The influence of controlled fire on the mobilization of Potentially Toxic Elements (PTE) in a mined landscape: Implications for land management and environmental health

This thesis submitted in total fulfilment for the requirements of the degree of Doctor of Philosophy (PhD)

By

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Cover Photo:

Controlled fire conducted at the Maldon study area on 20th August 2015 – taken by Joji Abraham

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STATEMENT OF AUTHORSHIP

Except where explicit reference is made in the text of the thesis, this thesis contains no material published elsewhere or extracted in whole or in part from a thesis by which I have qualified for or been awarded another degree or diploma. No other person's work has been relied upon or used without due acknowledgement in the main text and bibliography of the thesis.

Signed:________________	Signed:________________
Dated: 01 May 2018	Dated: 01 May 2018
Joji ABRAHAM	**Associate Professor Kim DOWLING**
Candidate	**Principal Supervisor**

CHAPTERS OF THESIS PUBLISHED IN REFEREED JOURNALS AND CANDIDATE'S CONTRIBUTION IN EACH PUBLICATION

This thesis-by-publication is structured into nine chapters and the published works within this body of thesis are presented in Chapters 2–8. Candidate's contributions toward each of these published works are in Table i, and a more detailed description of the thesis format and chapter content are depicted in Chapter 1: Introduction.

CHAPTER 2 - The unquantified risk of post-fire metal concentration in soil: A Review

Abraham, J., Dowling, K., & Florentine, S. (2017). Water, Air, and Soil Pollution 228:175. https://doi.org/10.1007/s11270-017-3338-0

CHAPTER 3 - Risk of post-fire metal mobilization into surface water resources: A Review

Abraham, J., Dowling, K., and Florentine, S. (2017). Science of the Total Environment 599-600:1740-1755. https://doi.org/10.1016/j.scitotenv.2017.05.096

CHAPTER 4 - Assessment of potentially toxic metal contamination in the soils of a legacy mine site in Central Victoria, Australia

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CHAPTER 5 - Application of Pollution Indices in the Soil Metal Contamination Assessment - Maldon Legacy Mine Site, Central Victoria, Australia

Abraham, J., Dowling, K., and Florentine, S. International Journal of Environmental Science and Technology (submitted).

CHAPTER 6 - Controlled burn and immediate mobilization of potentially toxic elements in soil, from a legacy mine site in Central Victoria, Australia

Abraham, J., Dowling, K., and Florentine, S. (2018). Science of the Total Environment 616-617: 1022-1034. https://doi.org/10.1016/j.scitotenv.2017.10.216

CHAPTER 7 – Effects of prescribed fire and post-fire rainfall on mercury mobilization and subsequent contamination assessment in a legacy mine site in Victoria, Australia

Abraham, J., Dowling, K., and Florentine, S. (2018). Chemosphere 190:144-153. https://doi.org/10.1016/j.chemosphere.2017.09.117

CHAPTER 8 – Influence of controlled burning on the mobility and temporal variations of potentially toxic metals (PTMs) in the soils of a legacy gold mine site in Central Victoria, Australia

Abraham, J., Dowling, K., and Florentine, S. Geoderma – the global journal of soil science (accepted for publication).

Table i Summary of published chapters

Chapter No	**Title of the paper**	**Source**	**Status**	**Candidate contribution**
2	The unquantified risk of post-fire metal concentration in soil: A Review	Water, Air, and Soil Pollution	Published	85%
3	Risk of post-fire metal mobilization into surface water resources: A Review	Science of the Total Environment	Published	90%
4	Assessment of potentially toxic metal contamination in the soils of a legacy mine site in Central Victoria, Australia	Chemosphere	Published	90%

5	Application of Pollution Indices in the Soil Metal Contamination Assessment - Maldon Legacy Mine Site, Central Victoria, Australia	International Journal of Environmental Science and Technology	Submitted	80%
6	Controlled burn and immediate mobilization of potentially toxic elements in soil, from a legacy mine site in Central Victoria, Australia	Science of the Total Environment	Published	90%
7	Effects of prescribed fire and post-fire rainfall on mercury mobilization and subsequent contamination assessment in a legacy mine site in Victoria, Australia	Chemosphere	Published	90%
8	Influence of controlled burning on the mobility and temporal variations of potentially toxic metals (PTMs) in the soils of a legacy gold mine site in Central Victoria, Australia	Geoderma	Accepted	85%

ABSTRACT

Controlled fires conducted in fire prone areas are an efficient and economic option to reduce the frequency and intensity of wild fires that result in damage to human property, infrastructure and ecosystems. However, in a similar way to wild fires, controlled fires affect many of the physical and bio-geochemical properties of the forest soil, and may remobilize Potentially Toxic Elements (PTE) from vegetation and soil organic matter. The objective of this study is to investigate the mobilization of PTEs in a mined landscape after a controlled fire and to describe their temporal variations in concentrations. Soil samples were collected two days before and two days after the controlled fire, at the end of each season, and after a major rainfall in September 2016, from a legacy mine site in Maldon, Central Victoria, Australia, and analysed for PTE concentrations.

The results revealed PTE mobility after the controlled fire, and most of the PTEs (As, Cd, Cu, Mn, and Zn) evidenced an increase in concentration (1.2, 1.5, 1.1, 2.9, and 1.7 times respectively) and other PTEs (Hg, Cr and Pb) shown a decrease (1.4, 1.1 and 1.1 times respectively) immediately after the fire. The increase in PTE concentration immediately after the fire is postulated to be associated with the addition of PTE enriched ash to the soil and the reduction is due to the volatilization of elements during fire. The PTEs, which increased their concentrations immediately after the fire show a temporal decrease in concentration in the post-fire soil environment due to the removal of ash and surface soil by rainfall runoff, leaching and wind activity. However, Hg shows an increase in concentration after the major rainfall event.

Although, median concentrations of As, Hg, Pb, Cu and Zn exceeded the Australian and Victorian top soil averages, only As and Hg are considered to be a risk to human and aquatic ecosystems health due to their elevated concentration and toxicity. Climate change and the resulting projection for increased forest fire frequency illustrates a growing concern given the expected concomitant increase in PTE mobilization. Preparing appropriate land and water management strategies, and addressing environmental health practice and policy, specifically at the legacy mining areas require a review. This study highlights the significant risk these sites pose.

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Introduction

1.1 Context and objectives

Mining and ore processing occupies a significant place in the economic prosperity and development of civilizations around the globe (Wellmer and Becker-Platen, 2002; Vidal et al., 2017). Mining supplies the necessary raw materials for commercial activities, improves the standard of living in many communities, and provides millions of job opportunities world-wide (Zeballos and Garry, 2010; Hruschka and Echavarria, 2011; Jorgenson et al., 2017). However, potentially toxic elements (PTEs), including As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn, formed from mining and ore processing create a substantial risk to human and ecosystems health in the vicinity of mine sites and also to distal areas (Sultan and Dowling, 2006; Navarro et al., 2008; Pearce et al., 2010; Cobbina et al., 2011, 2013; Park et al., 2014; Antoniadis et al., 2017; Martin et al., 2017).

Mine waste materials consist of metals and minerals include PTEs that were not captured during processing, crushed rock fragments, tailings and overburden materials. If mine waste is not contained or rehabilitated, possible consequences include contaminated soil, water and air environments with subsequent negative impacts on human and ecosystems health (Navarro et al., 2008; Taylor et al., 2010; Cobbina et al., 2013; Kim et al., 2014; Park et al., 2014; Antoniadis et al., 2017; Fan and Wang, 2017). It is reported that mining and metal processing constitute three of the top 10 toxic pollution problems across the globe and the health and well-being of more than 14 million people are at risk from mining activities (Mills-Knap et al., 2012). The degree and extend of PTE contamination around a mine site depends on geochemical characteristics of the mine waste and the due diligence used in mining to minimise impacts (Johnson et al., 2000; Schaider et al., 2007; Navarro et al., 2008).

PTE contamination is more significant in legacy mining areas, where limited or no environmental regulations existed during active mining and at mine closure (UNEP, 2001; Pearce et al., 2012; Park et al., 2014; Martin et al., 2016). This results in the accumulation of millions of tonnes of un-rehabilitated mine waste materials, which may contaminate all compartments of the environment, and act as continuous source of PTE contamination long after mine closure (Plumlee and Morman, 2011; Castillo et al., 2013; Foulds et al., 2014; Stefanowicz et al., 2014; Martin et al., 2014, 2017). More than a million legacy mine sites exist across the globe and more than 50,000 sites exist on the Australian continent highlighting the significance of PTE contamination from legacy mining activities across the globe and in Australia specifically (UNEP, 2001; Unger et al., 2012; Park et al., 2014).

Legacy gold mining in the Central Victoria has had a dramatic effects on the landscape with piles of waste rocks (mullock heaps) scattering across the region with extreme As levels (1900 mg kg^{-1}), high Pb (78 mg kg^{-1}), Cu (202 mg kg^{-1}) and Zn (1393 mg kg^{-1}) levels in soil, include high As levels in plants (6 mg/kg of dry weight), posed a threat to the human and environmental health (Sultan, 2006, 2007; Pearce et al., 2010; 2012; Martin et al., 2014, 2016). Any natural disturbances such as rainfall, drought and forest fire, including controlled fires, a practice used as a fire risk reduction strategy, may remobilize PTEs from soil as well as from organic matter, including vegetation. This PTE remobilization is an emerging concern due to their potential toxicity, bioaccumulation tendency and environmental persistence (Adriano, 2001; Clark et al., 2001; Ignatavicius et al., 2006; Schaider et al., 2007; Burke et al., 2010; Taylor et al., 2010; Burke et al., 2013; Burton et al., 2016; Nunes et al., 2017; Wu and Taylor, 2017).

Among forest fires, wild fire is considered a catastrophic phenomenon, as it may result in human life loss and property destruction with significant impacts on atmosphere, terrestrial and aquatic ecosystems, however it is a natural event in many terrestrial ecosystems (Lavorel et al., 2007; Cerda and Doer, 2008; Melendez-Perez et al., 2014; Nunes et al., 2017). Due to the catastrophic impacts, government authorities in a number of countries conduct controlled fires in forest areas, in order to reduce fuel load with the subsequent reduction in the frequency and intensity of wild fires. Though the intensity and areal extent is less than that of wild fires, it is hypothesised that controlled fire may also be able to remobilize PTEs from soil organic matter and vegetation, in a similar manner to wild fires (Burke et al., 2010; Odigie and Flegal, 2011; Burke et al., 2013; Melendez-Perez et al., 2014, Odigie and Flegal, 2014; Campos et al., 2015, 2016; Nunes et al., 2017). Moreover, it is reported that the frequency and areal extend of the controlled fire may increase in the near future as communities respond to the effect of climate change and the resulting increase in wild fire (Pausas, 2004; Hennessy et al., 2005; Westerling et al., 2006; Moreira et al., 2009, 2011; Odigie and Flegal, 2011; IPCC, 2013; Odigie and Flegal, 2014; Campos et al., 2015, 2016). Therefore, the objectives of this study are (i) to assess the PTE contamination in the soils of a legacy mining affected landscape in the Maldon area in Central Victoria, Australia, in comparison with Victorian and Australian top soil averages, (ii) to assess the PTE contamination in terms of number of pollution indices and the subsequent ecological risk assessment by potential ecological risk index (PERI) method, (iii) to investigate the influence of controlled fire on the immediate mobilization of PTE concentrations in the soils of the same legacy mine site in Maldon, Victoria, Australia, (iv) to understand the effects of prescribed fire on soil Hg concentration and its temporal change in concentrations in the post-fire environment, specifically after a major rainfall event, and (v) to understand the temporal variations in concentrations of PTEs in the post-fire environment include physico-chemical characteristics of the soils such as pH, electrical conductivity (EC), soil organic matter (SOM) and carbonate content. The correlation between the soil physico-chemical characteristics and PTE concentrations in the soil in the pre-fire and immediate post-fire environments are also highlighted. In this respect, the Central Victorian historical district proves an excellent environment to investigate the interaction between changing landscapes and historical mine waste materials.

1.2 Central Victorian mining history

The economic prosperity of the Central Victorian region started with the gold discovery at Clunes, in 1850 (Mudd, 2007). In the region, gold formed in the quartz-vein systems in low grade metamorphic Palaeozoic and younger turbidite terrains, in association with sulphide bearing minerals such as arsenopyrite (FeAsS), pyrite (FeS_2), pyrrhotite (FeS), sphalerite (ZnS), galena (PbS) and chalcopyrite ($CuFeS_2$) (Cox et al.,1987, Gray, 1988; Cox et al., 1991, 1995). In the first half of 1850s, mining concentrated in places such as Clunes, Ballarat, Creswick, Daylesford, Maryborough, Castlemaine and Bendigo, and moved to the west (St. Arnaud, Ararat and Stawell) and to the mountains in the east (Beechworth, Jamieson and Walhalla) (Fig. 1.1) during the second half (Mudd, 2007; ERV, 2017). Victoria's gold rush was ended in 1860s as the miners moved to New South Wales, Queensland and to Western Australia (ERV, 2017). During this period, quartz-vein system and the derived alluvial deposits in the region yielded in excess of 2000 t of gold (Ramsay and Willman, 1988). Mining interest was renewed in 1990's due to the high gold price, technological developments in mining and ore processing such as large-scale-low cost mining mechanisms, and new cyanide and milling processes, resulting in the opening of new mines with significant expenditure on exploration activities (Close, 2002; McDonald and Powell, 2008).

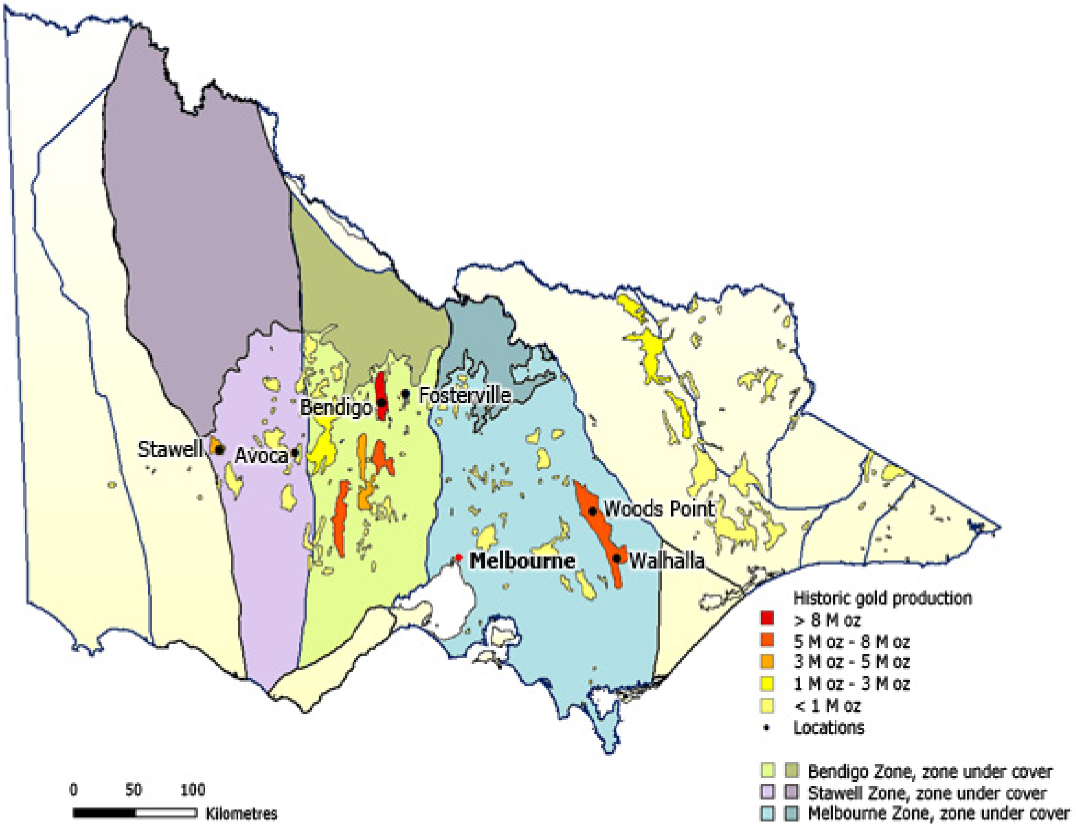

Fig. 1.1 Map of Central Victoria showing the major gold fields (Geoscience Australia, 2007).

To date Victoria has produced over 2500 t of gold (32% of Australia's share) both from alluvial deposits and from quartz-vein deposits (ERV, 2017). Thus, gold mining has occupied a central space in the history of Victoria's economic development, including cities and towns, and the development of the landscape. Mining also accumulated and deposited tonnes of mine waste materials rich in elevated PTE concentrations (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn) creating potential problems to human and ecosystems health, specifically for future generations (Sultan, 2006, 2007; Pearce et al., 2010, 2012; Martin et al., 2014, 2016).

1.3 Characteristics of mining affected landscapes

Historically, mining landscapes were left without any remediation when extraction activities ceased. During gold processing, only a minor percentage of gold is recovered, resulting in the accumulation of immense quantities of crushed rock fragments, overburden materials, mine tailings, mill waste water, together known as mine waste materials (mullock heaps). These accumulations of mine waste materials are scattered across much of the Central Victoria (Fig.1.2). The mine waste materials and the areas around these mine waste accumulations are often contaminated with PTEs in elevated quantities (Adriano, 2001; Sultan, 2006, 2007; Pearce et al., 2010, 2012; Doronila et al., 2014; Martin et al., 2014). After biogeochemical weathering and transformation, these mine waste materials and the accumulated PTEs can acts as an obvious source of contamination to surrounding ecosystems and residential areas through wind-borne dispersal of fine particles and water-borne transport of dissolved and particulate elements (Schaider et al., 2007; Martin et al., 2014, 2016, 2017). A conceptual model of PTE transformation, migration pathways from mine waste piles to biological receptors is shown in Fig.1.3, and this mobility has health impacts on human and ecosystems (Lim et al., 2008; Pearce et al., 2010, 2012; Martin et al., 2016; 2017).

Fig.1.2 Mine waste (mullock heap) from Creswick area, Central Victoria, Australia.

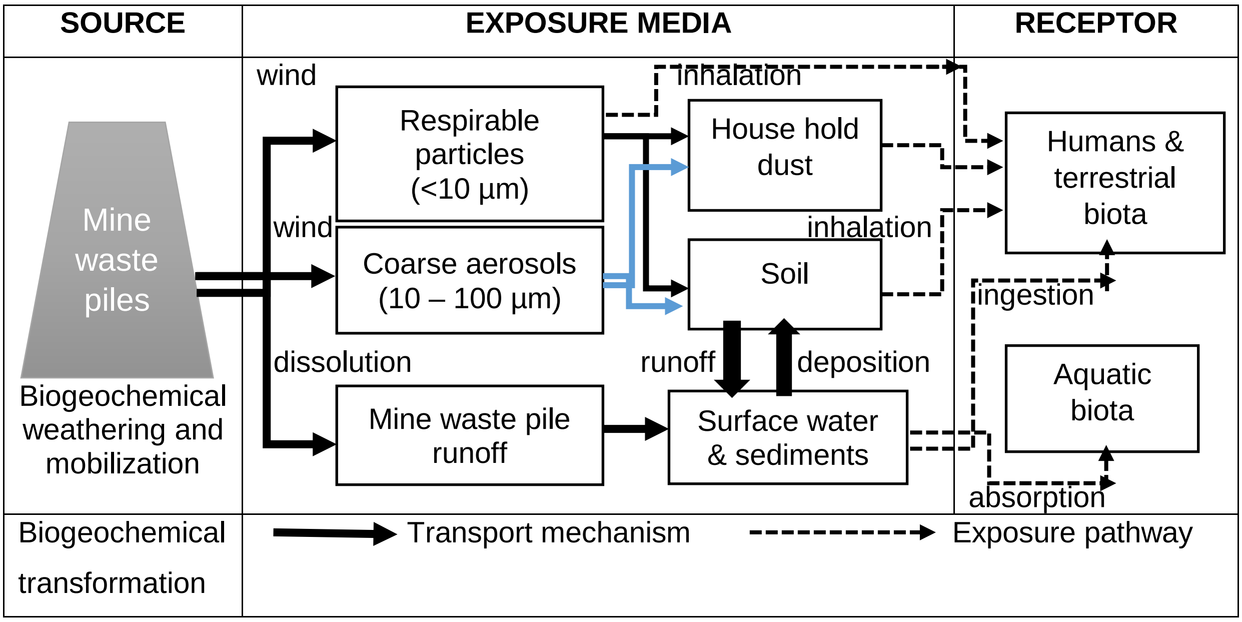

Fig.1.3 Conceptual model showing the biogeochemical cycling, fate and transport of PTEs, and pathways of exposure (modified from Schaider et al., 2007).

PTE contamination and health risks in mining areas affects not only workers, but the whole community including children and the elderly as well as plants and animals, and it continues to be a risk through exposure, even after mine closure (Qu et al., 2012). The exposure pathways of PTEs are direct ingestion, dermal contact, inhalation of soil particles and surface soil vapour, and vegetable ingestion (Zhuang et al., 2014; Zhang et al., 2015), and the risk is characterised using the hazard quotient (HQ). If the PTE contaminants increase/decrease in the biosphere, subsequent increase/decrease can be observed in the human body (Odigie and Flegal, 2014), and the prolonged absorption of PTE in the human body can cause severe health effects (Lim et al., 2008; Pearce et al., 2010, 2012; Martin et al., 2016; 2017). For examples, As absorption by residents including children has been recently reported from Central Victoria and highlighted a link between soil As concentration and cancer risk in humans in the region (Pearce et al., 2010, 2012; Martin et al., 2014, 2016, 2017). Similar to many other legacy mine sites across the globe, most of the un-rehabilitated legacy mine sites in Central Victoria are located in forest areas, where PTE may have an affinity with soil organic matter (Hernandez et al., 2003; Wei and Yang, 2010). In this normal situation, forest fires of any kind can influence the PTE mobility by burning the soil organic matter and vegetation (Odigie and Flegal, 2014; Burton et al., 2016; Odigie et al., 2016; Nunes et al., 2017; Wu and Taylor, 2017).

1.4 Forest fire and controlled fire

Forest fire is a global phenomenon and a natural component of forest and scrubland ecosystems in arid, semi-arid, boreal and tropical environments such as those found in the South-Western United States, Western South Africa, Chile, Northern Spain, Portugal and South-Eastern Australia (Neary et al., 1999; FAO, 2001; Hasson et al., 2008; Beganyi and Batzer, 2011; Stein et al., 2012). The Australian environment has thousands of years of natural association with fire and fire has been significant in shaping much of the landscape of Victoria (ERV, 2017). Many Australian ecological systems are dependent upon some form of “fire regime” to maintain ecosystem health and biodiversity. There is evidence of fires occurring throughout the Tertiary and Quaternary Periods (Pechony and Schindell, 2010; Bowmann et al., 2011; CFA, 2017). Aboriginal people used fire for many thousands of years as a tool for hunting, to reduced levels of fuel and facilitated easy travel through the bush (DELWP, 2017; CFA, 2017). Climatic conditions and vegetation types make many of Australia’s forested catchments susceptible to fires and causes a significant threat to life, property, infrastructure and natural resources (Smith et al., 2011).

The total land area of the State of Victoria in Australia is approximately 22.7 m ha, which is approximately three per cent of Australia’s total land mass. Around 7.7 m ha (one third of the total area of Victoria) land area in Victoria comprise of State forests (45%), national parks and other conservation area (together 55%). Fires in Victoria burned a combined area of over 3 million hectares across largely forested upland regions in 2003, 2006-07 and 2009 (CFA, 2017). The parks and forests in Victoria contains wide variety of ecological vegetation groupings, which include rain forests, Mallee woodlands, grassland and heathlands, and each of these vegetation groups pose various challenges for fire management (ENRC, 2008). In order to reduce the possibility and severity of wild fire, controlled burning of naturally accumulated leaf litter and vegetation is practicing in Australian landscape in autumn and or spring seasons (occasionally in late winter), including in Central Victorian regions.

Controlled burns are low to moderate intensity fires used for reduction in forest fuel levels, land preparation prior to agriculture, tree-regeneration, and weed and insect control purposes (Arocena and Opio, 2003; Fernandez and Botelho, 2003). It is applied in specific meteorological conditions such as low temperature, high humidity and low wind, when soil is moderately moist, and atmospheric condition allows optimum smoke dispersion and optimal control of the fire (Certini, 2005; Mataix-Solera et al., 2011; Weinhold, 2011). It may be used to promote the renovation of the dominant vegetation through elimination of undesired species (Certini, 2005). Controlled burning is considered a common practice in agricultural and forest areas in many parts on the globe including USA, Australia, Portugal, Spain, Canada and India (Cordiero et al., 2002; Arocena and Opio, 2003). In Australia, early European settlers used controlled fire to clear forest and wood land areas for agriculture, specifically to silviculture during the early 20th century (CFA, 2017). In the modern days, land and forest managers apply controlled fire as a fire risk reduction strategy by burning forest floor litter and fuels. Apart from Australia, USA also conduct extensive controlled burning, specifically in the California region, where various agencies conduct controlled burns in an around 2.2 million acres annually in the last decade (2000–2010) (Weinhold, 2011).

The intrinsic character of any kind of forest fire is the process of heat release during biomass combustion (Bento-Goncalves et al., 2012), which controls changes to physical and biogeochemical properties include pH, EC, SOM, porosity, permeability, water repellency, aggregate stability, microbial communities and many other properties, including PTE mobilization (Arocena and Opio, 2003; Certini, 2005; Boerner et al., 2009; Ubeda et al., 2009; Granged et al., 2011; Verma and Jayakumar, 2012; Norouzi and Ramesanpour, 2013). Arocena and Opio (2003) considered the influence of fire on soil properties two years after a controlled burn and windrow burning treatments in British Colombia and found that higher soil pH, exchangeable Ca, Mg, K, Na and base saturation in burned plots compared to unburned, which facilitated the germination and growth of the desired forest species. Similar to soil property alterations, fire is able to release and remobilize PTEs from vegetation and SOM (Fig.1.4) (Kristensen et al., 2014; Odigie and Flegal, 2014; Burton et al., 2016; Nunes et al., 2017). After a fire event, greater surface exposure may enhance erosion by rainfall runoff and wind activity, which increases mobility and bioavailability of PTEs, and may generate water quality issues (Burke et al., 2010; Odigie and Flegal, 2011; Stein et al., 2012; Burke et al., 2013). This results in human and ecosystems health concerns owing to the possibility of PTE inhalation and ingestion (Burke et al., 2010;

Stein et al., 2012; Burke et al., 2013). A conceptual model outlining the sources of PTEs in the forest ecosystems, influence of fire on PTEs, including its mobility and pathways of exposure are depicted in Fig.1.4. Climate change may increase the frequency and areal extend of the fire across the globe resulting in increase in PTE mobility (Neary et al., 1999; Mouillot et al., 2002; Pausas, 2004; Certini, 2005).

