records display localised enrichment from silver mining in major
metallurgical centres of pre-Incan Bolivia dating from 400 CE (Cooke et al., 2008).
Mercury contamination in Peru commences earlier, however, at 1400 BCE (Cooke et al.,
2009). In most cases, the magnitude of pre-Roman period Pb pollution was low with EF <2,
except at Copper Falls where pre-historical EF were as high as ~4 times background.

Pre-Industrial contamination on the European continent appears to have become more
regionally significant after approximately 650 BCE, as indicated by the onset of
anthropogenic metal accumulation in polar ice records. Interestingly, however, enrichment
is not recorded until after 500 BCE in presented peat records from Spain, Scandinavia and
Northern Britain, (Cloy et al., 2008; Klaminder et al., 2003; Martínez Cortizas et al., 2002;
Shotyk et al., 2005a). However, other records from Northern Britain and Scandinavia where
Pb isotopes where measured record an earlier onset of Pb contamination, dating from the
Bronze Age (Brännvall et al., 1999; Le Roux et al., 2004). Most European archives record
the Roman smelting as a peak in EF of 2-10, before a decline in the Medieval Period.
Increases in Pb enrichment in Europe occurred at c.1000 and 1300-1400 CE associated with
the intensification of German mining and increased metallurgy and mining from the
Renaissance (Hong et al., 1994; Shotyk et al., 2005a; Shotyk et al., 1998; Zheng et al., 2007). Thus regional-scale Pb contamination in Europe became established well before the Industrial Revolution.

North America and Asia both have a long history of pre-industrial contamination associated with early metallurgy (Lee et al., 2008; Pompeani et al., 2013). However, in some records from these locations, Pb enrichment is not apparent until within the Industrial Period (Ferrat et al., 2012; Kylander et al., 2009; Lee et al., 2011), implying spatially variable pre-Industrial activity. In North America it is difficult to constrain the magnitude of pre-Industrial Pb enrichment as there are few records capturing broad regional emissions that fit the criteria of this study. In Asia, the Mt Logan ice core suggests pre-Industrial enrichment was up to 3 times background (Osterberg et al., 2008). South American archives also contain a pre-Industrial record of Pb pollution, where in some cases, the magnitude of enrichment is greater than that recorded during the Industrial Period, i.e., $EF = 3-14$ versus 4-6 (Cooke et al., 2008), although this is not universal (Fig. 2).

At a global-scale, metal pollution increased most significantly following the beginning of industrial methods of mining, manufacturing and associated consumption from c.1750 CE. In the majority of records from Europe and North America, the Industrial Revolution marks the onset of a significant metal pollution burden in the global environment, which continues to the present. In Europe, this is evident in two stages; 1) 1750-1890 CE where, for example, $EF$ rose to 40 and 50 in the Jura peat mire (Switzerland) and the Summit ice core (Greenland), respectively and; 2) 1890 CE to present during which the most rapid increases in $EF$ occurred, e.g. $EF$ reaching ~180 in Jura and >400 in Summit. The scale of metal pollution during the Industrial Period in Europe is illustrated by temporal patterns in emissions. For example, using $EF$ at Summit (to 1995) as a proxy for European contamination, 17% of cumulative Western European atmospheric Pb emissions occurred prior to 1800 CE, 37% between 1800-1925, and 46% between 1925 and 1995. This figure is in agreement with estimates of cumulative anthropogenic Pb in west-central European peat, where approximately 59-66% of total Pb content was deposited prior to 1925 CE (Shotyk et al., 2000; Zaccone et al., 2007).

The few Asian records do not show an abrupt change associated with the Industrial Revolution. In these records the most pronounced increase in $EF$ occurs later, during the mid-20th Century, and continues into the present (Fig. 3). Asia archives record lower magnitude pollution by comparison to Europe, however, the most significant metal pollution in the region is contemporary (Fig. 3 and 4).

In the Southern Hemisphere, Australian, Antarctic and some South American records show a pronounced change during the Industrial Period. The magnitude of maximum enrichment in the Industrial Period is generally an order magnitude less than Europe (Fig. 2 and 3), while the timing of onset of rapid increasing $EF$ is later at ~1850-1890 CE. Thus the Southern Hemisphere missed the first wave of Industrial pollution (from 1750 CE) due to the later timing of adaptation to industrial manufacturing and the timing of European colonization. For example, industrialisation of Australia post-dates European settlement.
(from 1788 CE), while the earliest Pb pollution is recorded almost immediately following
the development of the first economic mines in Australia, appearing simultaneously at c. 1850 CE in both the Snowy Mountains and the Antarctic.