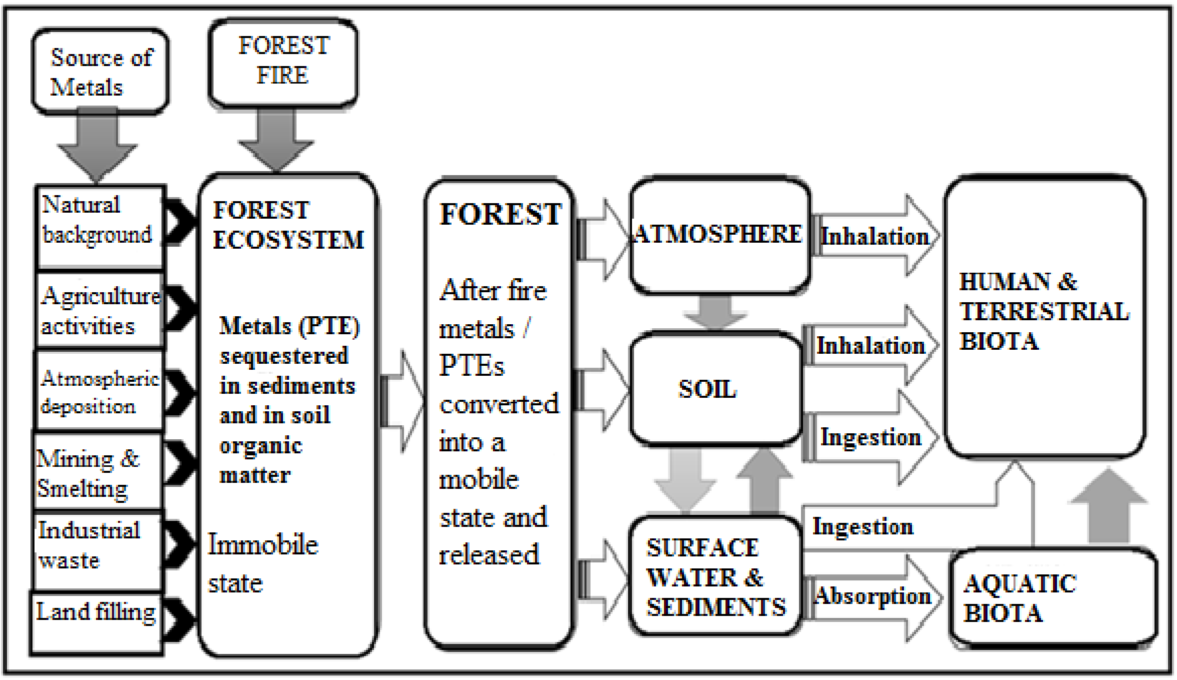

Fig.1.4 A conceptual model outlining the sources of PTEs to the forest ecosystems, influence of controlled burn on PTEs, their mobilization and pathways of exposure (Modified from Schaider et al., 2007).

1.5 Research problem

The Central Victorian region has large number of un-rehabilitated legacy gold mining sites, which are contaminated with elevated concentrations of PTEs in surface soil, surface waters, and in air (Sultan, 2006, 2007; Pearce et al., 2010, 2012; Martin et al., 2014, 2016, 2017). Pearce et al. (2012) reported some systematic As absorption by residents in the gold field regions of Victoria and Martin et al. (2013) demonstrated As uptake by children living in these areas using toenail As concentration as a biomarker. The potential for the remobilization of PTEs from this mining affected landscape during any kind of forest fire, including controlled burn is of concern as it may affect the health and well-being of the human and ecosystems particularly given that controlled burns are standard fire risk reduction strategy in Victoria. Though PTE mobility after wild fire has been studied in a number of occasions (Odigie and Flegal, 2011, 2014; Kristensen et al., 2014; Burton et al., 2016; Odigie et al., 2016; Nunes et al., 2017), the influence of controlled burn on PTE remobilization is limited and not reported from the Australian landscape, and specifically from any legacy mining affected landscapes.

The selected field location is Maldon in Central Victoria (study area details are noted in Chapter 4 to 8). It is a legacy mining affected landscape, where elevated PTE concentrations have been observed in residual soils. This study addresses the effect of controlled burn on the PTE concentrations in the surface soils, including the physico-chemical characteristics of the soil to assess the potential to release the PTEs from the surface soils and from vegetation. This also include its mobility, distribution, spatio-temporal variations in concentrations, and the influence on landscape management and environmental health. As a result, following research approach and study design is adopted.

1.6 Research approach and study design

1.6.1 Approach

The following approach is adopted for this study

- Review the existing literature on forest fires and its influence on soil and water with an emphasis on PTE distribution and mobility after fire.
- Site selection in consultation with Department of Environment, Land, Water and Planning (DELWP).
- Collection of pre-burn soil samples from the proposed study area two days before the controlled burn.
- Conduct controlled fire in the study area two days after the first sampling by DELWP and Parks Victoria crews.
- Collection of post-fire soil samples two or three days after the controlled fire.
- In the post-fire environment, collect soil samples at the end of each season and immediately after the major rainfall (September 2016) (pre-fire and all the post-fire sampling will be from the same sampling stations).
- Ash sample collection immediately (two days) after the controlled fire.

- Soil sample analysis for PTEs and physicochemical characteristics of soil such as pH, EC, SOM and carbonate content.
- Ash analysis for PTE concentrations and physicochemical characteristics.
- Data collation, statistical analysis and interpretation, in order to address the distribution and mobility of PTE contaminants.
- Publish the results in international peer-reviewed scientific journals.
- Make recommendation for better environmental, fire and water quality management of legacy mining affected landscapes and adjoining fire prone areas, including downstream watershed(s), to concerned authorities.

1.6.2 Study design

The research study is designed in the following way

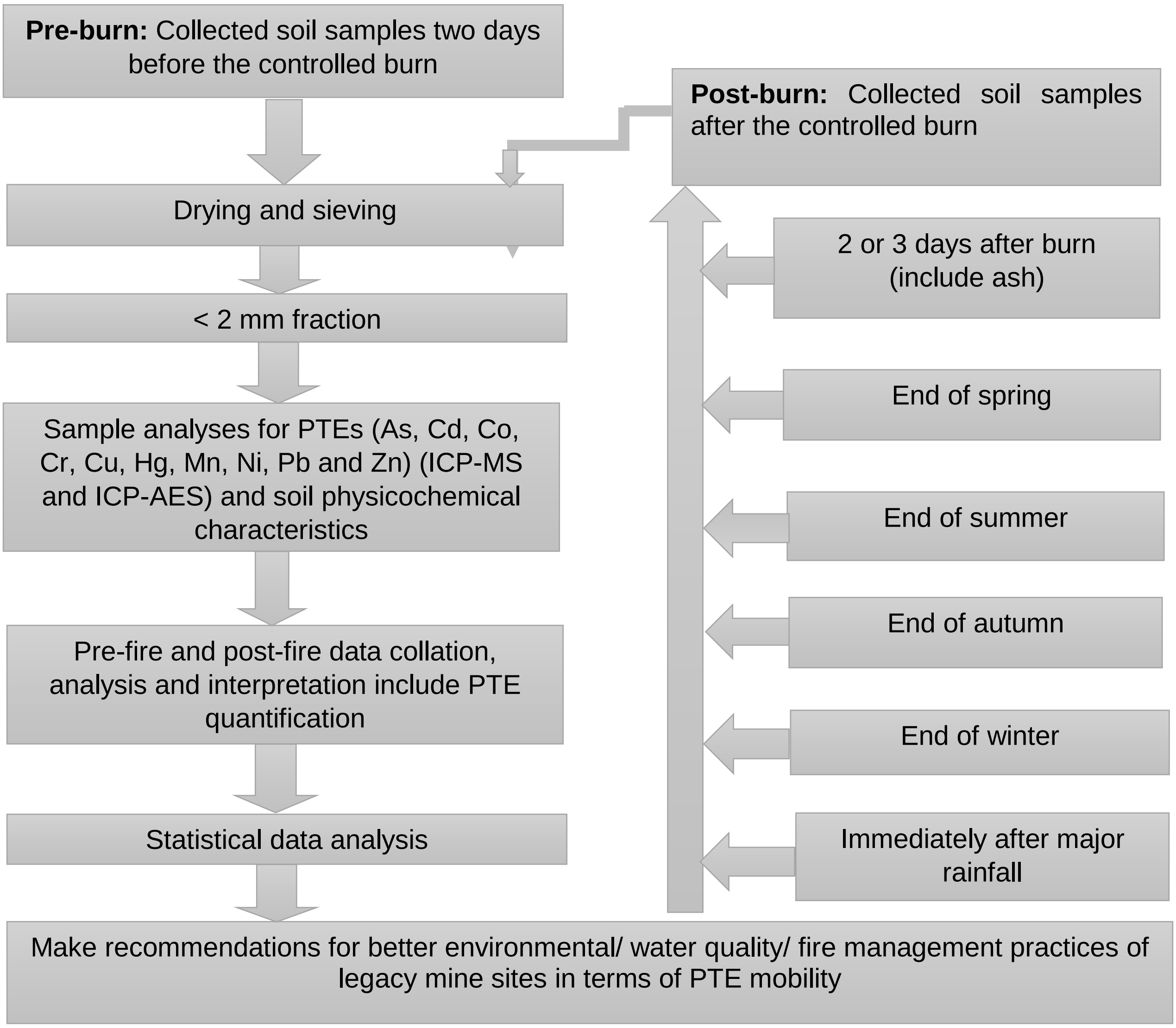

Fig.1.5 The research study design.

1.7 Knowledge gap and research justifications

A number of studies address the influence of fire on various soil characteristics such as pH, EC, bulk density, structural stability, SOM, and carbonate content (Certini, 2005; Hatten et al., 2005; Jovanovic et al., 2011; Verma and Jayakumar, 2012; Costa et al., 2014; Campos et al., 2016), but the influence of fire, specifically controlled fire on PTEs in soil is limited or missing (Certini, 2005; Pereira et al., 2011). Since 2005, various studies provide evidence that wildfire remobilize PTE contaminants such as Pb, Zn, Cd, Cr, Mn and Hg with a significant multi fold increase or decrease in their concentration after fire (Burke et al. 2010, Odigie and Flegal 2011; Burke et al. 2013; Kristensen et al. 2014; Odigie and Flegal 2014; Campos et al. 2015, 2016; Burton et al., 2016; Nunes et al. 2017; Wu and Taylor, 2017). However, these studies do not address distribution and mobility of PTEs after a controlled fire and within a mining related environment. In addition, fire influence on mining affected landscapes, specifically on unrehabilitated legacy mine site is unreported. Similarly, the ash generated as a result of the forest fire may contain variable amounts of PTEs, and is linked to the uptake of PTEs by plants. The contribution of PTEs from ash is also unreported in Australia context, with the exception of Pb (Kristensen et al., 2014; Wu and Taylor, 2017).

Due to its high toxicity and widespread environmental impact, As is listed as one of the six most toxic pollutants threatening human health and has become one of the most extensively studied elements in the field of metal toxicity (Flora, 2011). There is an urgent need to identify the potential mobility and distribution of PTE contamination after fire as there are not much information and data available on this regard, especially from mining landscapes where elevated concentrations of PTEs have been observed as in Central Victoria. This will help the land management practitioners in proper planning to improve the environmental health. The contribution of PTEs from post-fire runoff to receiving waters is also poorly understood in terms of magnitude of its potential effects and persistence of influence.

The increase in number and area of controlled burns in the region during spring and autumn generate concern as it may release PTEs at the time of intense rainfall events (DELWP, 2017). The increase in rainfall during autumn and winter may mobilize these

PTEs into the downstream surface water systems. Australian continent is prone to frequent and uncontrolled wild fires and their incidence and severity are predicted to increase due to climate change effects (Hennessy et al., 2005; Odigie and Flegal, 2011; Quintano et al., 2015). This study will address these knowledge gaps.

1.8 Significance and aim of the study

The influence of forest fire on many physical and biogeochemical soil properties are established (Certini, 2005; Verma and Jayakumar, 2012; Alcaniz et al., 2018), however, metals include PTEs have been poorly considered in these works. Some recent studies considered the mobilization of Hg (Biswas et al., 2007, 2008; Burke et al., 2010; Campos et al., 2015), Pb (Odigie and Flegal, 2011; Kristensen et al., 2014; Wu and Taylor, 2017) and other metals including Co, Cu, Mn, Ni, and Zn after the wild fire (Jovanovic et al., 2011; Shcherbov, 2012; Odigie and Flegal, 2014; Burton et al., 2016; Nunes et al., 2017). However, these studies did not consider the influence of controlled fire, specifically at Australian legacy mine sites and the distinctive soil profiles that develop over there, as observed in Central Victoria. This study will specifically address these issues.

PTEs are considered as major contaminants in gold mining landscapes. Mine wastes, tailings and associated soil containing PTEs may migrate into various compartments of the ecosystem, and this PTE mobility will increase in the post-burn environment as the fire has the capability to mobilize PTEs from SOM and vegetation (Kristensen et al., 2014; Campos et al., 2015, 2016; Wu and Taylor, 2017). Some of these PTEs can persists in soils for extended period of time and some may enter the food chain in significantly elevated concentrations, specifically Hg (Lee et al., 2005; Kelley et al., 2006; Mergler et al., 2007). Precipitation, subsequent runoff and wind activity can transport these fire affected contaminants to distal areas to reach human and terrestrial biota by way of ingestion and inhalation.

The absorption of PTEs for extended periods result in a wide range of deleterious systemic health effects in human (Mazumdar, 2008; Del Razo et al., 2011). The resulting health effects are peripheral and cardiovascular disease, hypertension, diabetes mellitus, hematologic-gastrointestinal-renal and respiratory disorders, hearing loss, developmental abnormalities (Centeno et al., 2007) and range of cancers, including bladder, colon, kidney, liver, lung and skin (IARC, 2004; Celik et al., 2008; ATSDR, 2011; Pearce et al., 2012; Carlos et al., 2014). Excessive intake of Pb (NTP, 2012; ATSDR, 2011; Zhang et al., 2012), Cd (Young, 2005; Solomon, 2008; ADWG, 2011; Cobbina et al., 2013), Cu (Cobbina et al., 2013), Mn (WHO, 2008; Cobbina et al., 2013) and Hg also cause severe effects on human health (Kelly et al., 2006; Mergler et al., 2007; Sunderland, 2010; Cobbina et al., 2013; Zhuang et al., 2014; Sundseth et al., 2017). Therefore, the overall aim of the project is to investigate the distribution and mobility of PTEs specifically As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn in and around mining affected landscapes after a controlled fire event, in order to understand the impact on community, fire fighters (CFA), land management and ecosystem health.

1.9 Contribution(s) to existing knowledge

Public awareness of issues relating to contamination from legacy and active mining areas, in terms of PTEs include their mobility and the subsequent health impacts is growing (Harvey et al., 2003; Burk et al., 2010, 2013). The current study provides information about the mobility of PTEs in the soils of a mining affected landscape in Central Victoria, specifically after the controlled fire, which is absent in the international scientific literature. The study addresses the temporal variations in PTE concentrations in the post-fire soil environment, for a period of one year, specifically in each season, which also addresses a gap in the literature. The PTE concentrations observed in ash samples after the controlled fire has also not been previously reported. The study also identifies the alterations in physicochemical properties of the soil such as pH, EC, SOM and carbonate content after the controlled fire, and supports the existing studies. The change in pH and EC of the creek water in the study area can provide information about how controlled fire can influence the surface water resources. This information is valuable for proper land management and sustainable environmental health.

The results of this study will be useful to land management practitioners, Department of Land Water and Planning (DELWP), Catchment Management Authorities (CMA), Parks Victoria, and Country Fire Authorities (CFAs), to formulate better environmental and fire management practices in the legacy mining landscapes of Central Victoria.

The results of this study will also help us to develop some key guidelines to the post-fire watershed management practices in terms of water quality, which will be helpful to water distribution managers. The result will also inform forest management plans, health advisory warnings and will contribute to improved environmental and human health in the region. It is also anticipated that the outcome from this research may be applied to mining affected landscapes in similar environments across the globe in characterising the PTE mobilisation after any kinds of forest fires.

1.10 Research Questions and Thesis Structure

This thesis by publication has been developed around a programmatic response to the major research question of influence of controlled fire in the PTE mobility, specifically in a legacy mine site. A suite of sub-questions has been developed to provide additional contributions to the knowledge regarding the controlled fire and PTE mobility in the soil environment. Each sub-question is independently addressed in the thesis in the form of a review or original research article.

1.10.1 Overarching research question

Does fire, specifically a controlled fire, influence the mobility and distribution of PTE (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn) concentrations in the soils of a legacy mining affected landscape at the Maldon area in Central Victoria, Australia?

1.10.2 Sub-questions

(i). What is known about forest fire, PTE mobility and the associated unquantified risks, specifically from the soil environment across the globe?

(ii). Does post-fire metal concentrations, including PTE mobilization, affects surface water quality?

(iii). What is the PTE distribution in the study area (Maldon mining affected landscape) before the controlled burn and what is the current contamination status based on the Australian and Victorian top soil averages and the established Australian guideline(s)?

(iv). How is the PTE contamination status in the study area addressed in terms of soil pollution indices such as enrichment factor (EF), geo-accumulation index (I-geo), contamination factor (CF), pollution load index (PI), pollution index (PI), integrated pollution index (IPI) and Nemerow integrated pollution index (NIPI).

(v). How does a controlled burn affect the PTE concentration in the soil? Does it influence the PTE mobility?

(vi). How does a controlled burn and post-fire rainfall affect the Hg mobilization in the soil? Does the controlled fire and rainfall influence the contamination level of Hg in a mining affected landscape?

(vii). What are the levels of PTEs in the soil environment immediately after a controlled fire, and their temporal variations in concentrations, specifically 3, 6, 9 and 12 months after the fire and immediately after the major rainfall?

1.10.3 Thesis Structure

This thesis comprises nine distinct but interrelated chapters which address the sub-questions noted above. These chapters provide a systematic study of the existing information regarding the forest fire, contamination status of PTEs in the study area, influence of controlled fire in remobilizing PTE concentrations, and their temporal variations in concentrations from the soils of a legacy mine site in Maldon area of Central Victoria, Australia.

Chapter 1 provides context with an introduction into Central Victorian mining history, characteristics of the mining affected landscape, an overview of the forest fire include controlled fire and its influence on soil property alterations, and PTE mobility after wild fires. This chapter also addresses the research problems, research approach and study design, gap in the literature, significance of this work and its structure, overarching research question include sub-questions and how the various chapters woven together.

Chapter 2 addresses sub-question (i). This chapter describes various factors such as behaviour of PTEs concentrations in the forest ecosystem, effects of fire on the PTEs in the forest ecosystems, composition and the level of PTE concentrations in the ash, conceptual models showing the fate and transport of PTEs in the post-fire soil environment and pathways of exposure. This review examine the post-fire PTE concentration in the soil environment with special reference to Hg mobilization and the formation of methyl mercury (MeHg). The chapter also summarizes the major studies linking forest fire and PTE mobilization, and temporal variations of PTE concentrations in soil, environmental implications and the risk of PTEs on human health. Impacts of climate change on forest fire and the resulting increase in PTE mobility is also addressed as it is concerns due to the negative impacts of PTEs to human and ecosystems health. This review adds emphasis to the need for studies to investigate the remobilization of metals/ PTE concentrations in soil during and after the fire and to understand their temporal variations in concentrations.

Chapter 3 addresses the sub-question (ii) through a review of the literature, which highlights the risk of post-fire PTE mobilization into surface water resources. This review critically analysed the key published works regarding: (i) human health risks of As, Hg, Pb, Cd, Cr, Cu, Zn, Mn and Ni (ii) metals specifically PTEs in the forest catchments (iii) influence of fire on PTE mobilization in forest catchments (iv) significance of ash in PTE mobilization (v) post-fire PTE mobilization into surface water resources include Hg mobilization. This review clearly identifies the post-fire mobilization of PTEs to downslope and downstream surface water resources and the resulting increase in concentration of PTEs, specifically Hg in fish, which is of concern due to the possible mobility of these potentially toxic metals to the humans through food chain mechanism

Chapter 4 addresses the sub-question (iii) with analysis of soil samples at the Maldon study area before the controlled burn, including physicochemical characteristics of the soil. The elevated concentrations of PTEs in the soil environment, are consistent with legacy mine waste materials. The PTE analyses results were compared with Australian and Victorian top soil averages and the established soil guidelines such as National Environmental Protection Measures (NEPM) and Department of Environment and Conservation (DEC) of the State of

Western Australia. The results demonstrated that the study area is contaminated with Hg and As, based on ecological investigation levels (EIL) of DEC and with As (based on residential health investigation levels of NEPM).

Chapter 5 addresses the sub-question (iv) by the application of pollution indices such as geo-accumulation index (I-geo), contamination factor (CF), pollution index (PI), pollution load index (PLI), integrated pollution index (IPI) and Nemerow integrated pollution index (NIPI). All these analyses revealed that the study area is moderately to extremely contaminated with PTEs, specifically with Hg (heavily to extremely contaminated), As (heavily contaminated) and Pb (moderately contaminated). This is of particular concern due to the toxicity of these PTEs to both human and ecosystems health and the proximity of the study area to residential areas. The elevated concentrations of PTEs in the study area provide a convenient starting point for the controlled fire related PTE remobilization investigations.

Chapter 6 addresses the sub-question (v). Controlled fire was applied to the study area in late August 2015 to investigate the remobilization of PTE concentrations in soil. Soil sample collection two days before and two days after the controlled fire and their analysis results revealed that controlled fire remobilize PTEs in the soil environment with Mn displaying highest mobility (229%) followed by Zn (65%). This creates particular health concern as the controlled fire and PTE mobility is postulated to increase in the near future due to climate change effects. Therefore, it is suggested that controlled fire should be carefully considered as a fuel reduction strategy in forest management.

Chapter 7 addresses the sub-question (vi) by analysing the soil Hg concentration in the pre-burn and post-burn soil environment. The soil analysis revealed the occurrence of Hg volatilization (27% average) during the fire and the Hg concentration displayed a difference before and immediately after the fire and in each post-fire sampling periods. It is seen that in the post-fire environment, immediately after the major rainfall, the mean soil Hg concentration increased 122% compared to the pre-rainfall level. This chapter also discussed the contamination assessment based on Hg mobility and the results revealed that majority of the study area is extremely contaminated with Hg. The Hg concentration in the pre- and post-fire environment is compared with the various soil quality guidelines and the potential ecological risk index also have been computed. This Hg mobilization is of specific concern due to the health impacts of Hg, specifically its neurotoxic effect.

Chapter 8 addresses the sub-question (vii) by analysing and reporting the PTE concentrations in the pre- and post-fire soil environment. In order to understand the temporal variations in PTE concentrations in the post-fire environment soil, samples collections were carried out two days after the fire, three, six, nine and twelve months after the fire and after a major rainfall in September 2016 (one year after fire). By analysing these soil samples, the temporal variations in PTE concentrations can be addressed. The soil analysis revealed the change in PTE concentrations with time. Most of the PTEs shown significantly increase in concentration immediately after the fire, but decrease with time specifically in autumn and after the major rainfall. The increase in PTE concentration in the immediate post-fire environment is attributed to the presence of ash, which have high PTE concentrations. The observed temporal decrease in PTE concentrations in the post-fire environment is due to the removal of ash and surface soil by precipitation and subsequent runoff, and wind activities.

Chapter 9 provide a synthesis of the key findings from chapter 2 to 8 and comments on the management implications associated with forest fire, specifically controlled fire, PTE mobility and their temporal variations in concentrations. This chapter draws on the literature presented in chapter 2 and 3 to contextualize recommendations that have been developed from the pragmatic research undertaken in this study, which will be of interest to land, forest, water and environmental managers, specifically in the fire prone regions.

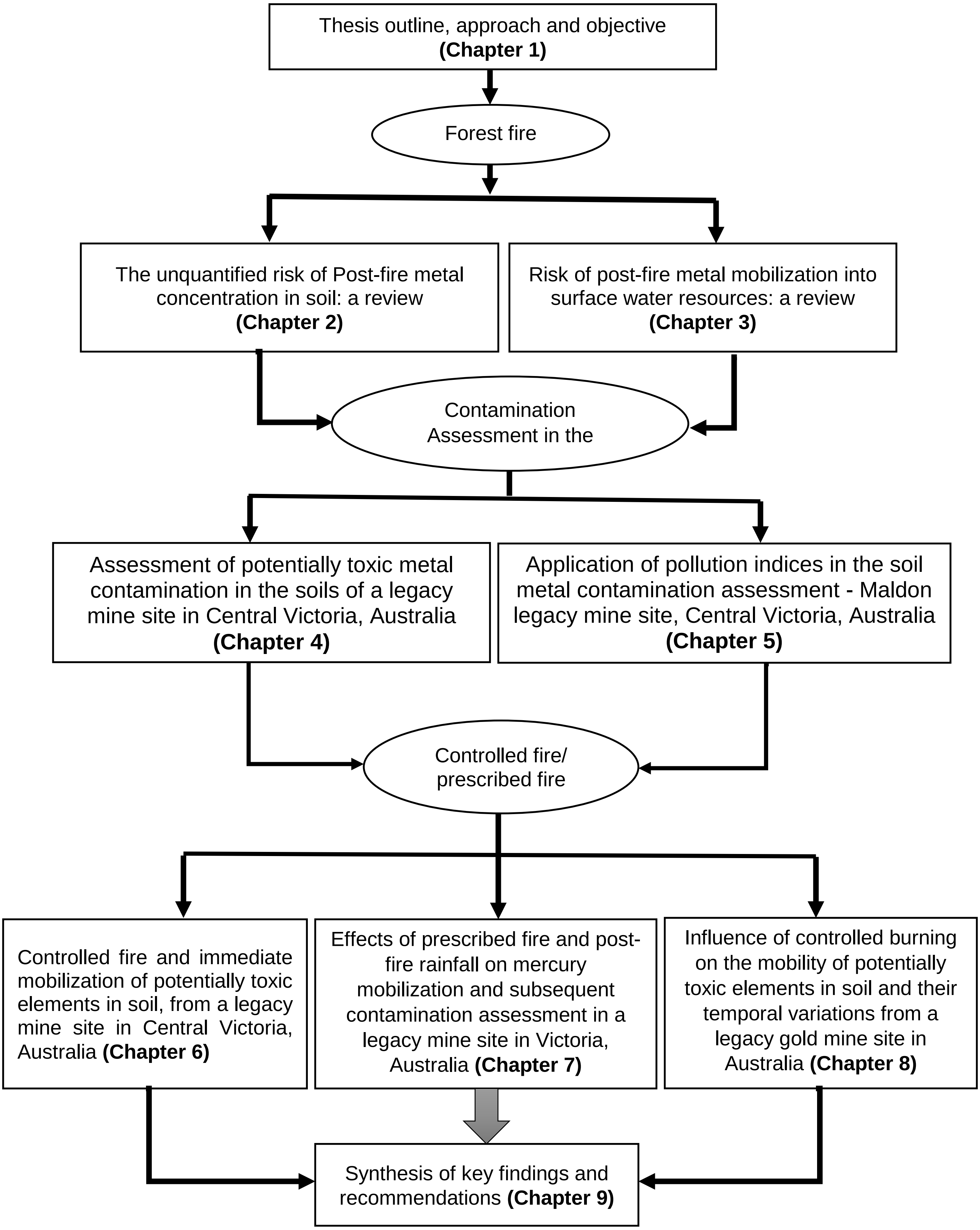

Fig. 1.6 Conceptual frame work of thesis structure.

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Chapter- 2

The unquantified risk of post-fire metal concentration in soil: A review

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The Unquantified Risk of Post-Fire Metal Concentration in Soil: a Review

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Abstract Forest fire is a natural disturbance that occurs in many terrestrial ecosystems specifically in the semi-arid environments and is considered to be an important cause of environmental change. Though many causes of fire are identified, including lightning, volcanic eruption, power line sparks, etc., human involvement is the most significant factor. Fire events are able to alter the physical, chemical and biogeochemical properties of the soil and surface materials and are able to release major and trace metals into the environment. This may be more significant in mining-affected and industrial landscapes, where elevated concentrations of metals present in the soil. After the fire event, metals become more mobile due to the increase in soil surface exposure and the mobility associated with ash dispersal. This mobility may increase the bioavailability of the metals, which may generate water quality issues and may contribute to human and environmental health concerns. Even though, the influences of fire on many soil properties are well established, the behaviour of metals with respect to fire is not well investigated. However, a few studies report that major and trace metals include Cd, Cr, Co, Cu, Hg, Mn, Ni, Pb, Zn and As are mobilized after fire with increased concentrations in soil and water resources and this might pose a risk to human health and ecosystems. Climate change may increase the intensity, frequency and areal extend of fire events and hence increase the metal concentrations and their potential health impacts. This paper reviews post-fire (wild fire) mobility of metals in soil common in contaminated forest ecosystems. The human and ecological health risks of these metals are also considered.

Keywords Climate change · Environment · Forest fire · Health risk · Metal mobilization · Soil

1 Introduction

Forest fire is a natural disturbance that is frequent in many terrestrial ecosystems, where meteorological conditions are characterized by higher temperature and low relative humidity (Pereira et al. 2005; Trigo et al. 2006; Dore et al. 2010). The majority of fires occur in semi-arid environments such as western and south-western United States, western South Africa, Chile, northern Spain, and Australia including boreal Russia and Canada (FAO 2001; Neary et al. 2005; Trigo et al. 2006; Beganyi and Batzer 2011; Stein et al. 2012). It has been estimated that more than 30% of the land surface is subjected to substantial occurrence of fire (Chuvieco et al. 2008) and each year fire burns nearly 650 M. ha of forest around the globe (Shcherbov 2012). Apart from climate change (Mouillot et al. 2002; Pausas 2004; IPCC 2013; Quintano et al. 2015), the immediate causes of forest fire are identified such as lightning, volcanic eruption and power line sparks; however, human involvement is considered to be the most

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significant (Shcherbov 2012; Syphard and Keeley 2015) including land-use change such as widespread planting of highly flammable tree species and land abandonment (Campos et al. 2012).

Forest fire is generally classified as either prescribed (controlled or light burn) for a specific purpose or wildfire. Prescribed burning of naturally accumulated leaf litter on forest floor is a standard practice to reduce fuel levels, and hence minimize the extent and severity of wild fire (Certini 2005; Castellinou et al. 2010; Pereira et al. 2011). This is regularly scheduled in autumn and/or spring season(s), whereas wild fire generally occurs in summer in the presence of abundant dry fuels, which may significantly contribute to the severity (Shcherbov 2012). In recent years, extreme fire seasons have significantly impacted on human lives and properties in Greece in 2007, in Australia in 2009, 2013, 2015, 2016 and 2017, in Canada in 2016 and in the USA in 2007, 2013, 2015 and 2016 (Hantson et al. 2015).

Modern society's view of forest fire is a catastrophic phenomenon that can considerably affect human lives and properties with significant impacts on atmosphere, terrestrial and aquatic ecosystems (Kelly et al. 2006; Cerda and Doerr 2008; Burke et al. 2010; Beganyi and Batzer 2011; Melendez-Perez et al. 2014). However, in reality, fire is a natural element of many terrestrial ecosystems, which can be well adapted to the effects of fire (Neary et al. 2005; Pereira et al. 2011) including low to moderate severity prescribed fire and high severity wild fire, both may renew essential nutrients for the long-term sustainable developments of the forest ecosystems (Arocena and Opio 2003; Pereira et al. 2011).

The direct impacts of fire are biomass combustion, volatilization of the nutrients and the release of some metals to the atmosphere, alterations in soil properties and the production of ash and charred materials (Shakesby et al. 1993; Andreae and Merlet 2001). The intrinsic character of fire is heat, released during the combustion of biomass and is a complex process (Bento-Goncalves et al. 2012). Severe fire results in heating of soil up to 30 cm depth (Debano 2000) and can alter the physical, chemical, biological and mineralogical properties of the surface materials and soil (Certini 2005; Shakesby 2011; Ginzburg and Steinberger 2012). These changes may be short-term or long-term (Arocena and Opio 2003) and some may be permanent (Certini 2005), depending on fire severity and duration (Dzwonko et al. 2015). Fire also bring about significant change in soil organic matter (OM), deterioration of soil structure, porosity, permeability and hydraulic conductivity, considerable loss of nutrients, increase in soil pH, electrical conductivity, leaching and erosion and significantly alter both quantity and composition of microbial and soil-dwelling invertebrate communities (Certini 2005, García-Marco and González-Prieto 2008; Verma and Jayakumar 2012).

Mobilization and deposition of major and trace metals occur through a complex interaction between combustion of vegetation, mineralization of the soil OM and through the heating and interactions of ash with the underlying soil (Jakubus et al. 2010; Pereira and Ubeda 2010; Jovanovic et al. 2011; Odigie and Flegal 2011, 2014; Costa et al. 2014; Campos et al. 2016). This is specifically relevant to mining-affected landscapes due to the presence of tailings and other mine wastes and from industrial wastes or other brown field sites, all of which have elevated metal content. Fire increases soil erosion up to 100-fold, depending on the surface soil exposure due to the burning and removal of vegetation, which leads to an increase in mobility and potential bioavailability of metals (Riggan et al. 1985; Cohen et al. 2005; Odigie and Flegal 2011; Stein et al. 2012; Warrick et al. 2012; Odigie and Flegal 2014; Campos et al. 2016). These metals may be transported downslope and downstream by surface runoff and impact surface water bodies (Shakesby and Doerr 2006; Smith et al. 2011; Campos et al. 2012, 2015, 2016). For example, Hg introduced by gold mining is mobilized by fire into downstream aquatic ecosystems, where the conditions may favour the formation neuro-toxic and immune-toxic mono methyl Hg (MMeHg), which bioaccumulate in the terrestrial and aquatic food web (Morel et al. 1998; Mahaffey 1999; Hightower 2004; Kelly et al. 2006; Mergler et al. 2007; Friedli et al. 2009; Foy et al. 2012). Recently burned areas experience increased overland flow (by decreasing infiltration) and the associated transport of metals, which can last many months and years (Cerda and Lasanta 2005; Moody et al. 2013). Leaching of metals through the soil profile can constitute groundwater contamination, specifically where groundwater levels are close to the surface (Reneau et al. 2007; Costa et al. 2014). Wind may also play a significant role in metal mobilization even up to great distances (Breulmann et al. 2002; Schaider et al. 2007). The intensity of surface and groundwater contamination depends on intensity of fire, pre- and post-fire metal concentration in the soil, distance to the water resources, frequency and intensity of rainfall, topography of the burned area, intensity and direction of the wind, and many other local factors.

Metals in the environment, particularly Cr, Cd, Cu, Hg, Mn, Ni, Pb, Zn and metalloid As (herein after called 'metal'), are of great environmental and human health concern due to their toxicity, environmental persistency and tendency to bioaccumulate and biomagnify in the food chain (Adriano 2001; Ignatavicius et al. 2006). Elevated metal concentration not only degrade the quality of the atmosphere, soil, water bodies and food crops, but also threaten the health and well-being of humans and other animals (Wang and Mulligan 2009; Nabulo et al. 2010). Deleterious health effects include cancer occur when metals are ingested or inhaled by humans (ATSDR 2011b; Pearce et al. 2012; Cobbina et al. 2013). For example, metals such as Cd, Hg and Pb are able to displace or replace essential metals (Cu, Fe and Zn) and interfere with the proper functioning of enzymes and associated cofactors, resulting in toxic effects (Gifford et al. 2004). It is also found that increased concentration of Pb in the blood (PbB) create hyperactivity and reduced intelligence in children (ATSDR 2011a) and As can create cancer incidence in many organs (Celik et al. 2008; ATSDR 2011b; Pearce et al. 2012). In the aquatic ecosystem, these metals can alter the structure and composition of resident microbial communities (Nipper et al. 1998; Beganyi and Batzer 2011; Minshall 2003) and can accumulate in fish species and may reach the human consumer (Kelly et al. 2006). Elevated metals also interfere with physiological functions of plants with disruption of gaseous exchange, CO_2 fixation, respiration, nutrient absorption and growth rate (Angelova et al. 1999, Kabata-Pendias 2011). In general, these metals either in deficiency or excess can impact on plants, animals and human health (Hindwood et al. 2003). Therefore, determining the concentration of potentially toxic metals in soil and their mobility in the environment is significant for assessing the health of the terrestrial and aquatic ecosystems include humans.

Some of the effects of fire on soil properties are well established; however, the behaviour of metals with respect to fire is not well investigated and documented (Certini 2005; Jovanovic et al. 2011, Norouzi and Ramezanpour 2013; Campos et al. 2016). Given the significant negative health impacts of increased metal concentration, further investigations are warranted. The influence of fire on Hg (specifically) (Caldwell et al. 2000; Kelly et al. 2006; Biswas et al. 2007, 2008; Burke et al. 2010; Melendez-Perez et al. 2014; Campos et al. 2015) Mn (Parra et al. 1996; Costa et al. 2014; Campos et al. 2016) and Pb mobilization (Odigie and Flegal 2011, 2014; Kristensen et al. 2014) has received some attention, but the influence of other metals such as Co, Cu, Cr, Cd, Ni, Zn and As is limited. This review considers global examples to illustrate the distribution and mobility of post-fire metal concentration in soils to facilitate analysis of suitable environmental and human health plans for actions during and after fire. Development of integrated fire and environmental risk management plans prior to the occurrence of any kind of fire would enable better coordination of management actions that are designed to mitigate post-fire environmental impacts (Smith et al. 2011). This is particularly significant in times of climate change, which increase forest fire frequency and areal extend (Mouillot et al. 2002; Pausas 2004; Westerling et al. 2006, IPCC 2013; Quintano et al. 2015).

2 Metals in the Forest Ecosystem

The forest floor is focal to forest ecosystem and includes organic matter and a mixture of minerals, which acts as a potential reservoir of metals, water-soluble organic compounds and biogenic substances (Shcherbov 2012). Though, many geogenic metal accumulation (volcanic eruption, atmospheric fall out, cosmic dust, weathering and soil erosion) affect the forest ecosystem, their concentration is low, compared to the anthropogenic accumulation (Nriagu 1989; Pacyna and Pacyna 2001). Metal mobility dramatically increased since the industrial revolution through activities such as mining and metal processing, metal and chemical industries, fuel combustion, transportation, household and industrial waste disposal, and so on (Wei and Yang 2010; Shcherbov 2012). These metals contaminate air, surface and ground water, terrestrial, lacustrine and marine environments (Boyle et al. 2005) and remain in the soil for a long time (Pereira and Ubeda 2010; Jovanovic et al. 2011). For example, emissions from the combustion of leaded gasoline accounted for approximately 75% of the global Pb aerosol during the second half of the twentieth century (Nriagu 1990; Dunlap et al. 2008).

The deposition and the subsequent accumulation of metals in the forest ecosystem are related to their sorption by soil OM, clay mineral fixation, and association with Mn oxide and Fe and Al hydroxides (Kaschl et al.

2002; Sipos et al. 2005; Kabata-Pendias 2011). Their behaviour is complex and is mainly controlled by adsorption and desorption processes including many specific physical, chemical and biogeochemical processes (Reis et al. 2015). Most of the metals in the forest ecosystem concentrated at the ground fuels (Shcherbov 2012) and organic layers of the soil as they (especially Hg, Cu and Pb) have an affinity towards soil OM (Hernandez et al. 2003), which significantly reduce their mobility (Siccama et al. 1980; Biswas et al. 2007; Obrist et al. 2008; Friedli et al. 2009). For example, around 90% of the Hg in the forest is found to accumulate and store in the surface organic layers of the soil (Grigal 2003). The reduction in metal mobility is characterized by high organic matter content, low levels of nutrients, normal pH and other physical anomalies (Chiu et al. 2006). Their binding mechanism and the resulting concentration in the forest ecosystem increases with humus formation (Shcherbov 2012) and depends on many other factors such as presence of other metals, soil pH and redox potential, landscape position, stand age and biota (Sposito 1989; Munthe et al. 1998).

The correlation of metals with soil pH and dissolved organic matter (measured as DOC) has been noted and it is established that pH is largely responsible for metal solubility, speciation (Drever 1988), mobility (Violante et al. 2010) and uptake by plants (Adriano 1986; Breulmann et al. 2002). Low pH increases the solubility and mobility, but decreases the organophyllic characteristics of some metals (Drever 1988). DOC forms strong bonds and complexes with metal ions as they have numerous functional groups with negatively charged sites (Ephraim 1992; Tipping 1998; Tipping et al. 2011). Among the selected metals, mobility of Zn, Cd and Ni are greatly influenced by soil pH and are considerably mobilized when the soil pH is low, whereas, mobility of Cu and Pb are strongly dependent on the solubility of the organic matter (Bergvist et al. 1989). Metals may also be associated with carbonate, oxide and hydroxide minerals (Intawongse and Dean 2006) and play a significant role in the biological activity of organisms (Hernandez et al. 2003). Microbial reduction of certain metals to a lower redox state (Cr(VI) to Cr(III)) is also possible, which reduces their mobility and toxicity (Gadd 2007).

Plants act as an intermediate reservoir of metals from primary sources (soils, water and air), through which they move onto other organisms and can have unforeseeable consequences to certain links in the food chain (Adriano 1986; Kabata-Pendias and Pendias 1992). Plant leaves extract dust particles including aerosols from atmosphere, but rain events wash out these particles from air and leaves and reach to soil, are then subject to uptake by plant roots (Rea et al. 2000, 2001, 2002; Frescholtz et al. 2003; Fay and Gustin 2007). This metal intake increases with mobility of metals and their concentrations in the soil. For example, Zn and Cd are very mobile and easily absorbed by plants, whereas Hg, Cu and Pb are strongly bound to soil particles that reduce their availability to plants (Obrist 2007; Jovanovic et al. 2011; Rutter et al. 2011; Driscoll et al. 2013). Plants can accumulate these metals without any noticeable signs of damage for an extended period, however, threshold toxicity exist. During fire, these sequestered metals either volatilize to the atmosphere (Hg) or accumulate on the soil surface with ash. Thus, forest ecosystem play a crucial role in the circulation of metals and forest fire is a significant contributor to metal mobility.

3 Fire Effects on Metals in the Forest Ecosystem

In a forest ecosystem, loss of organic matter by the combustion of vegetation is a significant consequence that soil experiences during fire, which convert the metals into a mobile state (Young and Jan 1977; Certini 2005; Biswas et al. 2007). Organic compound volatilization occurs at temperature 180–200 °C and nutrient volatilization begins when temperature reach to 200–400 °C (Neary et al. 1999), but amount of clays, cations, Mn and Fe oxides do not change until temperature reached approximately 450 °C (Knoepp et al. 2008). During fire, some metals (Co and Cu) can be enriched in the residues formed from the burning of biomass and some (Hg and Pb) can remobilize as airborne components (fly ash and dust) (even up to 85%) (Narodoslawsky and Obernberger 1996; Nzihou and Stanmore 2013). Co and Cu did not reveal higher concentrations in the burned soils, but shown significantly higher concentrations in ashes (Costa et al. 2014; Campos et al. 2016), and ash is considered as the major source of post-fire metal concentration, which can be easily transported to distal areas by way of wind (Hg, Cd and Pb) and surface runoff (Yarmonenko 2007; Campos et al. 2015, 2016). The airborne component consists of smoke and particulate emission through which a number of metals are released into the atmosphere, resulting in their redistribution happening throughout the burn (Young and Jan 1977; Biswas et al. 2007; Wiedinmyer and Friedli 2007; Shcherbov 2012). For example, during fire Hg stored in the forest soil and biomass can be volatilized into the atmosphere, in the form of elemental Hg^0 and an oxidized form of $HgCl_2$ (Veiga et al. 1994; Friedli et al. 2001; Almeida et al. 2005 Nzihou and Stanmore 2013).

The amount of metal released during forest fire is limited by their prior accumulation in the soil and the fire severity (Certini 2005; Biswas et al. 2007), which depends on the burn temperature and duration of heating (Debano et al. 1998; Debano 2000; Neary et al. 2005). For example, heating soils for 1 h at 180 °C released <10% of the Hg, while heating at 320 °C for 4 h released >95% of the Hg (Biswas et al. 2007). Severity is also affected by types of fuel and their availability, moisture content, topography of the area and weather pattern (Flannigan and Wotton 2001). Since most of the metals are concentrated at the middle and lower layers of the forest floor, moderate to high intensity fire is required to completely release the metals (Nriagu 1996; Shcherbov 2012; Sen and Peucker-Ehrenbrink 2012).

4 Ash—Composition and Metal Concentration

Fire leaves a footprint on the landscape, called ash. It is the most common residue on the soil surface in burned areas and is defined as materials remaining deposited on the surface from the burning of vegetation. Ash represents the accumulation of mineral matter stored in vegetation and in the soil organic horizon prior to burning (Biswas et al. 2007). It is a heterogeneous material composed of mainly particulate carbon, oxides and hydroxides of base cations (Ca^{2+}, Mg^{2+} and K^+), silica, phosphorous, nutrients, major and trace metals with other potential contaminants and is characterized by high alkalinity (Khanna et al. 1994; Amiro et al. 1996; Someshwar 1996; Johansen et al. 2003; Goforth et al. 2005; Plumlee et al. 2007; Campos et al. 2012; Wade et al. 2013; Campos et al. 2015, 2016). The concentrations of metals in ash varies and is dependent upon number of factors such as type, density and age of the vegetation, plant parts burned (leaves, bark, litter, etc.), soil types, soil OM, pre-fire metal concentrations in the soil, meteorological conditions, maximum temperature reached, fire intensity, duration and so on (Ulery and Graham 1993; Someshwar 1996; Pereira et al. 2009; Pereira and Ubeda 2010; Machado et al. 2015). Thickness of ash is found to relate to fire severity (Pereira et al. 2013a, b) with high intensity fire producing up to 10 cm with density varying from 1 to 5 kg m^{-3} (Doerr et al. 2008). Ash is also a key component that determines the post-fire hydrogeomorphological behaviour of fire-affected landscapes (Cerda and Doerr 2008). Immediately after the fire, infiltration is decreased due to the deposited ash and the formation of the hydrophobic layer at or near the surface (Debano 2000), which accounts for the increase in overland flow (surface runoff) (Jung et al. 2009).

Based on the colour, ash is described as either white or dark ash. White ash is the product of complete combustion, whereas dark ash is the product of incomplete combustion (Goforth et al. 2005). The different tones of ash colour provide information about fire severity. Black ash corresponds to low–medium severity, whereas grey and white ash suggest high severity fire (Pereira et al. 2014). During the forest fire, complete combustion of fuel takes place at or near 500 °C leading to the formation of light grey or white ash, which is composed mainly of alkaline earth oxides that over time react with atmospheric CO_2 and water vapour to form soluble hydroxides and carbonates (Ulery et al. 1993). In pine and oak plantation, Ca is the most abundant element in white ash (Ulery and Graham 1993). The white ash has significantly higher Munsell hue, value and chroma as well as colour lightness (Goforth et al. 2005). Black ash has a higher concentration of cations probably due to the high oxidation of the OM and incomplete combustion (Goforth et al. 2005; Liang et al. 2006). Goforth et al. (2005) found that variation in colour lightness of ash was correlated with variation in pH (r = 0.89), cation exchange capacity (CEC) (r = 0.82), total N (r = 0.74) and total organic C (r = 0.72). Both pH and CEC increased with lighter ash colour, whereas total N and organic C increased with darker ash colour (Goforth et al. 2005).

Major and trace metals such as Mn, Fe, Zn, Cu, Pb, Hg, Cd and As are reported from ash (Khanna et al. 1994; Someshwar 1996; Ferreira et al. 2005; Pereira and Ubeda 2010; Campos et al. 2016) with Mn returning highest concentrations (in a number of cases) (Parra et al. 1996; Costa et al. 2014) as it is mostly concentrated in the leaves. For example, Costa et al. (2014) reported highest concentrations of Mn in ash (121–448 mg kg^{-1}) after the Marao Mountain forest fire in Spain and Campos et al.

(2016) reported highest concentrations (57–598 mg kg^{-1}) after the Ermida fire in Portugal. Al is also observed as high concentration in rare cases. For example, after analysing the ash from the Lisbon (Portugal) fire (Jul 30, 2007) in the area dominated by *Pinus pinaster* and *Quercus suber* trees, Pereira and Ubeda (2010) mentioned that Al^{3+} was the metal released in higher quantities and Zn^{2+} was in lower quantities. Ash monitoring after the 2007 southern California forest fire showed significantly elevated levels of metals (As, Pb, Cu and Zn) that persisted at least a year following the fire (Plumlee et al. 2007).

The ash produced at high temperatures may have high pH value (Etiegni and Campbell 1991; Henig-Sever et al. 2001), and high $CaCO_3$ content (Ulery and Graham 1993, Goforth et al. 2005; Pereira et al. 2008) which inhibited the solubility of metals. The ash pH is predominantly higher than the underlying soil (even 8–14 pH values were noted) associated with increased concentrations of carbonates, oxides and hydroxides (Pereira et al. 2011). The higher percentage of carbon in ash may reflect a higher OM content in the soil and litter (Costa et al. 2014). Decreasing clay, soil OM and increase in pH during the burning process increase the mobility of these metals in the forest soil environment (Yoon et al. 2006).

5 Post-Fire Metal Concentration in Soil

Soil surface is significantly affected by forest fire (Mandal and Sengupta 2006; Odigie and Flegal 2011, 2014; Campos et al. 2015, 2016). Magnitude of these effects depends on a number of factors including metal concentration and bonding in the soil, types and density of vegetation, intensity of the fire, amount of ash produced and post-fire climatic conditions among others (Neary et al. 1999; Certini 2005; Maia et al. 2012; Verma and Jayakumar 2012). Metal mobility after fire increases the pathways to human ingestion and inhalation (Fig. 1). Many studies have focussed on Hg (Kelly et al. 2006; Biswas et al. 2007, 2008; Finley et al. 2009; Burke et al. 2010; Melendez-Perez et al. 2014; Campos et al. 2015), Pb (Odigie and Flegal 2011,

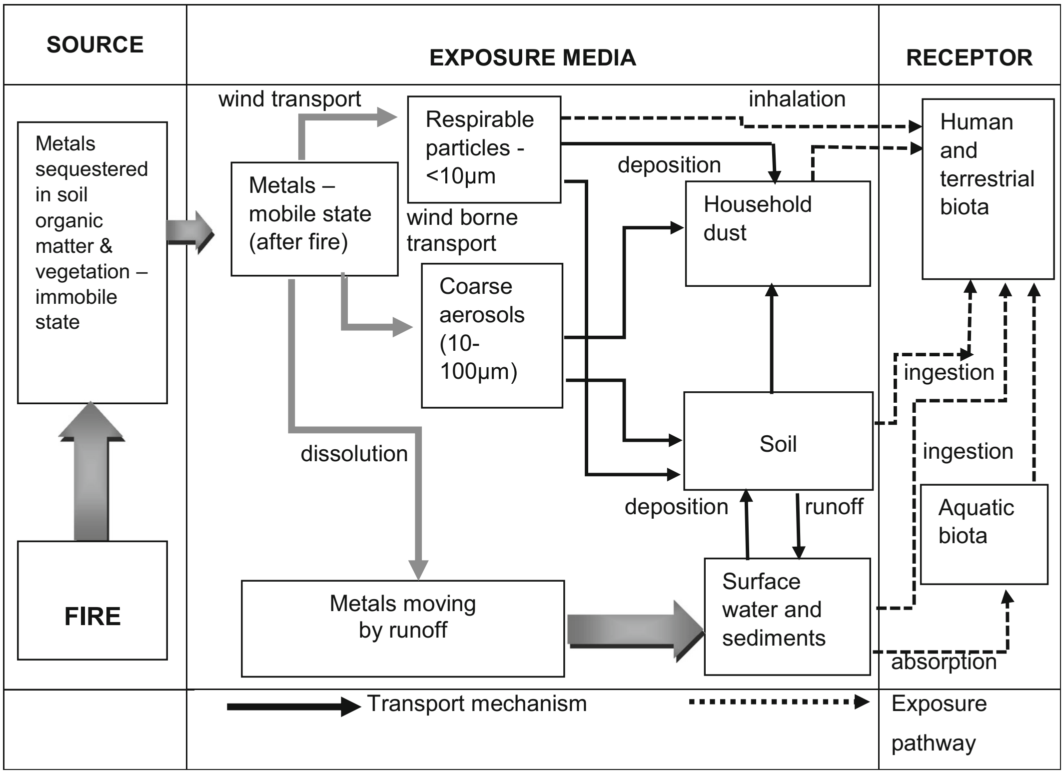

Fig. 1 Conceptual model showing the fate and transport of post-fire metals in soil and pathways of exposure (modified from Schaider et al. 2007)

2014; Kristensen et al. 2014) and Mn (Parra et al. 1996; Costa et al. 2014) mobilization, while other studies are about the mobilization of a group of metals which may or may not include Pb and Mn.

5.1 Mercury Post-Fire (Hg) Mobilization

Mercury exists in atmospheric, terrestrial and aquatic environments, and may be derived either from natural (weathering, volcanic eruption, geothermal activity, etc.) or anthropogenic (coal burning, metal mining and processing, petroleum refining, industrial activities, etc.) sources (Lindberg et al. 2007; UNEP 2013). Total global natural Hg emissions including re-emissions is estimated to be 5207 t year^{-1} (70% of the global Hg emission budget), and anthropogenic sources are estimated as 2033 t year^{-1} (Pirrone et al. 2010; UNEP 2013). Studies revealed that half of the natural emissions come from the terrestrial environment; however, the contribution from biomass burning is not well quantified (Pirrone et al. 2010; UNEP 2013). Hg enters the forest ecosystem by wet and dry atmospheric deposition and to a lesser extent by absorption through stomatal uptake (Rea et al. 2002; Fay and Gustin 2007; Bushey et al. 2008). Hg adsorbed to foliar surfaces enters the soil either by leaching by precipitation and by litter fall and subsequent litter decomposition (Munthe et al. 1998; Rea et al. 2002; Ericksen et al. 2003). During the forest maturation, forest soils accumulate Hg and store in association with OM in a complex way (Grigal 2003). This is supported by other studies, which demonstrated that around 90% of Hg in forest ecosystem is stored in the soil rather than associated with vegetation (Skyllberg et al. 2000; Biester et al. 2002; Grigal 2003).

Forest fire has been recognized as a major source of mercury (re-)mobilization from soil and vegetation, both living and dead (Artaxo et al. 2000; Friedli et al. 2001, Engle et al. 2006; Wiedinmyer and Friedli 2007; Friedli et al. 2009), and it appears that fire directly influences emission and deposition cycles by mobilizing it from soil and vegetation pools into the atmosphere (Biswas et al. 2007, 2008; Burke et al. 2010). The gaseous elemental Hg (Hg^0) is the dominant atmospheric species that has a relatively long residence time (~1 year) resulting in global distribution (Biswas et al. 2008). The released Hg from biomass burning is eventually deposited locally and globally, transported to aquatic ecosystems by runoff and wind, and when conditions favour, it may contribute to the formation of neuro-toxic and immune-toxic mono methyl Hg (MMeHg), generally known as methyl Hg (MeHg) (Wolfe et al. 1998; Kelly et al. 2006; Mergler et al. 2007; Friedli et al. 2009), which may bio accumulate and biomagnify in the food chain resulting in global health concerns (Morel et al. 1998; Caldwell et al. 2000; Amirbahman et al. 2004; Kelly et al. 2006; Mergler et al. 2007). Ash and post-fire soil contains generally low amount of total Hg (THg) compared with pre-fire soil Hg concentrations due to volatilization during burning and washing out process during the post-fire rainfall (Biswas et al. 2007; Mergler et al. 2007; Campos et al. 2015). For example, Biswas et al. (2007) noted 22–86% reduction in Hg concentration in the post-fire soil environment due to burning and Campos et al. (2016) noted 30–60% Hg reduction in ash after the first post-fire rainfall, related to the washing out process. Significantly higher concentrations of Hg were observed in the fine- and medium-grained size fractions of the soil after fire. For example, Burke et al. (2010) observed that in burned soil, 37.19% of Hg was recorded in the fine grained soils fractions, 35.43% in the medium, and 27.38% in the coarse material. This variability in the post-fire Hg distribution is attributed to many factors including slope of the land, land cover, fire-induced changes to the soil aggregates and soil OM (Burke et al. 2010).