European and North American records overwhelmingly show peak Pb enrichment between 1950-1980 CE, followed by a decline towards the present. This is broadly attributed to the introduction of cleaner production standards and the phase out of leaded gasoline (Harmens et al., 2007; McConnell and Edwards, 2008; Osterberg et al., 2008; Pacyna and Pacyna, 2001), although the later maybe less significant that commonly thought (see following paragraph). Despite this, the magnitude of Pb enrichment remains significant, e.g. average EF= 55 and 75 in European peat and in ice cores, respectively. In contrast, Southern Hemisphere records in general, show ongoing increasing Pb emissions (Fig. 2 and 4).

Increasing EF in the Antarctic and Australia likely reflects recent major increases in ore extraction from Australia in particular (Mudd, 2007). The South American records are more variable, however. Increasing Pb EF towards the present occurs in the Sajama Glacier record, but not in the Bolivian lakes or the Karukinka peat core. Asian records all show increasing metal pollution (e.g. contemporary EF=15 at Mt Logan), reflecting recent industrial growth across much of Asia (Li et al., 2012). This is expected to result in a delayed but significant increase in EF within the regions ecosystems, which is, so far, not apparent in the available records that predate the expected significant increases in emissions. It is worth noting, however, that recent Chinese Pb emissions are significantly below maximum historical Pb emissions in USA, Europe and Russia (Fig. 5), implying that current industrialisation of Asia is unlikely to result in a comparative environmental metal burden to that of Europe.

Despite the often cited contribution of leaded gasoline to the historic lead burden, its introduction in the 1920-1930s CE did not result in a stepwise change in Pb EF or Pb_e, in the presented records. Gasoline has undoubtedly contributed to the global pollution Pb load, as demonstrated by numerous Pb isotope studies (Bollhöfer and Rosman, 2002; Brännvall et al., 1999; Kylander et al., 2009; Shotyk et al., 2001), however, its contribution to Pb enrichment appears spatially variable and is less significant than Pb from other industrial sources in most of the presented studies. For example, EF at Summit, Greenland, is 247 during the early 20th Century prior to the introduction of leaded gasoline, compared to EF = 321 during peak gasoline emissions (1965-1975 CE). The contribution of leaded-gasoline to the total Pb pollution burden can be estimated from the difference between the actual Pb EF in 1975 (approximately peak Pb pollution emissions) and the predicted EF in the same year determined using the 1800-1920 CE trend, that is, the Pb contamination contribution derived from all other industrial sources. Using this approach, gasoline is estimated to have contributed 11% to maximum Pb enrichment at Summit. At other European or European pollution dominated sites, e.g. Jura, in the Swiss Alps and Devon Island (Canadian Artic), leaded gasoline contributed 17 and 32% of peak enrichment, respectively. By comparison, at Copper Falls in North America leaded-gasoline is estimated to have contributed 8% of peak emissions in c.1964 CE. In the remote USC mire in Australia the contribution of gasoline Pb is negligible by comparison other industrial activity (Marx et al., 2010),
however as previously pointed out, gasoline derived Pb was dominant in Australian cities (Chiaradia et al., 1997). Thus away from urban centres, it appears other sources of industrial Pb may be more significant than gasoline derived Pb.

Lead contamination therefore stands as ubiquitous globally from c.1890 CE. Consequently, the presented records imply that anthropogenic Pb, along with a likely suite of associated metals (Marx et al., 2010; Pacyna and Pacyna, 2001), form a distinct marker in any sedimentary archives receiving even a small atmospheric contribution. For example, based on average global enrichment in peat mires (EF=28), an atmospheric anthropogenic Pb flux of 0.8% would result in an EF of 1.2 by comparison to average Pb concentrations in upper continental crust, i.e. Pb=17 ppm (McLennan, 2001). In lakes, which receive more significant unpolluted sediment input, evidenced by their lower EF (Fig. 2 and 6), 4% atmospheric input is required to reach an EF of 1.2. This date (1890 CE), therefore stands a potential marker of the onset of the Anthropocene. A variety of dates for the Anthropocene onset have been suggested, ranging from the beginning of the Holocene, based on faunal and floral domestication across significant regions of the globe (Smith and Zeder, 2013), to the early 1950s CE, based on the global signal of anthropogenic radionuclide fallout and other human induced changes in Arctic lake cores (Wolfe et al., 2013). The former however does not result in a global signal, while the latter occurs within the ‘Great Acceleration’ (1945 to present), the greatest period of global change, rather than at its onset (Steffen et al., 2007). In addition, using c.1950 CE for the onset of the Anthropocene fails to take into account the very significant changes in Earth’s systems which occurred earlier than this date. The results of this compilation suggest globally ubiquitous anthropogenic Pb from c.1890 CE offers an alternative novel global marker (Uglietitia et al., 2014; Zalasiewicz et al., 2011).

5.0 Conclusion

The records presented in this compilation collectively document significant global changes in Pb concentration in the Earth’s critical zone associated with human activity. As a result, current Pb concentrations are perturbed by an average of 6-35 times natural background levels. Enrichment, however, varies spatially by two orders of magnitude. Enrichment in Europe and parts of North America exceeds 100 times background, whereas in Australia and Antarctica it is 4-15 times background. The commencement of Pb perturbation in the environment extends into pre-history in Europe, North America and East Asia, while in South America it occurs from the Middle Ages, associated with pre-Columbian metallurgy. On a global scale, the magnitude of this early Pb pollution is minor by comparison to the scale of environmental Pb enrichment which begins with the Industrial Revolution. In the presented records Pb contamination becomes globally ubiquitous after c.1850-1890 CE, when anthropogenic Pb begins accumulating in Australia and Antarctica. This date therefore stands as global sedimentary marker of industrial activity. Following this date, Pb contamination increases globally unabated for c.100 years. After c.1970 CE Pb contamination decreases in Europe and North America, associated with pollution controls and changing industrial activity, however in these locations pollution remains significant at >40 times background. In other parts of the globe, notably Asia and much of the
Southern Hemisphere, the Pb pollution load is growing due to increasing industrial activity.

Outside of Europe, significant data gaps occur, most notably from Africa, meaning the magnitude and specific patterns of Pb contamination are less clear or unknown. Despite this, the presented records demonstrate a significant metal pollution burden is ubiquitous in the global environment with likely associated implications for ecosystems and biogeochemical cycles.

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We thank Antonio Martínez-Cortizas, Charles Gobeil, Aubrey Hillman, Zhangdong Jin and David Pompeani who kindly made their data available for this compilation. All data are available via the original publications (see Table 1). We also thank two anonymous reviews whose comments greatly improved this manuscript.

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**Lakes**

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Figure 1. Map showing the location of records used in this compilation (full site details are presented in Table 1).
Figure 2. Lead concentrations (blue and red bars) and Pb enrichment factors (grey boxes and yellow and brown bars) in the presented sedimentary archives, for A) ice cores, B) peat mires and C) lake records. The grey boxes show Pb enrichment levels (EF) during the Industrial Period. The top of the box shows the maximum industrial EF, while the bottom of the box indicates the average industrial EF. The brown bars indicate the most recent EF. Where this is lower than the grey box it indicates a recent reduction in EF. Yellow bars indicate maximum pre-industrial EF. Dates for the period of industrial enrichment maximum industrial EF and most recent EF are indicated for each record (all dates represent CE ages). For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.
Figure 3. Current (late 20th and early 21st Century) Pb enrichment factors (EF) in global sedimentary archives. Arrows indicate major documented pollution plume pathways (after Marx and McGowan, 2010).
Figure 4. Trends in Pb enrichment (EF) during the Industrial Period (1750 CE to present) in selected archives. LGN = Mt Logan, DVN = Devon Island, SMT = Summit, DMM = Dumme Mosse, EGR = Jura EGR, HNG = Hongyuan; ERH = Erhai Lake; USC = USC; LAW = Law Dome; CTS = Coats Land; KKR = Karukinka; SJM = Sajama Glacier; CPR = Copper Falls; ESC = Point d’Escuminac (See Table 1).
Fig. 5. Reported atmospheric Pb emissions for selected regions during the late 20th/early 21st Century (EEA, 2013; EPA, 2008; Li et al., 2012; Pacyna and Pacyna, 2001).
Fig. 6. Comparative Pb enrichment (EF) recorded within lakes and peat mires which are within close proximity of one another.