A number of studies have been published (Allen et al. 2005; Kelly et al. 2006; Biswas et al. 2007, 2008; Mergler et al. 2007; Burke et al. 2010; Beganyi and Batzer 2011; Foy et al. 2012; Campos et al. 2012, 2015) about biomass burning and Hg release, mobility and the formation of MeHg and to a lesser extend impacts on human and ecosystems health (Kelly et al. 2006; Mergler et al. 2007). The post-fire soil Hg volatilization and subsequent deposition depends on many factors including fire intensity and types of vegetation (Biswas et al. 2007, 2008; Campos et al. 2015). High Hg loss occurs even at low volatilization temperatures and hence, the low soil temperatures (100–300 °C) that happen during most forest fire is sufficient to break the Hg-humic acid bonds (Biester and Scholz 1996). Laboratory study indicates that Hg is almost completely (95%) mobilized from organic matter by fire, predominantly in the gaseous elemental form (Hg^0) with the rest estimated to be associated with particulate matter (Friedli et al. 2001). Biswas et al. (2007) compared the Hg concentrations in soil profiles and in vegetation from burned forests with low, medium and high fire severities and compared with adjacent unburned control sites having similar vegetation types located in north-western Wyoming, USA. The areas were sampled (soil and foliage) in association with Boulder Creek Fire (Aug 2000), the Green Knoll Fire (Jul–Aug 2001) and the East Table Fire (Jul 2003) in order to determine the Hg concentrations over 0–8 cm soil depth in conifer, aspen and medow forest areas (burned and unburned). One of unburned conifer sites in the Boulder Creek area displayed total Hg (Hg_T) accumulation of 31.7 g Hg ha^{-1}, but the adjacent high severity burned area displayed 4.2 g Hg ha^{-1}, highlighted the release of 27.5 g Hg ha^{-1} (86.7%). In another conifer study site in the East Table land area, unburned soil displayed a Hg accumulation of 33.2 g Hg ha^{-1}, and the adjacent low severity burned area displayed 25.8 g Hg ha^{-1}, which highlighted the release of only 7.4 g Hg ha^{-1} (22.3%). Results suggest that the Hg release depends on the fire severity (Fig. 2). Greater fire severity associated with a greater percentage of Hg being released from 22.3% (low severity) to 86.7% (high severity); however, further work is needed to reconcile differences between the laboratory- and field-based studies.

It is also found that Hg release during forest fire depends on the tree species composition as noted by Campos et al. (2015) and Biswas et al. (2007). Campos et al. (2015) studied the post-fire Hg mobilization in eucalyptus- and pine-covered hill slopes in Portugal including one control site. After collecting and analysing the surface soil samples (0–2 cm), 4 and 14 weeks after the fire, Campos et al. (2015) demonstrated that burned eucalyptus forest released 1.1 g Hg ha^{-1}. Hg in the burned eucalyptus soils were twice the concentration registered in the burned pine soils (Campos et al. 2015). This is in consistent with the previous study of Biswas et al. (2007), whose study after the Rocky Mountain forest fire in USA revealed that conifer forest released 7.4 to 25.3 g Hg ha^{-1}, whereas medow forest areas released only 4.1 g Hg ha^{-1}.

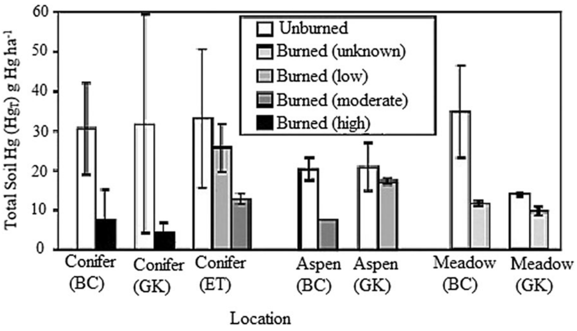

Fig. 2 Total soil mercury pool (g Hg ha^{-1}) of paired unburned and burned sites (*BC*, Boulder Creek; *GK*, Green Knoll; *ET*, East Table) (Biswas et al. 2007)

Quantification of Hg emissions is generally based on one of two methods: (i). soil profile method—where Hg release is estimated based on the difference in Hg stored in soil at paired burned and unburned (control) sites (Engle et al. 2006; Biswas et al. 2007; Michelazzo et al. 2010; Campos et al. 2015). (ii) Hg/CO method, where Hg release is estimated using the ratio of Hg^0 and CO in the smoke plume of a fire (Brunke et al. 2001; Friedli et al. 2001, 2003). Simultaneous measurement of Hg, CO and CO_2 made in a fire plume encountered at the Cape Point confirmed that biomass burning is a significant source of total gaseous Hg (TGM) at around 0.93 kt annually (Brunke et al. 2001). Michelazzo et al. (2010) considered Hg released in the Amazon forest, after a controlled burn and found that Hg present in the vegetation and in the O-horizon of the soil profile had been volatilized. Based on the Hg concentration and Hg burden in the soil, vegetation and litter before and after fire, the mass balance calculation revealed that the average Hg emissions of 3.5 g ha^{-1} is possible with 1.6 g ha^{-1} originated in the O-horizon and the remaining 1.9 g ha^{-1} from above ground vegetation (Michelazzo et al. 2010).

The Hg concentration in soil profile increments at burned sites was lower relative to unburned sites for the same vegetation types, when depth is considered. On the basis of an average 2.7 × 10^6 ha of forest and shrub land burned annually in the USA, Biswas et al. (2007) estimated that forest fire, including prescribed burn, in the USA releases 19–64 × 10^6 g of Hg annually. The same authors (Biswas et al. 2008) considered Hg storage in surface soils in a Central Washington conifer forest and estimated the release of Hg during the 2001 Rex Creek fire in the eastern Cascade Mountains, and compared this to unburned controlled sites in USA. Their study (based on paired burned and unburned samples) highlighted that the Rex Creek fire released 6.7 (±2.5) g Hg ha^{-1} equates to 146 (±55) kg of Hg into the atmosphere. This is significantly higher than the previous estimates of 2.9 (±1.5) g Hg ha^{-1} (based on the airborne measurement of Hg and CO concentration in smoke) by Friedli et al. (2003). It is also found that dry fuels emit almost no particulate Hg (PHg), while moist fuels emit nearly half of the total Hg as PHg (Obrist et al. 2008). Leached Hg from soil and ash is partially transferred into water courses and aquatic ecosystem, where it can be methylated to MeHg (Mergler et al. 2007; Melendez Perez et al. 2014).

5.1.1 Formation of Methyl Mercury (MeHg)

The post-fire Hg mobility in poorly drained soils and wetlands creates particular concern due to the possibility of MeHg formation and its significant health implications including neuro-toxic and immune-toxic effects (Lin and Pehkonen 1999; Caldwell et al. 2000; Amirbahman et al. 2004; Kelly et al. 2006; Michelazzo et al. 2010). Recent work suggest that litter fall and throughfall (direct deposition from atmosphere) as well as the dissolved fraction of the organic matter are the important controlling factors in Hg transport in undisturbed watersheds (Bushey et al. 2008). Areas of poorly drained soils and wetlands are favourable for the formation of MeHg (Grigal 2003) due to the fluctuating temperature and water levels and low dissolved oxygen (Richardson 1999; Scheuhammer et al. 2007). Therefore, it is important to determine the amount of Hg released during fire to assess the relative contribution of fire to the atmospheric Hg pool and investigate the potential for pulses of Hg to enter aquatic ecosystems following fire.

Many researchers (Caldwell et al. 2000; Amirbahman et al. 2004; Ravichandran, 2004; Kelly et al. 2006) measured elevated Hg levels in downstream waters of burned watershed, noting that much of the Hg is transported by suspended sediments and organic matter (Ullrich et al. 2001; Ravichandran 2004). Caldwell et al. (2000) measured large amounts of Hg mobilization in creek runoff in a freshly burned mixed coniferous forest, specifically a 6-fold elevation in the concentration of THg and a 30-fold elevation in MeHg concentration in the sediments of the receiving reservoirs near the creek input. The MeHg in the wetlands can bioaccumulate in fish via food web and may reach to human and other biota. Recent findings indicate that fish from lakes in partially burned catchments contain greater mercury (Hg) concentrations than fish from reference catchments (Kelly et al. 2006). A significant increase in Hg concentration was reported in rainbow trout muscle (68 ng g^{-1} wet weight (ww) Hg concentration before fire were increase to 140 ng g^{-1} dry weight (dw) after fire) and lake trout muscle (250 ng g^{-1} ww in 2001 increase to 391 ng g^{-1} ww after fire in 2003) compared with pre-fire concentrations (Kelly et al. 2006). Authors also determined that the forest fire caused a 5-fold increase in whole-body Hg accumulation in rainbow trout (*Oncorhynchus mykiss*) and smaller Hg increases in muscle of several fish species in a mountain lake in Canada (Kelly et al. 2006). The enhanced Hg accumulation was caused primarily by increased nutrient concentrations in the lake, which enhanced productivity, restructured the food web and increased consumption of fish and crustaceans (Kelly et al. 2006). Forest fire also caused a large short-term release of THg and MeHg into streams and the lakes, which initiated a small pulse of MeHg in invertebrates that contributed to enhanced Hg accumulation in fish. Garcia and Carignan (2005) mentioned that differential loading of organic matter-bound Hg can affect Hg cycling and found that in two partially burned lakes, the Hg concentration in two predatory fish species exceeded the WHO advisory limit (0.5 μgm wet^{-1} wt^{-1}) for human fish consumption. Increased MeHg concentration in fish can result in serious health problems for consumers due to the possible accumulation of Hg in their systems (EPA 1997, Cobbina et al. 2013). The elevated Hg concentration in downstream waters of burned watersheds depends on the fire severity, topography of the area, distance to the surface water body and other factors (Caldwell et al. 2000; Amirbahman et al. 2004; Kelly et al. 2006). Climate change, forest fire and prescribed burning to compensate for past fire suppression are predicted to increase future forest fire occurrences globally (Friedli et al. 2009, Campos et al. 2015, 2016) resulting in an increase in Hg concentration in water. In such an environment, MeHg accumulation in fish may have significant consequences (Kelly et al. 2006).

5.2 Post-Fire Lead (Pb) Mobilization

Post-fire Pb mobility has been reported by Odigie and Flegal (2011, 2014) and Kristensen et al. (2014). Odigie and Flegal (2011) considered Pb mobilization after the Jesusita Fire in the Santa Barbara County of California, USA, and reported relatively high levels of industrial Pb (formed from leaded gasoline; 4.3–51 mg kg^{-1}) observed in ash after the fire with increased bioavailability. In 2014, the same authors (Odigie and Flegal) reported the remobilization of industrial Pb (7–42 mg kg^{-1}) from the 2012 Williams Fire, Los Angeles, CA, USA, and noted the associated mobilization of other metals (Co, Cu, Ni and Zn).

Kristensen et al. (2014) collected ash and soil samples at three uncontaminated areas Waygara State forest (Tostaree fire), Darling Range Regional Park (Red Hill Fire) and Benyowla Regional Parks (Kelmscotte fire) across Australia, shortly after three large uncontrolled and intense wildfire events during early part of 2011 and analysed for Pb. In the Tostaree area of Victoria, Australia, though the total Pb concentration in the ash sample is low (1.6 mg kg^{-1}), the Pb isotopic composition indicates that Australian leaded petrol was the predominant Pb source in the ash, even though this relatively pristine area is approximately 340 km away from the nearest major city (Kristensen et al. 2014). Local surface soils (0–2 cm) collected adjacent to the burned forest also shows an isotopic composition consistent with leaded petrol. Authors reported that the isotopic composition of ash and surface soils (0–2 cm) from the Red Hill fire area of Western Australia were also significantly different from local background soils (40–50 cm). These differences are partially attributed to leaded petrol emission from the adjacent major Perth City. However, results do not support a simple two end-member mixing model of natural Pb and petrol Pb, suggesting supplementary Pb sources. The ash and soil sample analysis from the Kelmscott fire indicates that Pb content cannot be ascribed categorically to the influence of leaded petrol. Both the Redhill and Kelmscott fire areas are located directly in the trajectory of strong, seasonal south-westerly winds that have potentially transported aerosols from the Kwinana port, which handles slag, metal ores and other bulk commodities and is the site of a former leaded refinery. The results obtained from these three studies demonstrated that Pb is remobilized in ash during forest fire events.

5.3 Post-Fire Manganese (Mn) Mobilization

Many studies identified Mn as the highest remobilized metal in the post-fire soil environment (Parra et al. 1996; Costa et al. 2014.; Campos et al. 2016). Parra et al. (1996) studied the effect of forest fire on soil Mn concentrations in the Sierra de Gredos mountain range in Spain, where they collected soil samples 10 months after the fire, before any intense rainfall occurred. Results revealed very large increases of total Mn in the post-fire soil samples compared with control samples, both in the surface (0–5 cm) and sub-surface horizons (5–40 cm). The increase in Mn (471–1429 mg kg^{-1}) on the surface horizon is attributed to the contribution of ash from the burned vegetation, as many vegetation types are able to accumulate Mn in their leaves. It is considered that Mn might have moved to sub-surface horizons (303–757.6 mg kg^{-1}) in the form of organic complexes through the macro-pores of the soil (Khanna and Raison 1986). Similarly, Costa et al. (2014) assessed the metal concentrations in the soil after the Marao Mountain forest fire (Spain) in 2006. After analysing the post-fire soil and ash samples collected 5 months after fire, a 5-fold increase in Mn concentration is reported in ash samples compared to the underlying soil, which is attributed to derived from plant leaves. The increase in Mn concentration (67–598 mg kg^{-1}) in soil after the Ermida fire in Portugal is reported by Campos et al. (2016). Authors support the postulate that Mn in ash is linked to the typically high Mn concentration in tree leaves, especially in the needles of the resinous species as mentioned by Kabata Pendias (2011) and De Marco et al. (2005). Chambers and Attiwill (1994) artificially heated soil samples collected from the Healesville forest area in Victoria, Australia, and reported an increase in the concentration of Mn in the soil, probably due to the physiochemical breakdown of Mn complexed with soil OM (Boyd 1971; Liegel 1983).

Multiple fire events present a complex Mn picture. Brye (2006) observed a significant decrease in post-fire Mn concentration, as a result of 12 years of annual burning on all grass prairies and Norouzi and Ramezanpour (2013) reported no significant change in Mn concentration after their post-fire study in Iran. The decrease in concentration may be due to the water-soluble and easily leachable characteristics of Mn and the subsequent runoff, which is also mentioned by Costa et al. (2014) and Campos et al. (2016).

In general, Parra et al. (1996) observed an increase in Mn concentration of 100% and Chambers and Attiwill (1994) observed 279% in burned soils. Similarly, Costa et al. (2014) reported a 5-fold increase in concentration of Mn in the burned soils compared with underlying soil, which is supported by Campos et al. (2016) who found increase in Mn concentration of 10-fold compared with the underlying soil.

5.4 Post-Fire Mobilization of Other Metals

Elements such as Cd, Cr, Cu, Ni and Zn including As found to increase in burned soils when compared to unburned soils (Morrell et al. 1986; Parra et al. 1996; Mandal and Sengupta 2006; Plumlee et al. 2007;

Bogacz et al. 2011; Jovanovic et al. 2011; Campos et al. 2012; Costa et al. 2014; Campos et al. 2015, 2016) and present similar patterns to that of Pb and Mn.

In 1975, Young and Jan examined the possibility of metal remobilization after a large forest fire in the Angels National Forest, California, USA. The fire occurred in November 1975 and created a dramatic smoke plume roughly 100 km in width, which deposited a distinct layer of ash containing an increased concentration of nine metals (Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) (Young and Jan 1977), with possible mobilization to the adjacent aquatic environment. Followed by this, another study in Canada, where Auclair (1977) examined Cu, Mn and Zn concentrations in wetland plant tissues and in the soils of a Carex medow after a fire event and reported that these metals are mobilized by burning.

Similar atmospheric metal deposition was observed after the southern California (USA) forest fire, where deposition rates of Cu, Pb, Ni and Zn were observed to increase by factors of 4, 18, 13 and 6, respectively, over their mean flux (Sabin et al. 2005). Analysis of trace metal loads in the annual storm water discharge in a highly impervious catchment in the fire area (San Fernando Valley, Los Angeles, USA) emphasized that atmospheric deposition contributes to increased trace metal concentrations (57–100%) in the annual storm water discharge (Sabin et al. 2005). Followed by this, the U.S. Geological Survey (USGS) collected ash and burned soil samples from 28 sites in southern California forest fire areas during November 2007 and analysed for metals. Results revealed that the collected ash and burned soil samples contain elevated amounts of As (up to 140 mg kg^{-1}), Pb (up to 344 mg kg^{-1}), Cr (up to 354 mg kg^{-1}), Cu (up to 1370 mg kg^{-1}) and Zn (up to 2800 mg kg^{-1}) (Plumlee et al. 2007).

Similar to Hg, other metal concentration in ash also depends on a number of factors, such as burning intensity, types and density of vegetation and pre-fire metal concentrations in the soil. A study in an area of burned pine forest reported that concentrations of Fe and Al in the soil increased based on the fire severity (Groeschl et al. 1993). Significantly higher concentrations of Pb, Zn, Cu, Cr and Ni were observed on the post-fire surface soils, compared with pre-burn soils in two post-fire sites and two medow sites in Poland indicate mobilization of these metals (Bogacz et al. 2011). The 2012, Williams Fire burned about 1696 ha of forest area in the Angels National Forest, California, USA. Immediately after the fire, an increase in concentration of Co (3–11 mg kg^{-1}), Cu (15–69 mg kg^{-1}), Ni (6–15 mg kg^{-1}) and Zn (65–500 mg kg^{-1}) were observed in ash, attests to the pyrogenic remobilization of historic industrial metal contamination across an extensive geographic region (Odigie and Flegal 2014). Burton et al. (2016) analysed ash and burned soil samples collected from several locations within the perimeter of the 2009 Station Fire in USA and reported that most metals in storm water samples were elevated as a result of fire.

The immediate impact of post-fire metal mobility on humans is reported by Wolfe et al. (2004). In this study, urine analysis of 92 fire fighters and 135 non-fire fighters who were exposed to forest fire revealed that in both populations, urinary Ni, Ce, Cr and U concentrations were greater than the expected, compared with reference populations. Regression analysis demonstrated that for non-fire fighters (National Guard members) As and Cd levels were significantly related to smoke exposure, however only Ce was in the positive direction.

Similar to western and south-western USA, northern parts of Europe are also susceptible to forest fire due to the Mediterranean climate and fire prone vegetation like eucalyptus and pine. Pereira and Ubeda (2010) studied the metal mobility on a small burned plot in Portugal and reported that ash contained high amount of metals including Al, Mn, Fe and Zn and the specific metal present depends on plant species distribution and burning severity. Campos et al. (2016) studied the presence of major and trace metals in recently burned forest soils and their evolution with time since fire. Authors assessed the metal (Cd, Pb, Mn, Ni and V) concentration in ash and soil samples, which were collected immediately following the forest fire in north-central Portugal as well as 4 (after the first post-fire rainfall event), 8 and 15 months later from eucalyptus and pine plantations. It was determined that Mn (67–598 mg kg^{-1}) and Pb (52–122 mg kg^{-1}) attained the highest and second highest concentrations in ash and Co (1.8–4.8 mg kg^{-1}) and Cd (0.12–0.49 mg kg^{-1}) presented the lowest. It is reported that the concentration of Cd, Pb, Mn and Ni was consistently higher in the burned soils compared with unburned soils, and levels of Co and Cu showed no difference. After the first rainfall event, the concentration of Mn and Cd decline abruptly, whereas levels of Co and Ni increased during the first 8 months and Co and Pb showed little variation during the study. All metals show high concentration in ash immediately after the fire, but concentration declined sharply after 4 months.

The levels of Co and Ni in soil and ash were higher in the pine plantation than the eucalyptus (Campos et al. 2016).

The presence of metals in ash after the fire related directly to vegetation populations. Post-fire ash from the *Pinus densiflora* species found in the mountain regions of South Korea contain elevated Cd concentration, which is mobilized by wind and deposited in eastern coastal waters (Shin et al. 2002). The mobilized metals may affect terrestrial ecosystem. Comparison of major and trace metal concentrations in the leaves of *Dryobalanops ianceolata* plant species in the Lambir Hills National Park, Sarawak, Malaysia, in the years 1993, 1995 and 1997 revealed that certain metal concentrations (Co, Cu, Mn, Ni and Pb) increased in 1997 and is linked to atmospheric input of haze caused by the extensive forest fire raging in Borneo and other parts of Southeast Asia at that time (Breulmann et al. 2002). In 2009, fire removed vegetation covering the calcine sands in Bendigo, Australia, and exposed the sands to weathering processes. Investigations undertaken by Parsons Brinckerhoff identified that the levels of As in the exposed sands presented a potential risk to human health (Parsons 2011).

Around 30,000 forest fire break out happen annually in the boreal forest region in Russia, burning approximately 20 M. t of biomass in 5 M. ha of forest areas, releasing around 2 M. t of combustion products (Shcherbov 2012). Shcherbov (2012) highlighted that burns of any fire type release metals to the atmosphere, resulting in the redistribution of elements happening throughout the burn. He studied approximately 25 fire regions in Siberia and eastern Kazakhistan in (varied in fire age, type, size include immediately after fire, few years after the fire and some sites already have been reforested) between 2000 and 2010 and compared with unburned control sites and found that fire accelerated the migration of metals include Hg, Cd, As, Zn, Cu and Pb (Shcherbov 2012). He also reported that metals usually migrated typically by air and actively distributed within the burn or migrated adjacent to the burn and many submicron-sized particles travel to distal areas.

Similar to the existing studies, it is significant to get information regarding the historical post-fire metal mobilization in order to identify the metal contaminant areas and to understand their impacts on the aquatic ecosystem and the subsequent impacts to humans. Odigie et al. (2016) conducted one such kind of study in Chile. There, temporal change in metals in lake sediments correlated with charcoal abundance is used to locate the post-fire mobilization of contaminants. For example, results of the analysis of the age-dated sediments from the Lake Thompson in Patagonia, Chile, attest to the substantial post-fire remobilization of contaminants that occurred in Patagonia during the mid-1900s (Odigie et al. 2016).

The risk of contamination posed by forest fire including metal mobility is not limited in situ burned soils, but include surface and groundwater bodies, downstream of the burned areas (Cerdà and Lasanta 2005; Shakesby and Doerr 2006; Smith et al. 2011). The change in soil chemical properties during fire may affect soil functioning through their impacts on the composition and activity of microbial communities. Accumulation of major and trace metals in soils have been found to provoke toxic response in soil microorganisms (Certini 2005, Hart et al. 2005) by reducing the microbial biomass (Hartmann et al. 2005), decreasing the carbon mineralization and disturbing enzymatic activities (Frey et al. 2006). Relevant studies dealing with remobilization of metals after forest fire were summarized in Table 1. All the above studies revealed that forest fire is considered as one of the most important potential process for the global remobilization of metals (Odigie and Flegal 2011). These existing studies demonstrated that Hg is the most post-fire studied metals in the soil environment, followed by Mn and Pb including Zn, Cu, Ni and Cd. Mercury is of great interest in the post-fire soil environment because of volatility, toxicity, harmful impact on the environment and on human health, persistence and the relevance of the atmospheric compartment in the global Hg cycle (Alloway 1995; Cheng and Schroeder 2000; Huang et al. 2011; Campos et al. 2015).

All these studies highlighted that selected metals formed in ash are remobilized through wind and rain after fire events. Thus, fire must be considered as a vector for environmental change that may impact on human and ecosystem health. Overall increase in concentrations of major and trace metals in post-fire soil highlights that forest fire act as a source of metal contamination and ash is the primary agent in influencing the metal concentrations in the post-fire soils. Most studies revealed that fire intensity and types of vegetation are the primary factors in metal and nutrients mobilization during fire (Certini 2005; Knoepp et al. 2008; Pereira et al. 2011; Campos et al. 2012, 2015, 2016). Other factors which control post-fire metal

Table 1 Summary of major studies linking forest fire to the remobilization of selected metals

Authors	Study area/year fire occured	Scale affected (ha)	Metals involved/assessed	Results/remarks
Young and Jan (1977)	Angels National Forest Fire (22–28 November 1975), Southern California, USA	26,000 One of the largest fires in the decade	Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn	Distinct increase were observed in dry aerial deposition rates of metals along the sections of the southern California coast covered by a forest fire smoke plume.
Parra et al. (1996)	Sierra de Gredos Mountain Range, Avila, Spain	Wild fire	Mn	Fire increase total Mn concentrations in the surface and sub-surface soil, attributed to the contribution of ash from the vegetation
Wolfe et al. (2004)	Cerro Grande Fire (May 2003), Las Alamos, New Mexico, USA,	19,283 controlled burn became wild fire	As, Cd, Ce, in the urine samples of fire fighters	As and Cd levels were significantly elevated among national guard members—related to smoke exposure. Ce and As levels were elevated in fire fighters.
Ignatavicius et al. (2006)	Lithuania (Jul–Aug. 2002)	497 forest and peat bog fires	Cu, Pb and Zn	In August and September 2002 concentration of metals in the Lithuanian rivers increased by 21–80% compared with those averaged over the previous 08 year periods (1993–2001). Forest fires and peat bog fires increased metal concentrations in the aquatic environment. Metals released into the atmosphere through volatilization trapped in smoke particles or distributed as fly ash after combustion might have reached in the rives as well as the metals in the ash.
Kelly et al. (2006)	Moab Lake's catchment (Jul–Aug 2000)	1120	Hg	Forest fire caused 5-fold increase in whole-body Hg accumulation by rainbow trout and smaller Hg increases in muscle of several fish species in a mountain lake
Biswas et al. (2007)	(i). Boulder Creek Fire (Aug. 2000) (ii). Green Knoll Fire (Jul–Aug. 2000) (iii). East Table Fire (Jul, 2003) Western Wyoming, USA	1400	Hg	Hg (22.3–81.2%) released during fire. The greater fire severity associated with greater percentage of Hg being released from 22.3% (low severity) to 81.2% (high severity). It also depends on the tree species composition of the forest, which affect pre-fire Hg accumulation.
Biswas et al. (2008)	Rex Creek Fire (Aug. 2001), Central Washington forest, USA	20,234	Hg	Hg seems to be re-volatilized during fire. Loss of 6.7 g Hg ha^{-1} from the soil has been observed.
Witt et al. (2009)	Northern Minnesota, USA		Hg—total Hg, (THg) and methyl Hg (MHg)	Observed increase in both the species of Hg. Canopy type found to influence the magnitude of Hg mobilization.
Burke et al. (2010)	(i). Topanga Fire (Sep–Oct. 2005) (ii). Pine Fire (Sep, 2006) (iii). Day Fire (Sep–Oct. 2006) Southern California, USA	Medium size wild fires	Hg	Freshly burned soil exhibited lowest concentration of Hg at the soil surface (0–2.5 cm) subject to burn severity. Following the initial volatilization of Hg at the soil surface, the burned soil experienced an accelerated accumulation. Highest mobilization observed after the rainy season. Nearby watershed observed 4-fold increase in Hg concentration over the subsequent dry season.
Pereira and Ubeda (2010)	Lisbon, Portugal, Spain (Jul, 2007)	Medium size wild fire—study in a small	Al, Mn, Fe, and Zn	The ash contain high amount of metals and the metal release depends on species distribution and burning severity.

Table 1 (continued)

Authors	Study area/year fire occured	Scale affected (ha)	Metals involved/assessed	Results/remarks
		plot of burned area 27 × 9 m size		Over time the increase in pH, make the metals more mobile and released into soil solution.
Jovanovic et al. (2011)	Vidlic Mountain, Serbia, 2007	Severe wild fire	Cu, Pb, Cd and Zn	Fire caused increased concentrations and slightly increased bioavailability of the selected metals. More significant rise happened in metal amounts bound to oxides and organics. Sequential extraction showed that the increased content of metals occurred in the fraction that is available to plants.
Odigie and Flegal (2011)	Jesusita Fire (May, 2009), Santa Barbara, California, USA	1847	Pb	Relatively high levels of labile Pb (4.3–51 mg kg^{-1}) in ash from the fire were observed. Authors concluded that concentration of contaminants will increase with the projected increase in frequency and intensity of fire due to climate change.
Shcherbov (2012)	Considered 25 various fire regions in Siberia (Russia) and Eastern Kazakhstan during 2000–2010	Sites varied in fire size, age and fire types—include running surface to active crown fires	Hg, Cd, As, Zn, Cu, Pb, and Ni	Forest fire induced the migration of these metals. Elements distributed to the areas adjacent to the burn or elements redistributed within the burn. Author concluded that, in future the process will increase due to more fire in the region as a result of climate change.
Stein et al. (2012)	(i). Old Fire (Oct 2003) (ii). Simi Vallet Fire (Oct 2003) (iii). Day Fire (Apr 2006) (iv). Santiago Fire (Oct 2007) (v). Station Fire (Aug 2009), Urban fringe area, Southern California, USA	(i).36,940 (ii).43,790 (iii).65,840 (iv).11,490 (v).64,980	Cu, Pb, Ni and Zn	Mean flux of Cu, Pb, Ni and Zn from burned sites were increased 110-, 740-, 82- and 110-folds, respectively, compared to the respective flux in the unburned (control) site.
Norouzi and Ramezanpour (2013)	Lakan, Saravan, and Pilimbra areas, Iran (Jul 2009)	Medium wild fire events in artificial forests	Fe and Mn	Mobility and availability of Fe and Mn decreased after the wild fire events, that can be related to decreasing of clay, organic carbon (OC) and cation exchange capacity (CEC)
Kristensen et al. (2014)	(i). Tostaree Fire (Feb 2011), Waygara State Forest, VIC, Australia (ii). Red Hill Fire (Feb 2011), Darling Range Regional Park, Perth, Australia (iii). Kelmscott Fire (Feb 2011), Banyowla Regional Park Fire, Perth, Australia	11,365 All these three fires were uncontrolled large intense wild fire events	Pb Pb Pb	Pb composition in ash ranged from 1 to 36 mg kg^{-1}, remobilized during these wild fire events. Authors concluded that the concentration of the remobilized Pb will increase with projected increase in fire due to climate change effects.
Odigie and Flegal (2014)	Williams Fire (Sep 2012), Los Angeles, USA	1696	Co, Cu, Ni, Pb and Zn	Fire remobilized metals—Co (3 to 11 mg kg^{-1}), Cu (15 to 69 mg kg^{-1}), Ni (6 to 15 mg kg^{-1}), Pb (7 to 42 mg kg^{-1}) and Zn (65 to 500 mg kg^{-1})—in the forest soil. Authors concluded that in future climate change will exacerbate the forest fire and resulting metal mobilization.
Campos et al. (2015)		295	Hg	

Table 1 (continued)

Authors	Study area/year fire occured	Scale affected (ha)	Metals involved/assessed	Results/remarks
	(i). Ermida Fire, Portugal (26 Jul 2010) (ii). S. Pedro do Sul Fire, Portugal (06 Aug 2010)	5066		30% of the Hg retained in the eucaliptus soil escaped during the fire, corresponding to the loss of 1.0–1.1 g Hg ha^{-1}. Levels in burned eucaliptus soil were twice the values registered in burned pine soils. Rainfall caused a loss of 1.0 g Hg ha^{-1} from ashes.
Campos et al. (2016)	Ermida Fire, Aveiro district, Portugal (26 Jul 2010)	295	Cd, Co, Cu, Mn, Ni and Pb	Concentrations of metals were consistently higher in the burnt soils than in the unburnt soil (except Co and Cu—no difference). Mn and Cd declined abruptly after the first rainfall event, while Co and Ni increased after 8 months and Cu and Pb hardly changed. All metals revealed peak concentration in the ashes immediately after the fire, declined sharply 4 months later.
Nunes et al. (2017)	North-central Portugal (Jul 2013)	815	As, Cd, Co, Cu, Mn, Ni and Pb	Concerning levels of metals and polycyclic aromatic hydrocarbons in runoff and down stream water samples. Collected mosquito fish sample shown the pro-oxidative modifications

concentrations in soils are type of vegetation in the forest ecosystem, density and age of the vegetation, pre-fire metal concentrations in the soil, weather and climate include intensity and direction of the wind, frequency and amount of rainfall, etc.

6 Mobility and Temporal Variations of Post-Fire Metals in Ash

Forest fire is able to mobilize major and trace metals into the soil and atmosphere (Biswas et al. 2007; Plumlee et al. 2007; Biswas et al. 2008; Odigie and Flegal 2011; Smith et al. 2011; Campos et al. 2012; Costa et al. 2014; Kristensen et al. 2014; Silva et al. 2015; Santín et al. 2015; Nunes et al. 2017). The ash generated during fire may include a significant amount of suspended materials including major and trace metals (Khanna et al. 1994, Odigie and Flegal 2014; Campos et al. 2015, 2016). Heavy rainfall and strong winds during the initial post-fire period can play a significant role in the mobilization of these metals from ash and soils, including mobilization into downstream surface water and groundwater resources (Burke et al. 2010, 2013; Smith et al. 2011; Costa et al. 2014). Thus, both the rainfall and wind activities reduce the concentrations of major and trace metals in the post-fire soil environment.

The altered physical and chemical properties of fire-affected soil produce strong hydrological and erosional responses, including formation of water repellent layers with a subsequent decrease in infiltration and an increase in the overland flow (Shakesby 2011; Moody et al. 2013). Increased overland flow and erosion facilitate rapid transport of remobilized metals raising contaminant levels in the downstream watersheds (Cohen et al. 2005; Stein et al. 2012). To illustrate this, after a 153-mm rainfall event which took place over a 6-day period, 3.6 cm thick ash layer was removed, only 3 weeks after a high severity fire in eastern Spain (Cerda and Doerr 2008). Stein et al. (2012) also examined the impact of fire and erosive capacity on contaminant loadings after the Williams fire, USA, and reported that the mean post-fire concentration of Cu, Pb, Ni and Zn in the first storm water event were three times greater than the pre-fire levels, with the increase attributed to ash fallout. The subsequent deposition in soil and water bodies has the potential to increase human, terrestrial and aquatic ecosystem exposure (Meyer et al. 1992). In general, surface runoff and associated sediments, nutrients, major ions and metals losses were found to peak during the first major rainfall event and it is strongly related to rainfall amount, intensity and duration (Machado et al. 2015; Campos et al. 2016).

The physiochemical parameters of soil also play a significant role in the mobilization and retention of major and trace metals (Chlopecka et al. 1996; Hernandez et al. 2003; Wang et al. 2010). Among them, soil pH exerts a strong influence on the absorption, retention and mobility of the metals, whereas EC and soil OM are considered as less effective (correlation between OM and EC with metals is weak) (Violante et al. 2010). Other factors which affect metal mobility include the percentage of clay and silt in the soil, characteristics of metals and presence of metal oxides, Eh (Sadique 1997), biological activities (Smedley and Kinniburg 2002), original concentration of metals in the soil, intensity and duration of the fire, land-use and topography of the area, frequency of rainfall, characteristics of wind and residence time in the air, residence time in the aquatic environment and so on (Fig. 3). Decreasing clay and organic matter content and change in pH during burning, increases the metal mobility (Norouzi and Ramezanpour 2013). Some of these mobilized metals can persists in soil for extended periods of time and some achieving global distribution with potential impacts to human by way of ingestion, inhalation and absorption (Schaider et al. 2007).

The mobility of major and trace metals occur through runoff in dissolved and/or particulate form, mostly attached with soil and ash organic matter particles (Prats et al. 2014; Malvar et al. 2011; Campos et al. 2016). Campos et al. (2016) revealed three different pattern of metal mobility in a study area in north-central Spain after the fire: (i). Abrupt decrease in concentration of Mn and Cd observed in the post-fire soil after the first rainfall event. (ii). Increased concentration of Co and Ni observed, 4 and 8 months after the fire. (iii). Cu and Pb persist in the same concentration, even 15 months after the fire, in the form of oxides, hydroxides and carbonates. The authors note that Mn and Cd exhibit greater solubility/mobility and easier desorption by ion exchange processes which might explain the increase in mobility of these metals (Harrison et al. 1981; Ingwersen et al. 2000). This is supported by Costa et al. (2014), who observed a decrease in Mn concentration in the post-fire soil environment 1 year after fire and an increase concentration in surface water within and downstream of the burned area. The mobility of Cd was investigated by Pagotto et al. (2001) through sequential extraction from road side soil samples. The observed increase in concentration of Co and Ni, 4 and 8 months after fire is addressed by Campos et al. (2016) indicting that they are less soluble and mobile than Mn and Cd and persist in the soil environment. The enrichment factor (EF) of these metals was slightly above 1, which suggests the transference of Co and Ni from ashes to soils (Campos et al. 2016). Cu and Pb stay in the post-fire soils in the same concentration in the form of oxides, hydroxides and carbonates and enhanced their accumulation in the surface soils, which limit their leaching capacity (Harrison et al. 1981; Pagotto et al. 2001).

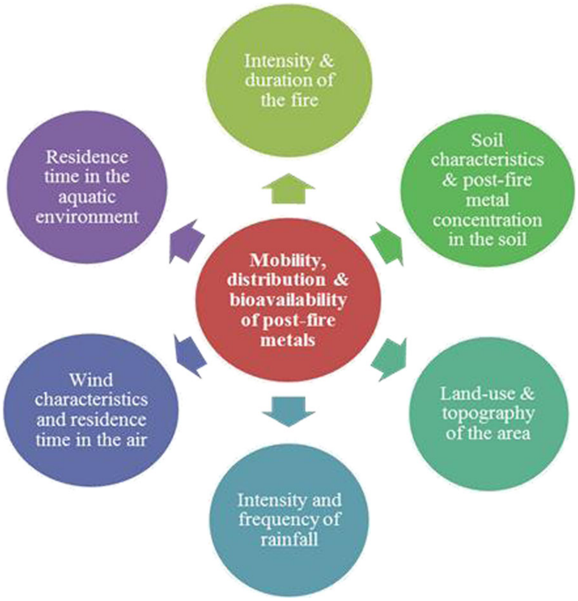

Fig. 3 Major factors which controls mobility, distribution and bioavailability of post-fire metals in the soil environment

Among the selected metals, Cu and Pb are the most difficult to mobilize in the post-fire soil environment (Campos et al. 2016). Pagotto et al. (2001) supported this and reported that Cu and Pb are very unresponsive to physicochemical variations of pH and salinity and are very immobile, with a retention time in the soil environment (Harrison et al. 1981). Among the selected metals, Zn is considered to be more mobile with the solubility of Zn depends on the pH value of the soil and is more sensitive to pH changes than other soil properties (Chirenje et al. 2006). The solubility and mobility of Zn are found to increase when soil pH < 5 (Scokart et al. 1983) and has high capacity to be adsorbed by minerals and organic compounds (Gibert et al. 2005). The presence of other metals in the soil also decreases the mobility of Zn, especially oxides and hydroxides of Al, Fe and Mn because these metals may act as co-precipitants (Gibert et al. 2005). Microbial activity may also play a significant role in the temporal variations of major and trace metal concentration in the post-fire soil environment by sorption into microbial biomass, their ingestion and intracellular sequestration and the subsequent precipitation in the form of organic and inorganic compounds (oxalates and sulphates) (Alkorta et al. 2004; Gadd 2004; Campos et al. 2016).

7 Forest Fire and Metals—Environmental Implications

Forest fire can dynamically change ecosystem structure and function and may take years to recover (Beganyi and Batzer 2011). Changes may include a shift in the dominant invertebrate taxa (De-Szalay and Resh 1997; Minshall 2003), an increase or decrease in nutrient levels (Scrimgeour et al. 2001; Kelly et al. 2006; White et al. 2008; Miao et al. 2010) and release of major and trace metals. Among the metals, Hg is of particular concern in wetlands because the physiochemical conditions are conducive to the formation of methyl Hg (Zillioux et al. 1993; Richardson 1999; Scheuhammer et al. 2007), which has severe neurological implications for organisms (Sharma and Agrawal 2005; Martin and Griswold 2009). Accumulation of 0.001–0.01 mg L^{-1} of Hg in an ecosystem can create acute toxicity in some invertebrate communities in their developmental stages (Boening 2000).

Published studied demonstrated that forest fire can remobilize metals into soil and air and can reach surface water (creeks, rivers, estuaries, dams and lakes) and groundwater resources and oceans, through wind borne disposal of fine particles and water-borne disposal of dissolved matter (Burke et al. 2010, 2013; Smith et al. 2011; Burton et al. 2016, Campos et al. 2016; Nunes et al. 2017). This metal mobility has significant implications in the environment as it affects all aspects of biota from soil microbes to terrestrial and aquatic vertebrates including humans. Post-fire rainfall events and loss of nutrients through surface runoff provide significant impacts on the soil microbial communities, soil productivity and has implications for ecosystem resilience in general (Hernández et al. 1997; Pardini et al. 2004; Campos et al. 2016; Muñoz-Rojas et al. 2016). The presence of metals in the soil may provoke a toxic response in soil microorganisms (Certini 2005; Hart et al. 2005) and this metal stress may change the structure and diversity of microbial communities by disturbing enzymatic activities and reducing microbial biomass (Hartmann et al. 2005; Frey et al. 2006). Specifically, increased forest fire activity combined with intensified post-fire rainfall events are significant threats to the environment due to changes in soil productivity, nutrient loss by erosion, increasing metal impact on microbial communities in soil and the larger ecosystems both locally and downstream with impacts for ecosystems resilience.

8 Risk of Metals on Human Health

Many metals are essential for human, animal and plant health (Wintz et al. 2002); however, excess amounts have negative effects including toxicity (Jankaite 2009). Metal toxicity affects survival, activity, growth, metabolism and reproduction of an organism (Wright and Welbourn 2002). Increased concern has focussed on children, as their immature body systems and different behaviour patterns put them at increased risk (Riewert et al. 2000).

Remobilization of metals during and after fire presents a risk due to the impacts of these metals to the human and ecosystem health. The health risks in metal contaminant areas affect not only industrial, mining and agricultural workers, but the entire population including children and the elderly. It is estimated that millions of people may be exposed to excess metals around the globe (Qiu et al. 2012), specifically from mining, industrial, agricultural activities include forest fire. The exposure pathways of metals include direct ingestion, dermal contact, inhalation of soil particles and surface soil vapour and vegetable ingestion (Zhuang et al. 2014; Zhang et al. 2015). If the metal contaminants decrease in the biosphere, subsequent decreases can be observed in the human body as well (Odigie and Flegal 2014). The risk of metal contamination may be characterized using hazard quotient (HQ), which is the ratio of the average daily dose (ADD) of a chemical to a reference dose (RfD) defined as the maximum tolerable daily intake of a specific pollutant that does not result in any deleterious health effects and is reported as milligram per kilogram per day (Lim et al. 2008). The value of HQ ≤ 1 suggests unlikely adverse health effects whereas HQ >1 suggest the probability of adverse health effects. An

HQ >10 is considered to be a chronic risk (Leung et al. 2008). Therefore, regulatory authorities around the world have established a risk based soil and water screening levels for potentially toxic metals to address these concerns (CEC 1986; EPA 1996; WHO 1996; ANZECC 2000; ATSDR 2011a, b, 2012, 2013).

8.1 Selected Metals and Their Health Effects

Numerous studies (Lee et al. 2005; Rodriguez et al. 2009; Nobuntou et al. 2010; Harmanescu et al. 2011; Zhuang et al. 2014) focussed on the negative human health impacts of metals (Fig. 4), including cancer incidence (Pearce et al. 2012). Over time, exposure to As by ingestion and inhalation can result in a wide range of deleterious systemic health effects such as peripheral and cardiovascular disease; hypertension; diabetes mellitus; hematologic and gastrointestinal disorders, renal and respiratory disorders; hearing loss; developmental abnormalities (Chen et al. 1996; Centeno et al. 2007; Mazumdar 2008; Smith and Steinmaus 2009; Del Razo et al. 2011; Carlos et al. 2014) and range of cancers, including bladder, colon, kidney, liver, lung and skin (Scholz and Ellerbrock 2002; IARC 2004; Celik et al. 2008; ATSDR 2011b). Long-term low level As exposure can cause darkening of the skin and the appearance of small corns or warts on the palms, soles and torso (Martin and Griswold 2009). Inorganic arsenite As(III) and arsenate As(V) are the major As species creating health effects. The health effects of these species are varied as As(III) is 20 times more toxic than As(V) and 70 times more

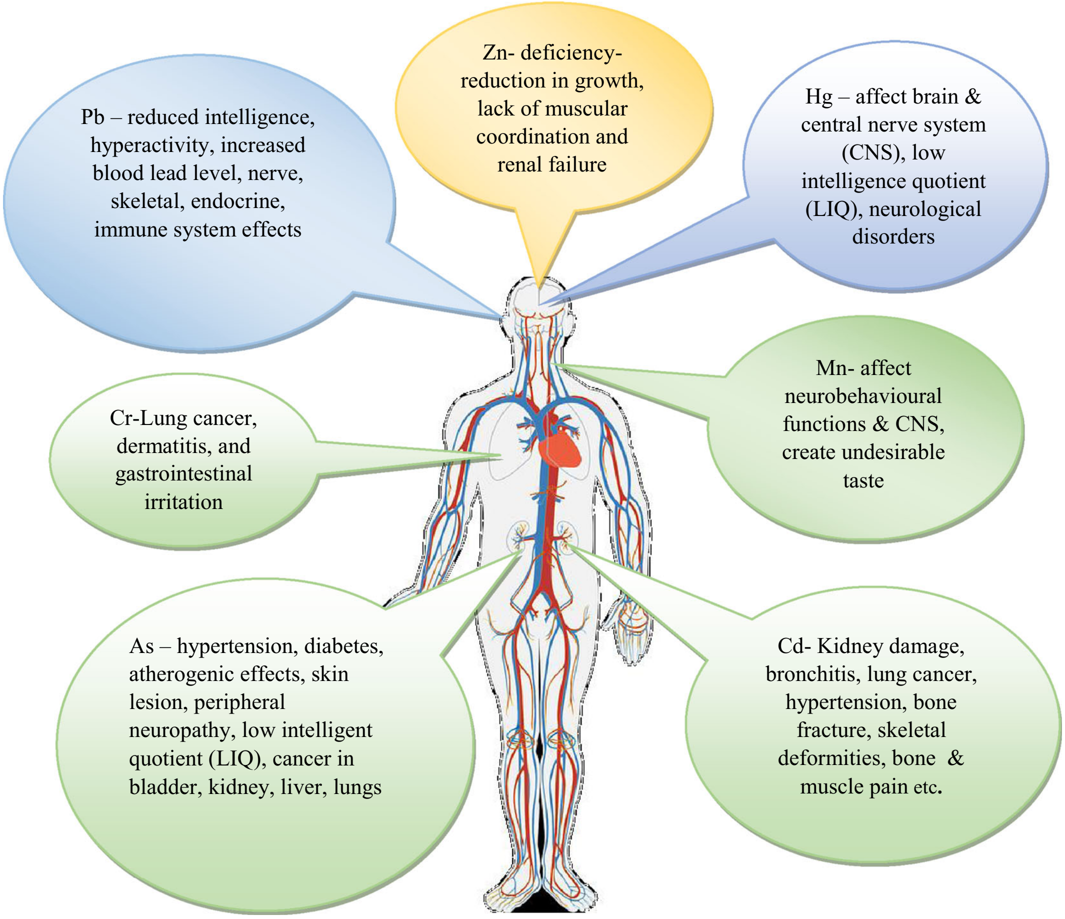

Fig. 4 Some of the impacts of metals on human health (based on Chen et al. 1996; IARC 2004; Young 2005; Centeno et al. 2007; Celik et al. 2008; Mazumdar 2008; ADWG 2011; ATSDR 2011a, b, 2012, 2013; Del Razo et al. 2011; NTP 2012; Zhang et al. 2012; Cobbina et al. 2013)

toxic than organic species (Rakhunde et al. 2012). Known negative health effects have prompted regulatory authorities to limit the concentration of As in drinking water as 0.01 mg L^{-1} (Martin and

Table 2 Some of the human health effects of selected metals and As

Metals	Health effects	Reference(s)
As	Low intelligent quotient	Cobbina et al. (2011)
	Cancer in several organs including bladder, kidney, lungs and liver	IARC (2004); Valenzuela et al. (2005); Celik et al. (2008); ATSDR (2011b)
	High level exposure—peripheral neuropathy/vascular disease	Zukowska and Biziuk (2008)
	Skin lesion	Valenzuela et al. (2005)
	High level exposure—death	USDL (2004)
	Chronic iAs ingestion—diabetes	Coronado-Gonzalez et al. (2007); Del Razo et al. (2011)
	Chronic iAs ingestion—cardiovascular disease	Chen et al. (1996); Mazumdar (2008)
	Hypertension, artheriogenic effect	Chen et al. (1996)
Hg	Neurological disorders, total damages to the brain and central nervous system (CNS)	Cobbina et al. (2013)
	Low intelligent quotient	Cobbina et al. (2011)
	Minamata disease—impaired hand-eye coordination, memory and speech loss, blurred vision, blindness, muscle weakening and spasms, death in some cases	Solomon (2008)
	Structural damages to the brain	
	It can crosses the placenta and can affect foetuses	Bradl (2005); Brown and Austin (2012)
Pb	Nerves, skeletal, circulatory, enzymatic, endocrine and immune system effects	Zhang et al. (2012)
	Hyperactivity, cognitive impairment, reduced intelligence and increase behavioural problems	Solomon (2008); NTP (2012)
	Cardiovascular, developmental, gastrointestinal, haematological, musculoskeletal, neurological, ocular, renal, reproductive effects	ATSDR (2011a, b)
	Decreasing life expectancy	Lacatsu et al. (1996)
	Increase in blood lead level (BLL)	Pirkle et al. (1994)
	It can cross placenta resulting in miscarriage, stillbirths, birth defects and neurological damage,	Solomon (2008)
Cd	Pulmonary adenocarcinomas, prostatic proliferative lesion, bone fracture, kidney dysfunction and hypertension	ADWG (2011); Cobbina et al. (2013) Scholz and Ellerbrock (2002)
	Very low exposure level—kidney damage, bronchitis, and osteomalacia	Young (2005)
	Itai-Itai disease—joint, borne and muscle pain, kidney dysfunction	Young (2005); Solomon (2008)
	Skeletal deformities, bone loss, kidney damage and generalized pain, anaemia	Solomon (2008)
	Category 1 human carcinogen	Bradl (2005)
Mn	Impairment of neuro-behavioural functions and affect CNS	WHO (2008); Cobbina et al. (2013)
Cr	Dermatitis, lung cancer, nasal septum atrophy, lactate dehydrogenase in bronchioalveleor lavage fluid	Offenbacher (1994)
	Mouth ulcers, nosebleeds, kidney disease, low white blood cell count—depressed immune system, miscarriages and variety of cancers, babies born with deformed spines	Wright and Welbourn (2002); Bradl (2005)
Zn	Deficiency reduction in growth, high dose create Cu deficiency	Chesters (1997)
Cd, Hg, Pb and Zn	Affect human nerves, pulmonary renal system	Kim et al. (2002)
Cd, Hg, Pb, Zn and As	Cognitive impairment in children	Cobbina et al. (2013)

Griswold 2009). The toxic effects of selected metals on human health are summarized in Table 2.

Methyl mercury in water and mercury oxide in the air find ways to humans through inhalation and/or ingestion of water or mercury contaminated fish or food (Cobbina et al. 2011, 2013). Consumption of Hg-contaminated fish or other food items by humans, and other organisms, incorporates the accumulated Hg into the consumer's tissues, which can cause nerve and brain damage, intellectual impairment, neonatal dementia and mental retardation (Wolfe et al. 1998; Mergler et al. 2007; Liang et al. 2014). Children and newborns exposed to MeHg in utero or in the early childhood are at an increased risk of lower neurological status and slower development (Crump et al. 1998; Barbone et al. 2004). Current health advisories discourage Hg-contaminated fish consumption for pregnant women and children, and recommend limits for adults, based on Hg concentrations in the fish (EPA 1997).

Environmental Protection Authority (EPA) of USA determined that Pb is a probable human carcinogen (Martin and Griswold 2009) and noted that children are particularly susceptible (Sharma and Agrawal 2005). Exposure to high Pb levels can damage the brain and kidneys and can affect the human reproduction by damaging the sperm production in men and increasing miscarriage in woman (Martin and Griswold 2009). Childhood Pb exposure was estimated to contribute to about 600,000 new cases of children with intellectual disability annually (WHO 2009). The global burden of diseases from Pb exposure estimated to be 143,000 deaths and 8,977,000 DALYs (Disability-adjusted Life Year) (WHO 2009). Human exposure to Pb contributes cardiovascular diseases, mild mental retardation from childhood exposure leading to reduced intellectual functions (Fewtrell et al. 2004).

Cd is a toxic metal targeting the lung, liver and kidney (Bernard 2008; Liu et al. 2009) and International Agency for Research on Cancer (IARC) classified it as a human carcinogen (Waalkes 2003). Long-term exposure to Cd leads to cardiovascular disease, anaemia and may also affect renal tubular functions (Waalkes et al. 1988; McLaughlin et al. 1999; Barbier et al. 2005). Cd absorption in conjunction with Ca, Fe, Zn, protein, fat and vitamin D deficiencies leads to ostomalacia and bone fracturing (McLaughlin et al. 1999; Bernard 2008). Acute exposure via inhalation results in pulmonary oedema and respiratory tract irritation, and ingestion results in stomach irritation leading to vomiting and diarrhoea (Waalkes 2003). EPA limits Cd in drinking water as 0.005 mg L^{-1}. (Martin and Griswold 2009).

Zn is an essential element needed by the human body and is commonly found in many food types and nutritional supplements; however, toxicity issues exist (ATSDR 2005). Symptoms of acute Zn toxicity in humans include vomiting, dehydration, drowsiness, lethargy, electrolytic imbalance, abdominal pain, nausea, lack of muscular coordination and renal failure, whereas chronic Zn exposure results in an increased risk of anaemia development, damage to the pancreas, lowering of the HDR cholesterol levels and increase in LDL and may possibly increase the symptoms of Alzheimer's disease (Athar and Vohora 1995). Inhaling large amounts of zinc (as zinc dust or fumes from smelting or welding) can cause a specific short-term disease called metal fume fever (ATSDR 2005).

Cr compounds bind with soil and are do not easily migrate into water (Martin and Griswold 2009). Excess Cr concentration in the body creates liver nercosis, nephrites, gastrointestinal irritation, nasal and mucous membrane ulcers and dermatitis including skin ulcers and allergic reactions (Costa and Klein 2006; ATSDR 2013). Long-term exposure results in liver, kidney, circulatory and nerve tissue damage (Athar and Vohora 1995, Martin and Griswold 2009), including lung cancer, which is the most serious long-term effect (Lewis 2004; Smith and steinmaus 2009). Repeated skin contact with Cr dusts can produce incapacitating eczematous dermatitis with oedema (ATSDR 2013).

Ni is a known haematotoxic, immunotoxic and neuro-toxic agent and affects modifications in DNA bases (Das et al. 2008). Ni induces embryo toxic and nephrotoxic effects, allergic reactions and contact dermatitis (EPA 2002). It may also cause conjunctivitis, eosinophilic pheumonites and asthma (Athar and Vohora 1995). It is a potential carcinogen for the lung and may cause skin allergies, lung fibrosis and cancer of respiratory tract in occupationally exposed humans (Kasprazak et al. 2003; Salnikow et al. 2004; Cempel and Nikel 2006; Phillips et al. 2010) and may create death in the case of high fleeting exposure due to adult respiratory distress syndrome (ARDS) (Phillips et al. 2010).

Mn is a normal constituent of air, soil and water. Mn has a relatively low toxicity to humans, but may cause poisoning at higher concentrations with noted effects to

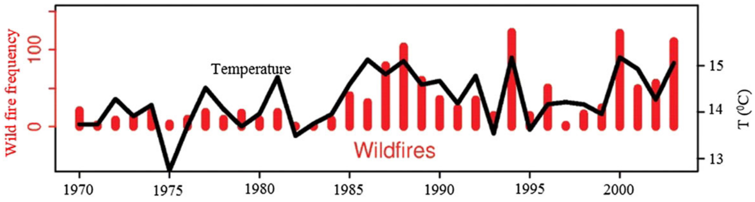

Fig. 5 Showing the relationship between forest fire frequency (>400 ha burned as *bars*) and mean spring-summer temperature (as *line*) in Western United States (Westerling et al. 2006). Note the increase in fire frequency associated with rise in temperature

the lung, cardiac system, liver and reproductive systems and reduction in systolic blood pressure (Crossgrove and Zheng 2004; ATSDR 2012). Gastrointestinal effects are noted in humans for lower Mn concentrations (WHO 2008; NHMRC 2011). Mn also affects the central nervous system (CNS) and may be associated with to Parkinson's disease (Levy and Nassetta 2003; Crossgrove and Zheng 2004, Michalke et al. 2007; ATSDR 2012) and may also impacts on the aesthetic of drinking water with changes to taste, colour and staining of pipes and fittings (WHO 2008; NHMRC 2011).

9 Impacts of Climate Change on Forest Fire

Global analysis of current, historical and palaeo fire activities provides insights into the interaction between climate change and forest fire (Flannigan et al. 1998; Bowman et al. 2011). To illustrate this, Westerling et al. (2006) analysed the spring-summer temperature and forest fire data from the west and south-western USA and reported that fire regimes directly respond to change in climate (Fig. 5), a correlation which is supported by Marlon et al. (2009) and Quintano et al. (2015). Numerous studies note the relationship between climate change and global fire activity and specifically states that global fire activity increases, when the Earth's climate warms and decreases when climate cools and climate change is considered to be the primary control of global fire activity over extended time periods (Swetnam 1993; Hasson et al. 2008; Marlon 2009; Liu et al. 2010; Pechony and Shindell 2010; Bento-Goncalves et al. 2012, IPCC 2013).

Concern over the potential impacts of climate change on fire severity is noted (Fried et al. 2004). Pechony and Shindell (2010) concluded that there is an impending shift to a temperature-driven global fire regime in the twenty-first century, with a rapid acceleration after 2050, consistent with the study by Mouillot et al. (2002), who projected a large increase in burned areas in the Iberian Peninsula. Similarly, Weinhold (2011) predicted an increase in acreage burned in California, USA, and Tedim et al. (2015) predicted large-scale fires in Portugal during the twenty-first century. Studies revealed both an increased number of days of 'high fire danger' (Brown et al. 2004) and the possibility of more frequent and more intense fire in areas such as northern California, USA (Fried et al. 2004).

The expected increase in fire frequency, intensity and areal extend due to climate change (Hennessy et al. 2005; IPCC 2007; Liu et al. 2010; IPCC 2013) may have broad implications in the forest ecosystems and adjoining areas and in particular for the remobilization of metals, which may contaminate soil (Odigie and Flegal 2011, 2014, Kristensen et al. 2014, Campos et al. 2016), water (Burke et al. 2010, 2013) and air (Weinhold 2011) with consequent effects on human health (Taylor et al. 2010; Weinhold 2011; Carlos et al. 2014), ecosystems health and biodiversity (Schaider et al. 2007; Zhuang et al. 2014). Given the pervasive nature of metal emission in the environment and the expected increase of fire due to climate change, many authors (Odigie and Flegal 2011; Shcherbov 2012; Kristensen et al. 2014; Odigie and Flegal 2014) reported the possibility that more metals will remobilize in the near future.

10 Conclusion

Millions of hectares of land including forest areas across the globe are contaminated with major and trace metals associated with anthropogenic activities such as mining, agriculture, landfilling, industrial waste disposal and many others. Despite improved legislation and practice, metal contamination continues today. The major and trace metals present in the forest ecosystem are generally sequestered in sediments, surface organic layers and vegetation, where they are relatively immobile, but any disruption or change to surface conditions such as fire may result in liberation of these metals into ash and other mobile phases. Metal enriched ash acts as a persistent toxic metal source to surrounding residential areas and the ecosystems through the wind-born dispersal of fine particles and water-borne transport of dissolved and particulate metals. This mobility may increases the bioavailability of these metals, which substantiate human and ecosystems health concerns and may generate water quality issues, especially in forested potable water catchment areas.

Substantial evidence supports the theory that our planet is experiencing a time of climate fluctuation or climate change (Mouillot et al. 2002; Westerling et al. 2006; Pechony and Shindell 2010; Tedim et al. 2015) and with increasing temperatures results in increasing forest fire frequency and areal extension. Global temperature increase and increased fire incidence strongly correlate, as does the need for controlled burns to mitigate the catastrophic risk of large uncontained fires. Much fire research has focused on changes to the post-fire soil properties and carbon signature with little work devoted to metal mobilization. Authors demonstrate that fire has the potential to affect the soil profile, which hosts metals in the contaminated forest soil, resulting in the liberation of metals with extensive redistribution, sometimes hundreds of kilometres from the original source. Ash enriched in metals may travel extensive distances in air and water and significantly impact on these distal landscapes and the human and the ecosystems there. The increase in mobility and potential bioavailability of these metals highlights the need to reconsider the action of fire on human and ecosystems health in all areas that are affected by fire.

Public awareness of issues relating to environmental contamination including metal contamination is growing, but when fire occurs, imminent threat to life and health of the people and their properties become the focus of responders and other public authorities. We in no way criticize this focus but suggest scientist and legislators must take a longer-term view and consider the effect of fire in a broader context. This is particularly true for first responders to any fire and is also true for authorities that manage controlled burns. The potential for harm has been demonstrated and research is now required to consider ways to minimize harm and quantify risk associated with metals.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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Chapter- 3

Risk of post-fire metal mobilization into surface water resources: A review

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Review

Risk of post-fire metal mobilization into surface water resources: A review

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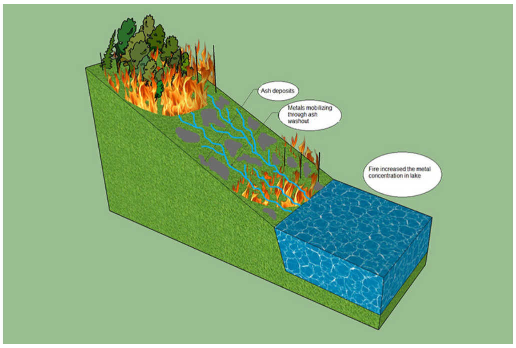
HIGHLIGHTS

- Forest catchment supply high quality water to a number of communities around the world.
- Forest fire release sequestered metals from soil organic matter and vegetation.
- Post-fire erosion rapidly transports these metals to downstream soil and water bodies.
- Their deposition in the water bodies affects the water quality and aquatic biota.
- This metal contamination may reach to human being as a consumer.

GRAPHICAL ABSTRACT



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ABSTRACT

One of the significant economic benefits to communities around the world of having pristine forest catchments is the supply of substantial quantities of high quality potable water. This supports a saving of around US$ 4.1 trillion per year globally by limiting the cost of expensive drinking water treatments and provision of unnecessary infrastructure. Even low levels of contaminants specifically organics and metals in catchments when in a mobile state can reduce these economic benefits by seriously affecting the water quality. Contamination and contaminant mobility can occur through natural and anthropogenic activities including forest fires. Moderate to high intensity forest fires are able to alter soil properties and release sequestered metals from sediments, soil organic matter and fragments of vegetation. In addition, the increase in post-fire erosion rate by rainfall runoff and strong winds facilitates the rapid transport of these metals downslope and downstream. The subsequent metal deposition in distal soil and water bodies can influence surface water quality with potential impacts to the larger ecosystems inclusive of negative effects on humans. This is of substantial concern as 4 billion hectares of forest catchments provide high quality water to global communities. Redressing this problem requires quantification of the potential effects on water resources and instituting rigorous fire and environmental management plans to mitigate deleterious effects on catchment areas. This paper is a review of the current state of the art literature dealing with the risk of post-fire mobilization of the metals into surface water resources. It is intended to inform discussion on the preparation of suitable management plans and policies during and after fire events in order to maintain potable water quality in a cost-effective manner. In these times of climate fluctuation and increased incidence of fires, the need for development of new policies and management frameworks are of heighted significance.

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Contents

1. Introduction

Catchment management is an overarching premise for water regulation and policies which governs the oversight of the hydrology and hydrochemistry of surface and groundwater resources (Ferrier and Jenkins, 2010). Healthy forest catchments with moderate to high annual precipitation and low contaminant concentrations are essential for the provision of potable water, together with irrigation, industrial and recreational uses around the globe. In addition, they also provide significant aquatic habitats (Neary et al., 2009; Smith et al., 2011). Many urban areas and cities rely heavily on the water provided by forest catchments including two-thirds of the municipalities in the USA and one-third of the world's largest cities including Melbourne, Sydney, Tokyo, Los-Angeles and Rio de Janeiro (CHIFM, 2008). Over 4 billion ha of forest catchments (31% of the total landmass) around the globe store, filter and provide high quality water that provide substantial economic benefits including an estimated US$ 4.1 trillion annually by limiting the cost for purifying and sanitizing water treatments and associated infrastructure (Bladon et al., 2014). However, the ongoing challenge of supplying substantial quantities of high quality water to communities is significantly increased by the impacts of both natural and anthropogenic activities including forest fire.

Fire is a natural disruption that affects many forested catchments in tropical, temperate and boreal regions (González-Pérez et al., 2004; Neary et al., 2006; Shakesby and Doerr, 2006; Beganyi and Batzer, 2011). It has been estimated that >30% of the land surface is subjected to substantial fire occurrence (Chuvieco et al., 2008) and each year fire burns nearly 650 M·ha of forests around the globe (Shcherbov, 2012). Recent studies highlight that climate change will increase the frequency and areal extent of fire particularly in association with other factors such as rural depopulation, land abandonment and afforestation with fire-prone species (Pausas, 2004; Hennessy et al. 2005; Westerling et al., 2006; Moreira et al., 2009, 2011; IPCC, 2013, Campos et al., 2015, 2016).

Fire can substantially effect a range of physical and biogeochemical properties of soil and is able to both release and redeposit metals on the soil surface (Certini, 2005; Odigie and Flegal, 2011; Campos et al., 2012, 2015, 2016). This may be either as the result of combustion of vegetation and soil organic matter (resulting in the breakdown of metal complex organic compounds) or through the interactions of fire on the soil surface resulting in ash and charcoal deposition (Bitner et al., 2001; Certini, 2005; Goforth et al., 2005; Jovanovic et al., 2011; Costa et al., 2014). Fire also alters catchment behaviour by affecting key hydrological factors, which control infiltration and surface runoff (Ellis et al., 2004; Knoepp et al., 2008; Shakesby and Doerr, 2006). The formation of a temporary water-repellent layer during fire, at or near the soil surface reduces infiltration, which increases overland flow, peak discharge, and overall water yield (when compared to pre-burn conditions) and hence the magnitude and timing of stream flows (DeBano, 2000; Benavides-Solario and MacDonald, 2001, 2005; Kunze and Stednick, 2006; Shakesby and Doerr, 2006; Moody et al., 2009). On the other hand, water repellency is sometimes very low or removed by fire, specifically in twice burned plots (Keesstra et al., 2016a). This overland flow increases the erosion rate and sediment load consequently increasing toxic and other metal concentrations in downstream water resources. These processes affect water quality parameters including pH, electrical conductivity (EC), turbidity, dissolved oxygen, major ions, nutrient loading (for example nitrate, sulphate, phosphate) and major and trace metal concentrations (Wallbrink et al., 2004; Kunze and Stednick, 2006; Shakesby and Doerr, 2006; Scherer, 2008; Moody and Martin, 2009; Campos et al., 2015, 2016).

Leaching of contaminants, including metals occurs throughout the soil profile and may result in groundwater contamination, specifically where groundwater levels are close to the surface (Reneau et al., 2007; Costa et al., 2014). Wind may also play a significant role in metal mobilization resulting the effects being dispersed over great distances (Breulmann et al., 2002; Schaider et al., 2007). The enhanced metal mobility occurs particularly during or immediately after the first major post-fire rainfall event(s) and has elevated impacts if the fire occurs on a landscape with already raised contaminant levels. This metal mobility has the potential to significantly impact on the quality of water from forest catchments and their associated rivers and water storages and introduces potential health impacts on human and ecosystems (Kelly et al., 2006; Sillins et al., 2009a; Smith et al., 2011; Nunes et al., 2017). However, it should be noted that all forest fires do not necessarily result in major changes such as soil erosion, increased runoff and raised sediments load together with enhanced pollutant connectivity and transport. Exceptions to these severe effects are found in low-intensity prescribed fires and fires which occur on flat lands and areas with low precipitations. Post-fire erosion and runoff and the resulting metal mobility of the area, are influenced by number of factors such as fire severity, post-fire metal concentration in the soil, frequency, intensity and duration of the rainfall, soil surface exposure, hydrological properties of the soil, distance to the water resources, slope of the land, intensity and direction of the wind together with a number of other minor local factors (Smith et al., 2011). In all the environments, the physical dynamics of the location strongly control the localised effects and magnitude of fires impacts.

There is a widely held view that forest fire is a catastrophic phenomenon that affects human lives and properties and which has significant impacts on the atmosphere and terrestrial and aquatic ecosystems (Kelly et al., 2006; Lavorel et al., 2007; Cerda and Doerr, 2008; Burke et al., 2010; Beganyi and Batzer, 2011; Melendez-Perez et al., 2014; Nunes et al., 2017). However, fire is a natural phenomenon of many terrestrial ecosystems and these systems may have adapted to require fire at some level in order to thrive. The effects of fire including moderate increases in erosion, runoff, sediment load and pollutant transport, which are all considered as a part of the natural temporal changes (Neary et al., 2005; Pausas and Keeley, 2009; Pereira et al., 2011). Low to moderate severity prescribed fires and high severity wild fires may even renew essential nutrients for long-term sustainable developments of forest ecosystems (Arocena and Opio, 2003; Pereira et al., 2011). Nevertheless, although fire may be natural and part of an evolved ecosystem, increased rates of fire coupled with increased contamination of surface materials present a significant risk to catchment systems and may have a significant impact on human populations.

It is recognised that fire is not the end of the forest ecosystem. As it is a natural phenomenon, most forests will recover from fire after several years. In most cases plants will succeeded in recolonising the burned forest area and most of the soil properties will return to pre-fire levels and in some cases the event will enhance the forest environment (Certini, 2005). Herbaceous plants and shrubs are reported to be the type of vegetation that most easily regenerate in the post-fire environment and may quickly dominate the landscape (Costa et al., 2014). After two years regeneration of the trees becomes apparent (Costa et al., 2014). In this respect, Lane et al. (2008) reported a link between vegetation recovery and post-fire alteration in surface water chemistry.

Metals in the environment, particularly Cr, Cd, Cu, Hg, Mn, Ni, Pb, Zn and the metalloid As (herein after called a 'metal') are of great environmental and human health concern due to their toxicity, environmental

Table 1
Some of the human health risks of As and selected metals including their guideline values.

Metals	Guideline value (mg L^{-1}) – WHO (2008)	Human health risk	Reference
As	0.01	(1) Low intelligent quotient	(1) Cobbina et al. (2011)
		(2) Hypertension and artheriogenic effect	(2) Chen et al. (1996)
		(3) Skin lesions	(3) Valenzuela et al. (2005)
		(4) Cancer in several organs including bladder, kidney, lungs and liver	(4) Gallaher et al. (2002); Leak et al. (2003); IARC (2004); Valenzuela et al. (2005); Celik et al. (2008); ATSDR (2011)
		(5) Chronic iAs ingestion –diabetes	(5) Coronado-Gonzalez et al. (2007); Del Razo et al. (2011);
		(6) Chronic iAs ingestion -cardiovascular disease	(6) Chen et al. (1996); Mazumdar (2008)
		(7) High level exposure -peripheral neuropathy/vascular disease, and even death	(7) USDL (2004); Zukowska and Biziuk (2008)
Hg	WHO – 0.006 (inorganic Hg) Australia - 0.001 (total Hg)	(1) Low intelligent quotient	(1) Cobbina et al. (2011)
		(2) Neurological disorders	(2) Cobbina et al. (2013)
		(3) Create toxicity to kidney	(3) Gallaher et al. (2002)
		(4) Total and structural damages to the brain and central nervous system (CNS)	(4) Cobbina et al. (2013)
		(5) It can cross the placenta and can affect foetuses	(5) Bradl (2005)
		(6) Methyl Hg may create neurological disorders and mental disability	(6) Gallaher et al. (2002)
		(7) Minamata disease - Impaired hand-eye coordination, memory and speech loss, blurred vision, blindness, muscle weakening and spasms – leads to death in some cases	(7) Solomon (2008)
Pb	0.01	(1) Increase in blood lead level (BLL)	(1) Pirkle et al. (1994)
		(2) Decreasing life expectancy	(2) Lacatsu et al. (1996)
		(3) Effects on CNS	(3) Gallaher et al. (2002); Leak et al. (2003)
		(4) Nerves, skeletal, circulatory, enzymatic, endocrine and immune system effects	(4) Zhang et al. (2012)
		(5) Hyperactivity, cognitive impairment, reduced intelligence, and increased behavioural problems	(5) NTP (2012); Solomon (2008)
		(6). Cardiovascular, developmental, gastrointestinal, haematological, musculoskeletal, neurological, ocular, renal and reproductive effects	(6) ATSDR (2011)
		(7). It can cross placenta resulting in miscarriage, stillbirths, birth defects and neurological damage	(7) Solomon (2008)
Cd	0.003	(1) Very low exposure level leads to kidney damage, bronchitis, and osteomalacia.	(1) Young (2005)
		(2) Pulmonary adenocarcinomas, prostatic proliferative lesion, bone fracture, kidney dysfunction and hypertension	(2) Scholz and Ellerbrock (2002); ADWG (2011); Cobbina et al. (2013)
		(3) Cognitive impairment in children	(3) Cobbina et al. (2013)
		(4) Skeletal deformities, bone loss, kidney damage and generalised pain, anaemia	(4) Solomon (2008)
		(5) Category 1 human carcinogen	(5) Bradl (2005)
		(6) Affects human nerves, pulmonary renal system	(6) Kim et al. (2002)
		(7) Itai-Itai disease giving joint, bone and muscle pain, kidney dysfunction	(7) Young (2005); Solomon (2008)
Cr	0.05	(1) Dermatitis, lung cancer, nasal septum atrophy, lactate dehydrogenase in bronchioalveleor lavage fluid	(1) Offenbacher (1994)
		(2) Mouth ulcers, nosebleeds, kidney disease, low white blood cell count and depressed immune system, miscarriages and variety of cancers. Babies may be born with deformed spines	(2) Bradl (2005); Wright and Welbourn (2002)
Cu	2.0	(1) Gastrointestinal symptoms at low concentrations	(1) Gallaher et al. (2002))
		(2) Poisoning may occur at high concentrations	(2) Gallaher et al. (2002)
Zn	3.0	(1) Essential element for human consumption but a very high concentration may have aesthetic and gastrointestinal effects	(1) Gallaher et al. (2002)
		(2) Deficiency reduction in growth, and a high dose creates Cu deficiency	(2) Chesters (1997)
		(3) Affects human nerves, pulmonary renal system	(3) Kim et al. (2002)
Mn	0.4	(1) High concentrations may have an aesthetic effect and it stains plumbing fixtures	(1) Wasson et al. (2003); Townsend and Douglass (2004); White et al. (2006)
		(2) Impairment of neuro-behavioural functions and affects CNS	(2) WHO (2008); Cobbina et al. (2013)
Ni	0.07	(1) It may cause conjunctivitis, eocinophilic pheumonites and asthma.	(1) Athar and Vohora (1995)
		(2) May induce embryo toxic and nephrotoxic effects, allergic reactions and contact dermatitis	(2) US-EPA (2002)
		(3) It is a potential carcinogen for lungs and may cause lung fibrosis and cancer of respiratory tract in occupationally exposed people	(3) Kasprzak et al. (2003)

persistency and tendency to bioaccumulate and biomagnify in the food chain (Adriano, 2001; Ignatavicius et al., 2006; Kelly et al., 2006; Campos et al., 2012, 2015, 2016; Nunes et al., 2017). Elevated metal concentrations not only degrade the quality of the atmosphere, soil, water bodies and food crops, but also threaten the health and well-being of humans and other animals who reside on the land or consume water and food from the affected area (Wang and Mulligan, 2009; Nabulo et al., 2010; Cobbina et al., 2013). Deleterious health effects such as cancer, hyperactivity, reduced intelligence, reduction in physical growth, gastrointestinal-renal-respiratory disorders, hearing loss, developmental abnormalities, cognitive impacts including mild mental retardation and many others may occur when metals are continuously ingested or inhaled by humans (Table 1) (Chen et al., 1996; Centeno et al., 2007; Mazumdar, 2008; ATSDR, 2011; Del-Razo et al., 2011; Pearce et al., 2012; Cobbina et al., 2013). In aquatic ecosystems metals can alter the structure and composition of resident microbial communities (Nipper et al., 1998; Minshall, 2003; Beganyi and Batzer, 2011) and can accumulate in fish species which may reach the human consumer (Kelly et al., 2006). Elevated metals also interfere with physiological functions of plants with disruption of gaseous exchange, CO_2 fixation, respiration, nutrient absorption, and growth rate (Angelova et al., 1999, Kabata-Pendias, 2011). Increased forest fire frequency combined with intensified post-fire rainfall, wind and the resulting metal mobility is thus viewed as a threat to human and ecosystems health owing to the toxicity and bioaccumulation properties of the metals (Hernández et al., 1997; Pardini et al., 2004; Goberna et al., 2012; Guénon et al., 2013; Muñoz-Rojas et al., 2016). In general, these metals either in deficiency or excess can impact on plants, animals and human health (Hindwood et al., 2003). Therefore, determining the concentration, distribution and mobility of toxic metals in soil and water both pre- and post-fire environment is required to assess the health of the terrestrial and aquatic ecosystems and to devise strategies to minimize impacts.

During fire, mobilization and deposition of metals occur through complex interactions involving combustion of vegetation, mineralization of the soil organic matter and causing interactions of hot ash with the underlying soil (Jakubus et al., 2010; Pereira and Ubeda, 2010; Jovanovic et al., 2011; Odigie and Flegal, 2011, 2014; Costa et al., 2014; Campos et al., 2016). Studies from the USA (Bitner et al., 2001; Sabin et al., 2005; Burke et al., 2010; Stein et al., 2012; Burke et al., 2013; Burton et al., 2016; Nunes et al., 2017), Australia (Leak et al., 2003; Wasson et al., 2003; Lane et al., 2008; Kristensen et al., 2014), Portugal (Campos et al., 2012; Costa et al., 2014; Campos et al., 2015, 2016; Nunes et al., 2017), Chile (Odigie et al., 2016), Lithuania (Ignatavicius et al., 2006) and Korea (Shin et al., 2002), have reported on metals (Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn and As) in burnt forest soils and ash, and the capacity of rainfall runoff and storm events to produce flows carrying large sediment loads enriched with metals into surface water resources. However, the post-fire impacts on water quality (in terms of metals), including the magnitude of their potential effects, the persistence of their influence and their impacts on organisms (including humans) are not well investigated and documented. Understanding the dynamics of metal concentrations between the land and the water interface is essential for appropriate health risk assessments for quantifying agricultural impacts and for long-term ecosystem management and sustainability planning.

This paper is a review of the state of the art literature dealing with the risk of post-fire mobilization of selected metals into surface water resources. The articles related with this topic have been selected using standard search tools including 'ISI Web of knowledge' and 'Google scholar' interrogated with key words and phrases related to forest fire and metal mobilization. Global examples have been used to illustrate the distribution and mobility of post-fire metal concentrations into water resources and the resulting impacts on ecosystem and human health, in order to promote further discussion on the preparation of suitable management plans in catchment areas during and after significant fire events. The findings of this review will help United Nations (UN) to achieve their sustainable development goals (Keesstra et al., 2016b).

2. Metals in the forest catchments

The forest floor is a dynamic component of the forest ecosystem and includes organic matter and a mixture of minerals, which act as a potential reservoir of metals, water soluble organic compounds and biogenic substances (Shcherbov, 2012). Metals are geogenically introduced into the terrestrial environment (through weathering and soil erosion, volcanic eruption, atmospheric fall out and cosmic dust), and they find their way into forest and aquatic environments in varying concentrations (UNEP, 2013). Metal concentrations have dramatically increased since the industrial revolution through anthropogenic activities (fossil fuel-based power generation, manufacturing, increased rates and modes of transportation, mining and smelting activities, inorganic agricultural practices, waste incineration and unmonitored land filling) (Nriagu, 1989; Pacyna and Pacyna, 2001; Wei and Yang, 2010). Metals liberated or mobilized by these activities can contaminate air, surface and ground water, terrestrial, lacustrine and marine environments (Boyle et al., 2005). They are often persistent of pollutants in the ecosystems tendency to accumulate in sediments with long persistence times (Pereira and Ubeda, 2010; Jovanovic et al., 2011; Soliman et al., 2015). If these metals remain sequestered in soil or sediment, their impact is limited. However, mobilized and ingested by animals and humans significant damage may follow (Jain et al., 2008).

The deposition and the subsequent accumulation of metals in the forest ecosystem is related to their adsorption by soil organic matter, clay mineral fixation and their association with Mn oxide and Fe and Al hydroxides (Kaschl et al., 2002; Sipos et al., 2005; Kabata-Pendias, 2011). Their behaviour is complex but is dominantly controlled by adsorption and desorption processes including many specific physical, chemical and biogeochemical processes (Reis et al., 2015). Once these metals enter a catchment, they may be (i) concentrated in the organic layers of the soil (especially in the case of Hg, Cu and Pb) (Shcherbov, 2012), (ii) sequestered in sediments, (iii) compounded with soil organic matter (Rea et al., 2000; Biester et al., 2002; Grigal, 2003), and (iv) be absorbed by plants and hence become fixed in the system, significantly reducing their mobility (Hernandez et al., 2003; Biswas et al., 2007; Obrist et al., 2008; Friedli et al., 2009). For example, approximately 90% of the Hg in the forest is found to be accumulated and stored in the surface organic layers of the soil (Grigal, 2003). The binding mechanisms that hold them in place, and the resultant concentration in the forest ecosystem, both-increase with humus formation (Shcherbov, 2012). The presence of other metals, soil pH and redox potential, landscape position, stand age, and biota spectrum all affect humus formation (Sposito, 1989; Munthe et al., 1998). It is generally agreed that Cr, Cu, Pb are strongly binding with soil organic matter, whereas, Cd, Co, Mn, Ni and Zn are weakly binding (Tipping, 1998; Lawlor and Tipping, 2003). Immediately after their deposition metals are generally enriched on the surface layer of the forest soil, then slowly migrate to the lower layers. Consequently, their concentrations decrease rapidly with depth (Xin-Ling et al., 2008, Shcherbov, 2012).

Plants are an intermediate reservoir of metals which are taken from the primary metal sources of soils, water and air and if subsequently ingested by animals or humans, they are able to move into these organisms and can have negative health impacts (Adriano, 1986; Kabata-Pendias and Pendias, 1992; Kabata-Pendias, 2004, 2011). Plant leaves may also extract dust particles including metal aerosols from the atmosphere, and rain events wash these particles from the leaves allowing them to reach to soil, where they are subject to uptake by plant roots (Rea et al., 2000, 2001, 2002; Frescholtz et al., 2003; Fay and Gustin, 2007). This metal intake increases with the mobility of metals and their concentration in the soil. For example, Zn and Cd are very mobile and easily absorbed by plants, whereas Hg, Cu and Pb are strongly bound to soil particles which reduce their immediate availability (Obrist, 2007; Jovanovic et al., 2011; Rutter et al., 2011; Driscoll et al., 2013). Plants, dependent on species, age and other stress factors, may accumulate metals without any noticeable signs of damage for an extended period and fire liberates metals by either volatilization into the atmosphere (for example Hg) or accumulate on the soil surface within the ash. Thus, the floric forest ecosystem plays a crucial role in the accumulation and circulation of metals and forest fire is a significant contributor to subsequent metal mobility.

3. Impacts of fire and metal mobilization in forest catchments

During fire, the plant biomass and litter layers are typically consumed and the mineral soil is heated, which affects its physical and biogeochemical properties (Certini, 2005). These changes are either short-term or long-term (Arocena and Opio, 2003) while some may be permanent (Certini, 2005). The changes depend chiefly on the nature of the forest, the severity and frequency of fire events and post-fire climatic conditions (Certini, 2005). It has been established that fire is able to release and remobilize sequestered metals from plants and soil organic matter through a relatively complex set of processes (Biswas et al., 2007, 2008; Burke et al., 2010; Odigie and Flegal, 2011, 2014; Kristensen et al., 2014; Burton et al., 2016; Odigie et al., 2016). To illustrate this process, Parra et al. (1996) reported elevated levels of Mn (471 to 1429 mg kg^{-1}) in the post-fire soil environment in the Sierra de Gredos mountain range, and Costa et al. (2014) reported five-fold increase of Mn concentration in ash (compared to the underlying soil) after the Marao Mountain forest fire. Both of these observations were made in Spain. The increase in Mn (67 to 598 mg kg^{-1}) and Pb (52 to 122 mg kg^{-1}) concentration recorded in ash after the 2010 Ermida Fire in Portugal have also been highlighted (Campos et al., 2016). Moreover, a number of authors have reported that Hg stored in forest soil and biomass was volatilized in to the atmosphere in the form of insoluble and unreactive gaseous elemental mercury (Friedli et al., 2001, 2003; Engle et al., 2006; Obrist et al., 2008, Biswas et al., 2007, 2008; Burke et al., 2010; Woodruff and Cannon, 2010; Campos et al., 2015). The mobilized metals are transported to the downstream water resources by runoff and wind activities. For example, Hg introduced into the surface soils by gold mining is mobilized by fire into downstream aquatic ecosystems, where the conditions may favour the formation of the neurotoxic and immune toxic mono methyl Hg (MMeHg). This may then bioaccumulate in the terrestrial and aquatic food web (Morel et al., 1998; Mahaffey, 1999; Hightower, 2004; Kelly et al., 2006; Mergler et al., 2007; Friedli et al., 2009; Foy et al., 2012). Similarly, a three-orders-of-magnitude increase in Pb and Cd were observed (compared to pre-fire concentration) in an urban fringe watershed (Burke et al., 2013) and an increase in concentrations of As, Fe, Pb, Mn and Ni were observed in water samples collected from the burned area (Burton et al., 2016), both after the Station Fire in California (USA) in 2009.

Soil organic matter and pH are the two important parameters which controls the liberation and mobility of metals in the forest ecosystem. When metals enter the forest, they become associated with soil organic matter as most of the metals (Hg, Cu, Ag and Pb) have an affinity towards it and sequester within it with an immobile phase. Increase in the amount of soil organic matter in the forest ecosystem increases the metal concentrations. Soil organic matter shows variability in concentration immediately after the fire in number of occasions (Castro et al., 2011). During fire, elevated soil temperature is sufficient to decompose the metal-humic acid bond resulting in the release of metals onto the soil, air and water environments. Laboratory study indicates that some of the metals (for example Hg) can completely release from soil organic matter by fire (Friedli et al. 2001) and this metal release depends primarily on fire severity (Biswas et al., 2007). High pH value resulting from neutral or alkaline reactions attributes to the metal accumulation in the post-fire soil environment (Bogacz et al. 2011). However, decrease in pH few months after the fire (in most cases) due to intensive precipitation and runoff increase the metal mobilization. The accumulation of new acid products of plant decomposition on the soil surface may also intensify this process (Zaildeman et al. 1999).

Mobility and availability of metals in soils are generally low under high content of organic matter and clay (Yoon et al., 2006). The organic matter mineralization induced by fire, led substantial amount of metals in ash and soil ready to transport, which could be a source of downstream soil and water contamination (Ignatavicius et al., 2006; Pitman, 2006). This post-fire metal concentration depends on a number of factors: pre-fire metal concentration in the soil, types and density of vegetation in the area, fire severity, maximum temperature reached, duration of the fire, types of soil, plant parts burned and many more (Someshwar, 1996; Pereira et al., 2009). The post-fire contaminant soil with metals are characterised by low contents of soil organic matter, low levels of nutrients and pH imbalance (Chiu et al., 2006). The decrease in organic matter and clay and increasing pH during the burning process also increases the mobility of metals (Norouzi and Ramezanpour, 2013).

The correlation of metal concentration with soil pH and dissolved organic matter (measured as dissolved organic carbon) has been noted and it has been established that pH is largely responsible for metal solubility, speciation (Drever, 1988) and mobility (Violante et al., 2010). Low pH increases solubility and mobility, but decreases the organophyllic characteristics of some metals (Drever, 1988). Dissolved Organic Carbon (DOC) forms strong bonds and complexes with metal ions as they have numerous functional groups with negatively charged sites (Ephraim, 1992; Tipping, 1998; Tipping et al., 2011). Mobility of Zn, Cd and Ni are greatly influenced by soil pH and are considerably mobilized when the soil is observed to have low pH; alternatively, the mobility of Cu and Pb is strongly dependent on the solubility of organic matter (Bergvist et al., 1989). Field based studies in forest catchments also reveal that Cu and Pb show strong positive mobility relationships with DOC (Landre et al., 2009), while Cd and Zn mobility are dependent on pH (Bergkvist, 1987; Lazerte et al., 1989, Watmough and Dillon, 2007, Adkinson et al., 2008). This is supported by Oni et al. (2013), who reported a positive correlation between Cu and Fe mobility with DOC and negative correlations with soil conductivity and sulphate concentration.

The increase in forest fire events is linked to more numerous drought seasons, which also exposes large areas of soil surface suitable for erosion. Post-fire precipitation events and wind activities further increase soil erosion (up to 100-fold) with consequent increased runoff and mobilization of significant quantities of metals into downstream water resources. (Riggan et al., 1985; Cohen et al., 2005; Odigie and Flegal, 2011; Stein et al., 2012; Warrick et al., 2012; Odigie and Flegal, 2014; Campos et al., 2016). This significantly decreases water quality, increases the potential bioavailability of a range of metals and may elevate stress on the aquatic ecosystems (Schaider et al., 2007; Nunes et al., 2017). This is a multifaceted process and further complexed by availability of soil organic matter, soil and water pH, redox status, biogeochemical and hydrological processes, among others (Schindler, 2001; Landre et al., 2009) (Fig. 1).

The metals which reach the aquatic ecosystems may eventually deposit and reside in the bottom sediments of stream beds, river banks and flood plains, where they can adversely affect the ecosystem, especially within benthic populations and cause alterations in their community structure (Nipper et al., 1998; Urbaniak et al., 2008, Zhuang and Gao, 2014). Studies have shown that hydrological changes may trigger the migration of benthic-deposited metals back into water and these may be transported further downstream and act as a point of secondary metal contamination (Crossland and La Point, 1992; Kunze and Stednick, 2006). Water plants and plankton in the waterbody absorb these toxic metals from the benthic zone and this leads to an increase in metal availability to all aspects of the food chain resulting in multiple potential impacts to organisms including humans (Finlay and Callow, 1996). Apart from this food chain dynamic, human and terrestrial biota are able to absorb metals from the environment knowingly or unknowingly by way of direct ingestion and inhalation (Schaider et al.,

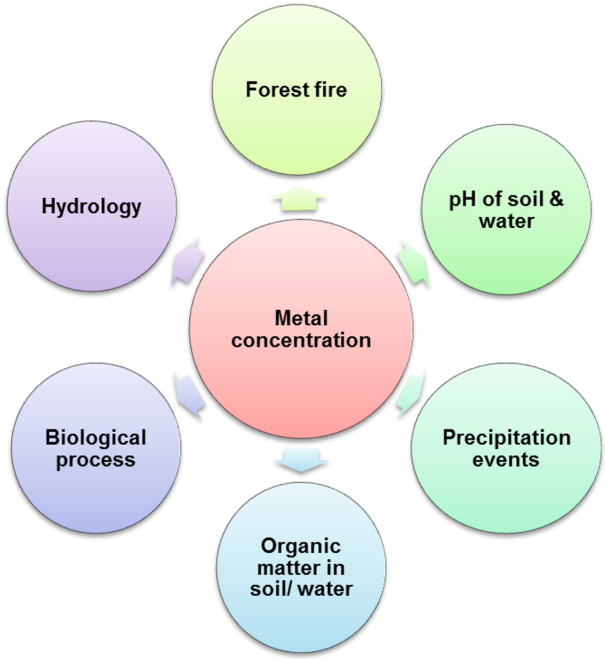

Fig. 1. Some major factors affecting the metal cycling and dynamics in the forest catchments.

2007; Pearce et al., 2012; Martin et al., 2014; Zhuang et al., 2014) (Fig. 2). Thus, metals in the catchments will contaminate the water system and can cause health impacts to human and terrestrial and aquatic biota. Therefore, there is a strong impetus to understand the factors and processes affecting metal dynamics in catchments linked to their prolonged residence time (100 to 1000 years) and their significant toxicity (Macklin and Klimek, 1992; Landre et al., 2009; Huang et al., 2011; Rose et al., 2012).

4. Ash – Remnant of forest fire

'Soil is the mother of all things'. This shows the importance of soil to life of all living creatures on earth (Doran and Parkin, 1994). Soil play fundamental roles in its functioning, linking the atmosphere, the subsurface and the aquatic compartments (Faber et al., 2013), and is the critical component of the natural systems both through its contribution to food, clean water and energy security and by mitigating biodiversity loss (Turbe et al., 2010; Kirkby, 2015). The vastness of the planet and the soil resources allowed agriculture to expand with growing population and store vast amount of groundwater resources, which may improve water quality (Amundson et al., 2015). Many factors and properties of soil such as soil moisture, structure, texture, pH, electrical conductivity, soil organic matter are regulating the micro-, meso- and macro-fauna of the soils (Heiden et al., 2016). Most fascinating thing about soil is that it is incredibly diverse both horizontally and vertically (Bardgett, 2016). Soil system is essential to all living beings on the Earth in such a way that the human management of soil with a holistic approach is mandatory. The future of humanity is intertwined with the future of the Earth's soil resources. Therefore, fifth of the December is celebrated annually as the "World Soil Day" to highlights the importance of soil.

Ash is considered as a part of the soil system. It is a complex mixture of organic and inorganic residues produced by fire which may be subsequently deposited on the soil surface in burned areas (Bento-Goncalves et al., 2012). It is a heterogeneous material composed mainly of particulate carbon, oxides and hydroxides of base cations (Ca^{2+}, Mg^{2+}, P and K^{+}), silica, phosphorous, nutrients (which promote plant recovery), major and trace metals and other potential contaminants (Pereira et al., 2014). Ash includes components from the accumulation of mineral matter stored in vegetation and in the soil organic horizon prior to burning (Biswas et al., 2007) and is characterised by high alkalinity and electrical conductivity (Goforth et al., 2005; Plumlee et al., 2007; Gabet and Bookter, 2011; Granged et al., 2011; Campos et al., 2012; Wade et al., 2013; Campos et al., 2015, 2016). Ash produced at high temperatures may have a high pH value (Etiegni and Campbell, 1991; Henig-Sever et al., 2001) and a high $CaCO_3$ content (Ulery and Graham, 1993; Goforth et al., 2005; Pereira et al. 2008) which inhibits the solubility of metals (Bodi et al., 2014).

The composition and properties of ash depends on number of factors such as fire temperature, types of fuel, plant species burned, vegetation structure, leaf types, plant parts burned, completeness of combustion and so on (Goforth et al., 2005; Gabet and Bookter, 2011; Bodi et al., 2014). The ash pH is usually higher than the underlying soil (even pH values of 8–14 have been noted) and is associated with increased concentrations of carbonates, oxides and hydroxides (Pereira et al., 2011). A high ash pH enhances the availability of some elements and can

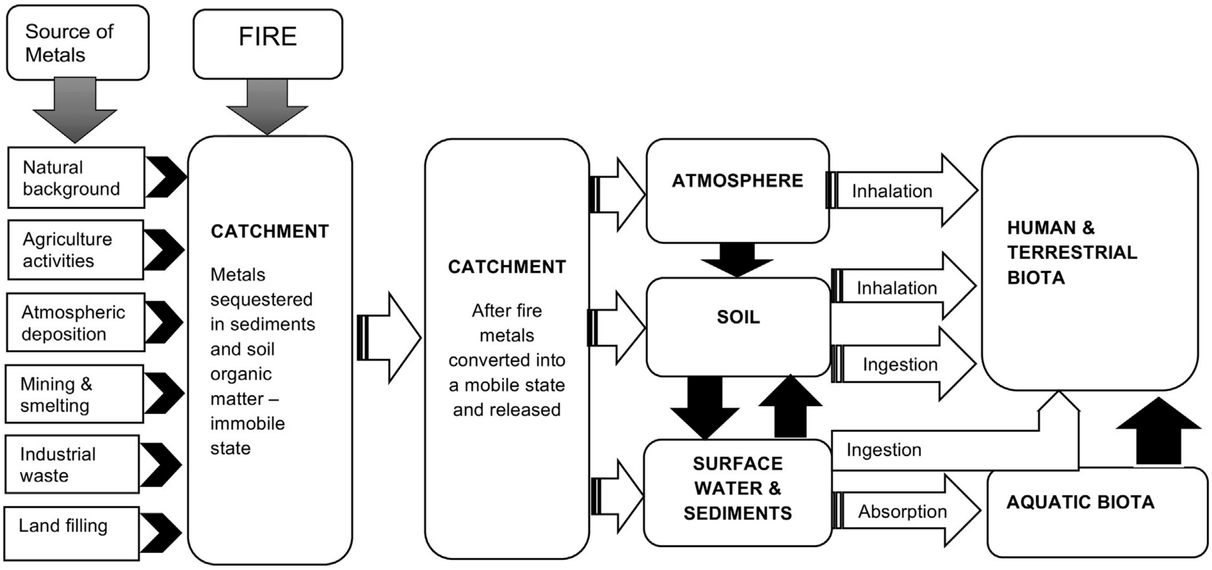

Fig. 2. A conceptual model outlining the sources of metals to the catchment, transport of these post-fire metal to water resources and pathways of exposure. Modified from Schaider et al. (2007).

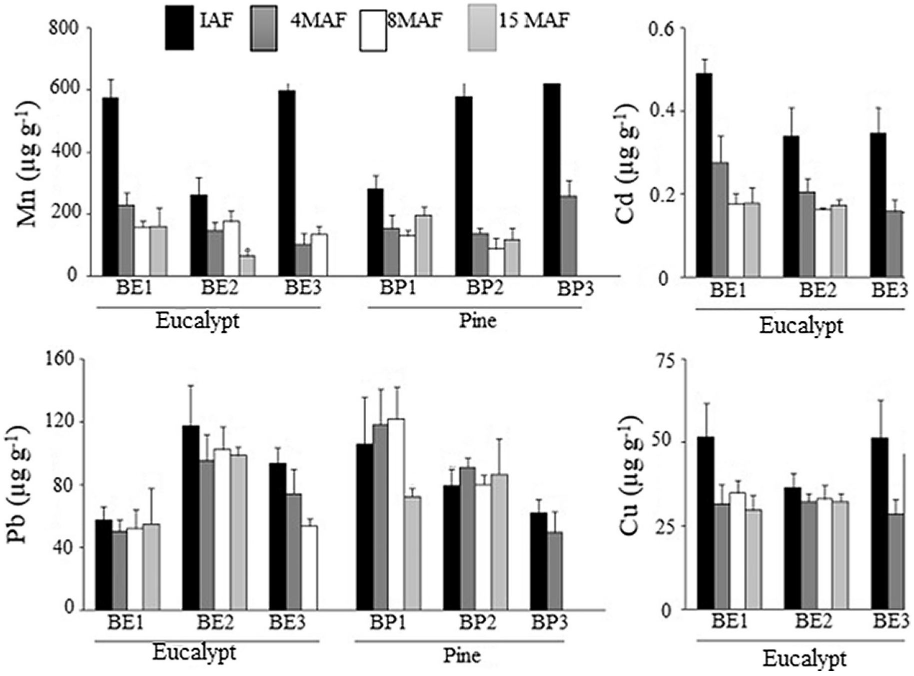

Fig. 3. Concentration of Mn, Cd, Pb and Cu in ash immediately after fire, 4, 8 and 15 months after the fire (IAF, 4MAF, 8MAF, 15MAF respectively) in Eucalypt and Pine plantations after the Ermida Fire (Portugal) in 2010 (Campos et al., 2016). Note the increase in concentration of metals immediately after the fire in most cases.

reduce the availability of others and ash can inhibit the germination of plants due to the alkaline pH and toxic effects of some ions (Bodi et al., 2014; Pereira et al., 2014). In addition, a high percentage of carbon in ash may reflect a higher organic matter content in the soil and litter (Costa et al., 2014). A decrease in clay and soil organic matter together with an increase in pH during the burning process increases the mobility of these metals in the forest soil environment (Yoon et al., 2006).

Ash can provide valuable information about the impacts of fire on the landscape and the colour of the ash is used to estimate the fire severity (Pereira et al., 2014). Black ash corresponds to low to medium fire severity, whereas grey and white ash are the result of high severity fires (Goforth et al., 2005; Pereira et al., 2014). During a forest fire, complete combustion of fuel takes place at or near 500 °C leading to the formation of light grey or white ash which is composed mainly of alkaline earth oxides that over time react with atmospheric CO_2 and water vapour to form soluble hydroxides and carbonates (Ulery et al., 1993). White ash has a significantly higher Munsell hue value and chroma (Goforth et al., 2005). Black ash has a higher concentration of cations probably due to the oxidation of organic matter and incomplete combustion (Goforth et al., 2005; Liang et al., 2006). Goforth et al. (2005) found that variation in colour lightness of ash was correlated with variation in pH ($r = 0.89$), cation exchange capacity (CEC) ($r = 0.82$), total N ($r = 0.74$) and total organic C ($r = 0.72$). Both pH and CEC increased with lighter ash colour, whereas total N and organic C increased with darker ash colour (Goforth et al., 2005).

The thickness of an ash layer is controlled by amount of available fuel and the fire severity. Areas where high fire severity is observed usually present with a thin cover of ash (Pereira et al., 2013). Ash produced at low temperature is more hydrophobic than ash at high temperature (Bodi et al., 2011). A long term ash study in the Mediterranean has highlighted that ash is the key component that determine the post-fire hydrogeomorphological properties of fire-affected landscape (Doerr and Cerdà, 2005).

Major and trace metals such as Mn, Fe, Zn, Cu, Pb, Hg, Cd and As are routinely reported in ash (Khanna et al., 1994; Someshwar, 1996; Ferreira et al., 2005; Pereira and Ubeda, 2010; Campos et al., 2016; Olsson et al., 2017) with Mn returning the highest concentrations (in a number of cases) as it is mostly concentrated in leaves (Parra et al., 1996; Costa et al., 2014; Campos et al., 2016). For example, Costa et al. (2014) reported high concentrations of Mn in ash (121–448 mg kg^{-1}) after the Marao Mountain forest fire in Spain and Campos et al. (2016) reported high concentrations (57–598 mg kg^{-1}) after the Ermida fire in Portugal (Fig. 3). Al is also observed in high concentrations in some rare cases dependant on vegetation type. For example, after analysing the ash from the Lisbon (Portugal) fire (July 2007) in the area dominated by *Pinus pinaster* and *Quercus suber* trees, Pereira and Ubeda (2010) noted that Al^{3+} was the metal released in the highest quantities and Zn^{2+} was the lowest. Ash monitoring after the 2007 southern California forest fire showed significantly elevated levels of metals (As, Pb, Cu and Zn) that persisted at least a year following the fire (Plumlee et al., 2007).

The concentration of metals in ash varies and is dependent upon a number of factors such as type, density and age of the vegetation, plant parts burned (leaves, bark, litter, etc.), soil types, soil organic matter, pre-fire metal concentrations in the soil, meteorological conditions, maximum temperature reached, fire intensity and duration (Ulery and Graham, 1993; Someshwar, 1996; Pereira et al., 2009; Pereira and Ubeda, 2010; Machado et al., 2015).The variable amounts of metals and other contaminants that are present in ash introduce potentially toxic components into the hydrologic network when the ash is washed into the stream and other water resources in the post-fire environment (Nieminen et al., 2005; Ignatavicius et al., 2006; Pitman, 2006, Smith et al., 2011; Santin et al., 2015).

5. Post-fire metal mobilization into surface water resources

Forest fire is demonstrated to alter physical and biogeochemical properties of the soil and is able to liberate, mobilize and redeposit metals from soil organic matter and vegetation in air, land and water environments. This may potentially impact the health of the terrestrial and aquatic ecosystems (Certini, 2005, Burke et al., 2010, 2013; Smith et al., 2011; Burton et al., 2016; Odigie et al., 2016, Nunes et al., 2017). This is most prominent in forests with already elevated background metal concentrations and fire-suppressed mature forests where metals may have accumulated for extended period of time (Woodruff and Cannon, 2010). Strong and prolonged drought increases the frequency and scale of the forest fire with subsequent post-fire precipitation and runoff being able to transport large quantities of sediments with metal contaminants to downstream surface water systems, thus changing the water quality and making it unfit for human consumption. This dynamic may exist for a few months or even years after fire and have significant consequences (Gallahar and Koch, 2004; Goforth et al., 2005; White et al., 2006; Smith et al., 2011; Stein et al., 2012; Costa et al., 2014). For example, in the last two decades, fires have affected the water supply catchments of Denver and other south-western US cities, four major Australian cities such as Sydney (2001), Canberra (2003), Adelaide (2007) and Melbourne (2009) including various regional towns by way of contamination (Smith et al., 2011; Martin, 2016). In regional Australia, the eastern Victorian Alpine Fire during 2003 generated debris flow in the upper Buckland River which recorded maximum Fe, As, Cr and Pb concentrations of 2467, 40, 18 and 98 times the respective guideline values (Leak et al., 2003). Similarly, in south-eastern Australia, a single post-fire (within first year) summer storm event (>2 h; 43 mm, peak 15 min with intensity of 80 mm h^{-1}) accounted for 127 t of total suspended sediment yield from a small wet eucalyptus forest mountain catchment (Lane et al., 2008). Moody and Martin (2004) also observed large post-fire (within one year) sediment yield of 50 t ha^{-1}, in a catchment area in the western US.

Many studies report on the presence of metals in burnt forest soils and the capacity of storm events in carrying large sediment loads with metals into surface water resources (Ignatavicius et al., 2006; Rulli and Rosso, 2007; Pierson et al., 2008, Burke et al., 2010, 2013; Burton et al., 2016; Odigie et al., 2016). In 1977, Auclair examined Cu, Zn and Mn concentration in wetland plant tissues and in the soils of Carex medow, in the Qubec Province of Canada and reported that these metals are significantly mobilized by burning (Auclair, 1977).

The Cerro Grande Fire in New Mexico, USA occurred in May 2000, and was one of the major fire events in the last decade. It burned almost 17,200 ha of forest land (Bitner et al., 2001) and 239 residential structures (Wolfe et al., 2004). The post-fire runoff events were monitored and water samples were collected at 40 ephemeral stream sites. The water analysis results (for metals) were compared with 20 years of pre-fire values (Bitner et al., 2001) and concentrations of Fe (560 mg L^{-1}), Mn (102 mg L^{-1}) and Zn (3.6 mg L^{-1}) were elevated at 1870, 255 and 1.2 times the WHO guideline values respectively. Elevated concentrations of As, Ba, Cr, Hg and Pb were also reported (Bitner et al., 2001). Similar to this, the 2002 Hayman Fire in a mature forest (along the Colorado side of the Rocky Mountains, USA) resulted in a 2 to 2500 times increase in concentrations of As, Al, Cd, Fe, Pb and Hg, which affected the drinking water quality (Ranalli and Stevens, 2004). Comparable results were also recorded at the Rodeo-Chediski Fire in Arizona, USA (Gill, 2004).

One year after the Hayman Fire, a major fire occurred in 2003 in the Lost Creek area of Alberta, Canada, which burned around 21,000 ha of crown land forest (Sillins et al., 2009a). Seven watersheds were examined to determine the effects of forest fire, including stream flow and water quality. Results obtained from this study showed elevated mean concentrations of a number of metals in the burned catchment areas (Sillins et al., 2009b). Two subsequent years of monitoring also emphasized that total Hg concentrations exceeded both chronic and acute provincial water quality guidelines on a number of occasions. For example, an extremely high Hg pulse of 265 μg L^{-1} (0.001 μg L^{-1} = maximum acceptable concentration in drinking water) was measured after a moderate precipitation (20 mm) several days after the fire event (Sillins et al., 2009b).

In addition to the above, a number of post-fire observations were recorded in California, USA, between 2003 and 2009. The contaminant loading from these fire events found that the mean Cu, Pb and Zn concentrations in storm water were between 112 and 736-fold higher in burned catchments (Fig. 4) (Stein et al., 2012) and ash fallout also showed a three-fold increase in metal concentrations (Stein et al., 2012). Similarly, elevated concentrations of Fe, Mn and Al were found after the 2010 Fourmile Canyon fire Colorado, USA (Writer and Murphy, 2012).

Recently, Burton et al. (2016) conducted a similar study in California after the 2009 Station fire (USA). Authors collected ash, burned soil samples, pre-storm and storm water samples after the fire and analysed for metals. They reported that the total concentrations of As, Pb, Zn and Ni were higher in those samples collected in burned areas, which indicates that fire played a major role in mobilizing these metals (Fig. 5) (Burton et al., 2016).

The post-fire sediment load and metal delivery in the Arroyo Seco watershed in California, USA, after a fire in 2009 were studied by Burke et al. (2013). A significant increase (three orders of magnitude) was observed in most metal concentrations during the peak discharge time, compared to pre-fire values (Fig. 6). The highest concentrations of Pb and Zn occurred during the rising limb of the hydrograph, immediately following the peak precipitation. Cd peaked earlier than Pb, immediately following the first pulse in precipitation, while the highest concentration of Cu occurred on the hydrographs' falling limb (Burke et al., 2013). The maximum metal concentration occurred during the

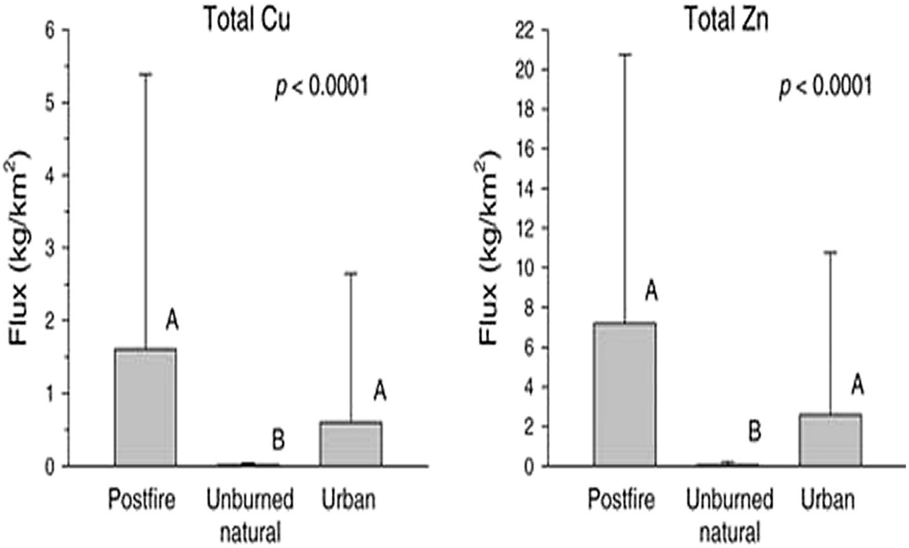

Fig. 4. Variation in concentration of Cu and Zn in pre- and post-fire storm water samples collected after the Southern California forest fire (in between 2003 and 2009). The bars represent the mean flux + standard deviation of individual storms. The letters indicate statistical similarities (Stein et al., 2012). Note the increase in concentration in the post-fire environment.

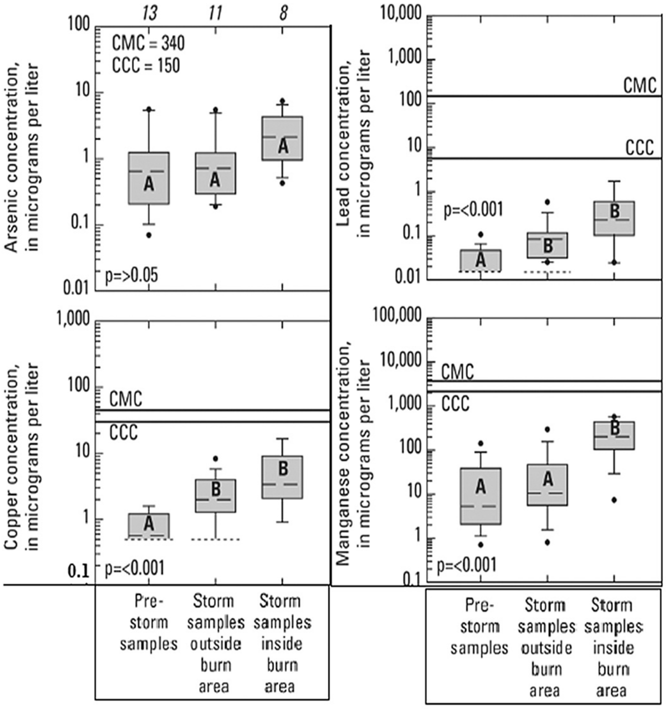

Fig. 5. Metal concentrations in water samples collected during and after the 2009 Station Fire California (CMC- Criteria Maximum concentration for aquatic species; CCC – Criteria Continuous Concentration for aquatic species) (Burton et al., 2016).

first rise in flow, well before the peak discharge and the authors suggest that this pattern should be taken into account in any post-fire storm water sampling program.

2003 is considered a disastrous year in the Earth's recent fire history, particularly in Australia. After a prolonged drought, extensive forest fire events occurred in the east of Victoria in Australia (2003), affecting 1.5 M·ha of land in the Eastern Victorian Alpines. An intense post-fire summer storm event in the catchment area of the Ovens River in North-Eastern Victoria (2003) resulted in an increase in concentrations of As, Cu, Pb, Cr, Fe and Zn that were 4, 32, 33, 40, 47, and >50 times respectively enriched when compared to the pre-fire concentration (North East Water, 2003). In the Upper Buckland River in north-eastern Victoria, a post-fire rainstorm event (38 mm for 2 h) delivered large amounts of sediments (59,000 mg L^{-1} suspended solids and 1,29,000 NTU) into a surface water system which supplies drinking water to Canberra. Analysis showed elevated concentrations of As (0.28 mg kg^{-1}, six times the guideline value (gv)), Fe (740 mg kg^{-1}, 2467 times the gv), Pb (0.98 mg kg^{-1}, 20 times the gv) and Cr (0.92 mg kg^{-1}, 18 times the gv) with all levels exceeding the WHO drinking water guidelines (Leak et al., 2003).

The fire also affected the Corin reservoir, located >500 km away from the core fire area. There, Wasson et al. (2003) estimated the individual post-fire event loads of Fe and Mn entering the Corin reservoir (197 km^2) which supplies water to Canberra and found that three post-fire storms within 2 months of the fire generated the following Fe/Mn loads (kg ha^{-1}): 0.007/0.002 (59 mm/1 day; 25.8 ML inflow), 0.04/0.001 (72 mm/2 days; 280 ML inflow), and 0.02/0.007 (rainfall data unavailable; 153 ML inflow). Similarly, post-fire monitoring of the Fe and Mn concentrations in the Bendora reservoir (supplying water to Canberra) on the Cotter River also demonstrated an increase in concentrations of Fe and Mn compared to all other previous studies by factors of three and five respectively (White et al., 2006). Similarly, Townsend and Douglas (2004) observed increased post-fire loads of annual Fe (1.2 kg ha^{-1}) and Mn (0.22 kg ha^{-1}) transport in a Savanna forest catchment in Kakadu National Park in Australia. The possible deleterious effects of the Eastern Alpine Fire (2003) on the quality of rainwater captured from roofs and stored in tanks for private supply were studied by Spinks et al. (2006). They found that concentrations of Cd (in two sample results; 0.0034 and 0.0067 mg L^{-1}), Fe (five sample results) and Zn (seven sample results) were above the Australian Drinking Water Guideline of 0.002, 0.03 and 3 mg L^{-1} respectively (ADWG, 2011) and there are indications that the forest fire smoke and ash may have contributed to these increases.

Linked to climate change and prolonged drought, a series of 497 fires (include land and peat bog fires) broke out in Lithuania between July and August 2002 (Sakalauskiene and Ignativicius, 2003). In August and September 2002 the concentration of metals in Lithuanian rivers increased by 21–80% compared to those averaged over the previous eight-year period (1993–2001). These increased metal concentrations in rivers (Fig. 7) are attributed to forest and peat bog fires in Jul–Aug 2002 and the subsequent mobilization of metals into water resources (Ignatavicius et al., 2006). Similarly, post-fire ash from the *Pinus densiflora* species found in the mountain regions of south Korea contained elevated Cd (0.089 to 0.946 mg kg^{-1}) concentration, which could be mobilized by wind and deposited in eastern coastal waters and subsequently affect the marine ecosystems (Shin et al., 2002).

The impact of wild fire on an ecosystems is sometimes so devastating that it can kill fish in the watershed. Recently Nunes et al. (2017) reported a study which highlighted the impacts of wild fire (the Talhadas fire in Portugal in 2013) which mobilized metals into the aquatic biota with Mosquitofish (*Gambusia holbrooki*) sued as the biomarker. The chemical analysis of water samples revealed concerning levels of metals in both runoff and stream water and were found to be harmful to organisms. Pro-oxidative modifications were the most recent toxic effects observed in the mosquitofish. Metabolic alterations related with toxicant conjugation with glutathione were also affected by the exposure to contaminated surface water and runoff, evidencing the defensive nature of triggered biological response (Nunes et al., 2017). Moreover, dead rainbow trout (*Oncorhynchus mykiss*) have been observed in the Big Tujunga Watershed in California during the 2009 Station fire (Burton et al., 2016).

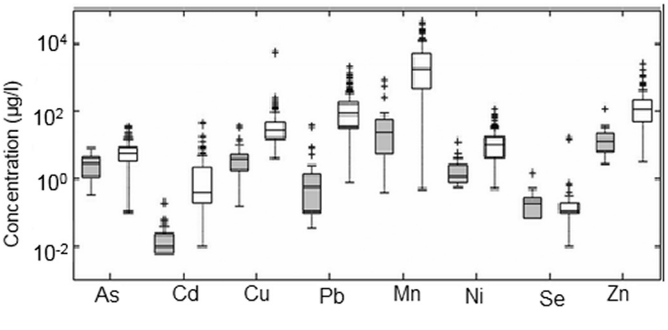

Fig. 6. Box plot show the concentrations of pre (grey fill) and post-fire (no fill) metals loads into Arroyo Seco forest catchment, USA, relative to the 2009 Station Fire (Burke et al., 2013). Note the increase in post-fire metal concentrations.

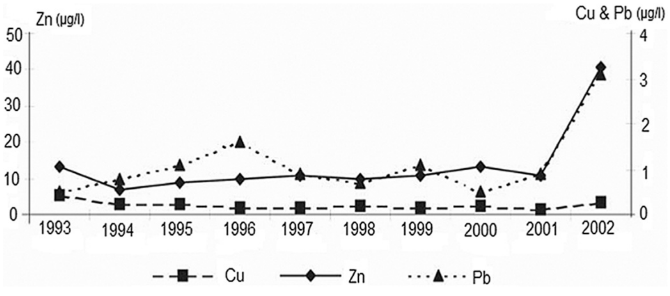

Fig. 7. Showing the increase in concentration of Pb, Zn and Cu in the Lithuanian rivers after a series of fires in Jul–Aug 2002 (Ignatavicius et al., 2006).

Information regarding the historical post-fire metal mobilization is essential to allow identification of the metal contamination of adjacent areas and to understand its impact on the aquatic ecosystem. Such studies were conducted in 2016 by Odigie et al. (2016) in Chile, South America. Temporal change in metals in lake sediments correlated with charcoal abundance was used to locate the post-fire mobilization of contaminants including metals of interest here. Results of the analysis of the age- dated sediments from Lake Thompson in Patagonia, Chile attest to the substantial pyrogenic remobilization of contaminants that occurred in Patagonia during the mid-1900s (Odigie et al., 2016).

Besides direct release onto soils, metals may also be released to the atmosphere during a forest fire. There have been concerns about the remobilization of previously deposited metals on the land and foliage to coastal and other aquatic ecosystems through areal fallout. The Angel's National Forest fire (Nov 1975) burned around 26,000 ha of forest land in the Los Angeles County Basin in the USA and created a dramatic smoke plume of roughly 100 km in width, which deposited a distinct layer of ash throughout the Basin. Distinct increases were measured in dry areal deposition rates of nine metals (Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) along the sections of the southern California coast in USA, which were affected by the forest fire smoke plume. These metals were possibly mobilized into the adjacent marine and other aquatic environments (Young and Jan 1977). Similarly, during the severe Southern California fire in the USA in 2003, the atmospheric deposition rates of Cu, Pb and Zn rose by factors of 4, 8 and 6 respectively compared with the unburned areas, which could reach soil and water resources by way of rain and subsequent runoff (Sabin et al., 2005).

5.1. Post-fire mercury mobilization

Among the post-fire metal mobilization Hg is of particular concern due to its volatility, toxicity and persistence in the environment (Huang et al., 2011). Forest fires have been recognised as a major source of mercury (re-)mobilization from soil, and living and dead vegetation (Artaxo et al., 2000; Friedli et al., 2001, Wiedinmyer and Friedli, 2007). Fire directly influenced the emission and deposition cycles by mobilizing it from soil and vegetation pools into the atmosphere (Biswas et al., 2007, Burke et al., 2010). The Hg release depends on number of factors including tree species composition (Biswas et al., 2007; Campos et al., 2016), moisture content in the fuel (Obrist et al., 2008), Hg concentrations in the soil and intensity of the fire (Engle et al., 2006). Ash and post-fire soil contains generally low amounts of total Hg compared with pre-fire soil Hg concentrations due to the volatilization of Hg (Biswas et al. 2007; Mergler et al., 2007; Campos et al., 2015). The released Hg from biomass burning is eventually deposited locally and globally, transported to the aquatic ecosystem by runoff and wind and when conditions are favourable it may contribute to the formation of neuro-toxic and immune-toxic methyl mercury (MeHg) specifically mono methy Hg (MMeHg) (Kelly et al., 2006; Friedli et al., 2009). This may bioaccumulate and biomagnify in the food chain resulting in global health concerns (Caldwell et al., 2000; Amirbahman et al., 2004; Mergler et al., 2007) since monomethyl Hg is the most toxic of the mercury compounds (Clarkson, 2002).

Many researchers (Caldwell et al., 2000; Amirbahman et al., 2004; Ravichandran, 2004; Kelly et al., 2006) found elevated Hg levels in downstream waters of burned watersheds, which it is thought have been transported by suspended sediments and organic matter (Ullrich et al., 2001; Ravichandran, 2004). Caldwell et al. (2000) measured large amounts of Hg mobilization in creek runoff in a freshly burned mixed coniferous forest, as well as noting a six-fold elevation in the concentration of total Hg and a 30-fold elevation in MeHg concentrations in the sediments of the receiving reservoirs. It is noted that this downstream sediment condition suits the formation MeHg. The elevated Hg concentrations in the downstream waters of the burned watershed were also shown to depend, among other things, on the fire severity, topography of the area, and distance to the surface water body (Caldwell et al., 2000; Amirbahman et al., 2004; Kelly et al., 2006). Areas of poorly drained soils and wetlands are favourable for the formation of MeHg (Grigal, 2003) due to the fluctuating temperature, water levels and the low dissolved oxygen content (Scheuhammer et al., 2007). Kelly et al. (2006) noted a large unexpected pulse of both total Hg and MeHg delivered to a reservoir system in the first post-fire storm event and found that the fish in the downstream reservoir exhibited elevated MeHg concentration that was attributable primarily to the food web restructuring. A study was conducted to examine the spatial and temporal variations of Hg concentrations in sediments of an arid-land reservoir in New Mexico, USA after a forest fire. The concentration of total Hg in the sediments increased from 7.5 ng g^{-1} to 46 ng g^{-1} and MeHg increased from 0.428 ng g^{-1} to 12.46 ng g^{-1} (Caldwell et al., 2000). The first rainfall after the fire caused an accentuated reduction of mercury levels in ash (30–60%) related to the washing out process. In such case the runoff produced after the rainfall may mobilize Hg into the adjacent terrestrial areas and in the water systems downstream and their study highlighted that forest fires and subsequent rainfall play a key role in the mobilization of Hg in the environment (Caldwell et al., 2000).

Litter fall and the dissolved fraction of organic matter are important factors in Hg transport in undisturbed watersheds (Bushey et al., 2008). This creates particular concern towards Hg mobility where conditions may be conducive for the formation of methyl mercury (MeHg) (Lin and Pehkonen, 1999; Caldwell et al., 2000; Amirbahman et al., 2004; Kelly et al., 2006). Therefore, it is important to determine the amount of Hg released during a fire event to assess the relative contribution of fires to the atmospheric Hg pool and to aid in the investigation of the potential for pulses of Hg to enter aquatic ecosystems following such fires. Increasing temperature in the tropical, temperate and boreal regions, where high Hg pools reside is expected to exacerbate Hg liberation and mobility because these regions are prone to frequent and large fires which is exacerbated by climate change and land-use pattern including afforestation with fire-prone species (Friedli et al., 2009; Campos et al., 2015; 2016).

A summary of the relevant studies linking post-fire mobilization of metals to water resources are provided in Table 2. All the post-fire metal mobilization studies clearly revealed that metals including As and Hg are mobilized after fire events and reach surface water systems primarily through runoff. Among the post-fire metals studied, Hg is the one which has received peak attention mainly because of its toxicity, persistence and health impacts to human and ecosystems and its ability to travel long distances through the air. The formation of MeHg in the wetlands and other surface water systems is also of concern as it is easy to mobilize into the human system through the food chain, where it is neuro-toxic and immune-toxic. Further studies are recommended in order to quantify the extent of mobilization of all the post-fire metals into wetlands and other surface water resources and to further understand their pathways of exposure towards aquatic ecosystem and humans through the food chain. Quantification is of particular significance in areas that are contaminated and hence are already defined as having elevated metal values.

6. Conclusion

Forests are vital elements of the water cycle, in that approximately 4 billion hectares of forest catchments (30% of the total land area) supply potable water resources to many major cities and communities around the world. Thus any kind of contamination, particularly metals have the potential to significantly affect the availability of high quality potable water supplies should those metals become mobilized.

Fire is a common phenomenon in forest catchments, and it can play a significant role in the release of metals usually sequestered in soil organic matter and vegetation. It can thus facilitate their movement into range of environmental contexts and measurably increasing their mobility and bioavailability. In addition, fire events increase soil erosion rate by as much as two to 100-fold, which allows rapid transport of

Table 2
Summary of relevant studies linking forest fire to the remobilisation of selected metals including As.

Authors	Study area/year fire occurred	Fire types/Scale affected (ha)	Metals involved/assessed	Results/remarks
Young and Jan (1977)	Angels National Forest Fire (22–28 November 1975) Southern California, USA	26,000 One of the largest fires in the decade	Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn	Distinct increases were observed in dry aerial deposition rates of nine metals along the sections of the southern Californian coast covered by a forest fire smoke plume
Bitner et al. (2001)	Cerro Grande Fire (2000) New Mexico, USA	17,200	Mn, Cu and Zn	The metal concentrations in the run-off water have been observed to increase after fire (compared with 20 years of pre-fire data)
Wolfe et al. (2004)	Cerro Grande Fire, (May 2003) Los Alamos, New Mexico, USA	19,283 Controlled burn became a wild fire	As, Cd, Hg, Ni and Pb in urine samples of fire fighters	As and Cd levels were significantly elevated among National Guard members which was related to smoke exposure Ce and As levels were elevated in fire fighters
Ignatavicius et al. (2006)	Lithuania, (Jul/Aug, 2002)	497 forest and peat bog fires	Cu, Pb and Zn	In August and September 2002, the concentration of metals in river waters increased by 21–80% compared with those averaged over the previous eight-year period (1993–2001). Forest fires and peat bogs increased metal amounts in the aquatic environment. Metals were released into the atmosphere through volatilzation and were trapped in smoke particles or distributed as fly ash after combustion
Spinks et al. (2006)	East Gippsland Fire, 2003 Victoria, Australia	1.5 million	As, Cd, Cr, Cu, Fe, Pb and Zn	Some Cd, Zn and Fe concentrations in the rainwater storage tanks were above the Australian Drinking Water Guidelines
Biswas et al. (2007)	(i).Boulder Creek Fire, (Aug, 2000) (ii).Green Knoll Fire, (Jul/Aug, 2000) (iii).East Table Fire, (Jul, 2003) Western Wyoming, USA	1400	Hg	Hg (22.3–81%) was released during the fires, and greater fire severity was associated with the greater percentage of soil Hg being released. It also depends on the tree species composition of the forest, which affects pre-fire Hg accumulation
Biswas et al. (2008)	Rex Creek Fire, (Aug, 2001) Central Washington forest, USA	20,234	Hg	Hg seems to be re-volatilized during fire. Loss of 6.7 g Hg ha^{-1} from the soil has been observed
Witt et al. (2009)	Northern Minnesota, USA		Hg – Total Hg and methyl Hg	Observed increase in both species of Hg. Canopy type of trees influenced the magnitude of Hg mobilization
Burke et al. (2010)	(i) Topanga Fire (2005) (ii) Pine Fire (2006) (iii) Day Fire (2006) California, USA	(i) 9800 (ii) 100 (iii) 66,000	Hg	Loss of Hg in the freshly burned soil was observed. Four-fold increase in surface Hg concentrations were observed in the Day Fire area. Following the initial volatilization of Hg during fire, the burned soil experienced an accelerated accumulation of Hg in the post-fire environment
Pereira and Ubeda (2010)	Lisbon, Portugal, Spain, (Jul, 2007)	Medium size wild fire – study in a small plot of burned area 27 × 9 m size	Al, Mn, Fe, and Zn	The ash contain high amount of metals and the metal release depends on species distribution and burning severity. Over time the increase in pH, make the metals more mobile and will released into soil solution.
Stein et al. (2012)	(i) Old Fire, (Oct, 2003) (ii) Simi Vallet Fire, (Oct, 2003) (iii) Day Fire, (Apr, 2006) (iv) Santiago Fire, (Oct, 2007) (v) Station Fire, (Aug, 2009) Urban fringe area, Southern California, USA	(i) 36,940 (ii) 43,790 (iii) 65,840 (iv) 11,490 (v) 64,980	Cu, Pb, Ni and Zn	Mean flux of Cu, Pb, Ni and Zn from burned sites were increased 110, 740, 82 and 110-folds respectively, compared to the respective flux in the unburned (control) site. Contaminant loading from the burned landscapes has the potential to make substantial contribution to the total annual load to downstream areas in several years following the fire
Burke et al. (2013)	Station Fire (2009) Angel's National Forest, Los Angeles, USA	6,66,000	As, Cu, Hg, Al, Fe, Ni, Zn, Cd, Mn and Pb	One (As, Cu), two (Al, Fe, Ni, Zn) and three (Cd, Mn, Pb) orders of magnitude increase were observed in fluxes between largest pre- and post-fire storm events
Burton et al. (2016)	Station Fire (2009) Angel's National Forest, Los Angeles, USA	6,66,000	As, Cu, Fe, Hg, Mn, Ni, Pb and Zn	Filtered concentrations of Fe, Mn and Hg and total concentrations of As, Cu, Hg, Ni, Pb and Zn were elevated as a result of the Station Fire.
Odigie et al. (2016)	Central South-Chile Fire records (20th century)	NA	As, Co, Cu, Mn, Ni, Pb and Zn	Temporal change in the amount of metals (As, Co, Cu, Mn, Ni, Pb and Zn) and their correlation with temporal change in charcoal abundance in age-dated sediments were collected from Lake Thomson, in Patagonia Chile. They attest to the substantial pyrogenic remobilization of contaminants that occurred in Patagonia during mid-1900s.

fire-released metals to downstream land and water resources carried by runoff and wind and which may consequently impact on water resource qualities. Water resources and watersheds contaminated with metals have the potential to pose a significant risk to downstream communities and ecosystems due to the effects of these metals on human and ecosystem health.

Climate change and associated processes include increased frequency of dry and warming weather events, while concomitant human impacts include land-use change (land abandonment, afforestation with fire- prone species) have recently exacerbated forest fire frequency and their extent in many forest catchments. The expansion of fire affected landscapes and the increase severity of events posing a threat to the sustainability of the landscapes and ecosystems. It is reported that fire and flood events will be more frequent and severe under the predicted climate change conditions, which may significantly increase the mobile metal concentration in the environment. Such an increase in metal concentration and its resulting mobility will impact on water resources and affect the potable water quality. Therefore, greater focus on metal concentration and mobility after fire together with their effects on human and ecosystem health should be reviewed to allow water authorities to predict and mitigate risk. These assessments should be based on the observed fire intensity, areal extent and frequency, the background metal concentrations, possible impacts on catchment hydrological processes, distance to the potable water source, intensity and frequency of post-fire rainfall events, and likely wind activity. This will facilitate the identification of communities with water supplies that might be most vulnerable following fire. Moreover, catchment management authorities and organisations responsible for catchment and water management should take some immediate and reasonable actions to reduce the negative impacts of fire such as: (i) construction and management of fuel breaks around the water catchment areas, (ii) regular conduct of controlled burning in fire-prone areas to reduce the chance and severity of wild fires, and (iii) avoiding the use of fire retardants near waterways and riparian zones in case of fire. These actions will reduce the ingress of contaminants include metals into water reservoirs to minimum level.

Conflict of interest

The authors declare that they have no conflict of interest.

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Chapter- 4

Assessment of potentially toxic metal contamination in the soils of a legacy mine site in Central Victoria, Australia

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Assessment of potentially toxic metal contamination in the soils of a legacy mine site in Central Victoria, Australia

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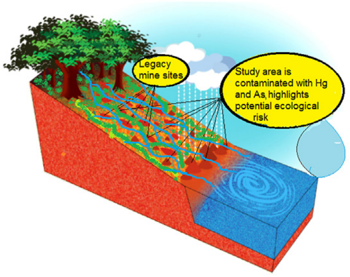
HIGHLIGHTS

- Legacy mining operated under limited or no environmental regulations.
- Legacy mining has resulted in tonnes of unrehabilitated mine wastes rich in metals.
- Mine waste has contaminated the surrounding environment, specifically with Hg & As.
- Metal mobility affects downstream water resources.
- Study area reflects a global portrait of more than a million legacy mine sites.

GRAPHICAL ABSTRACT



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ABSTRACT

The environmental impact of toxic metal contamination from legacy mining activities, many of which had operated and were closed prior to the enforcement of robust environmental legislation, is of growing concern to modern society. We have carried out analysis of As and potentially toxic metals (Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn) in the surface soil of a legacy gold mining site in Maldon, Victoria, Australia, to reveal the status of the current metal concentration. The results revealed the median concentrations of metals from highest to lowest, in the order: Mn > Zn > As > Cr > Cu > Pb > Ni > Co > Hg > Cd. The status of site was assessed directly by comparing the metal concentrations in the study area with known Australian and Victorian average top soil levels and the health investigation levels set by the National Environmental Protection Measures (NEPM) and the Department of Environment and Conservation (DEC) of the State of Western Australia. Although, median concentrations of As, Hg, Pb, Cu and Zn exceeded the average Australian and Victorian top soil concentrations, only As and Hg exceeded the ecological investigation levels (EIL) set by DEC and thus these metals are considered as risk to the human and aquatic ecosystems health due to their increase in concentration and toxicity. In an environment of climate fluctuation with increased storm events and forest fires may mobilize these toxic metals contaminants, pose a real threat to the environment and the community.

1. Introduction

Rapid industrialization and economic development inevitably bring with it land, water and air disturbance, which may include significant and toxic contamination with metals from

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anthropogenic activities, notably from mining and metal processing (Miller et al., 2004; Schaider et al., 2007; Qingjie et al., 2008; Florentine et al., 2016). In particular, the unrehabilitated by-products of mining activities include refinement tailings, discarded low grade ores in overburden materials, dump heap leachates, and residues of mill waste water and acid mine water, all of which may act as a persistent toxic metal source long after mining ceases (Schaider et al., 2007; Navarro et al., 2008; Esshaimi et al., 2012; Cobbina et al., 2013; Park et al., 2014). These sources have the potential to contaminate surrounding areas through the waterborne transport of dissolved and fine particulate metals, and together with windborne dispersal of dry fine particles (Adriano, 2001; Jung, 2001; Schaider et al., 2007; Doronila et al., 2014). These contaminant effects may extend to distal areas (Navarro et al., 2008; Esshaimi et al., 2012) with contamination is found to decrease with distance from the source (Roberts and Johnson, 1978; Park et al., 2014).

Mining related metal contamination is particularly pronounced in legacy mining areas, since no environmental regulations existed during the period of active mining nor at the stage of mine closure (Park et al., 2014). Central Victoria, in Australia has a long history of gold mining, which started in the 1850s with more than 2500 t of gold extracted and processed (McDonald and Powel, 2008; EER, 2015). At mine closing, many tonnes of mine waste materials rich in fine grained potential toxic metals (such as Cd, Cr, Cu, Hg, Pb, Zn and As) thus remained in the surface soil and present a constant source of contamination of soil, water, air and plants (Sultan, 2006, 2007; Pearce et al., 2010, 2012; Martin et al., 2013, 2014, 2017a, 2017b).

The potential toxic metal contamination from legacy mining sites across the globe has received increased attention in recent times (Zhou et al., 2010; Esshaimi et al., 2012; Zornoza et al., 2012). For example, closure of more than 1000 mines in a mineralised zone in Morocco resulted in the contamination of soil, water, plants and sediments with toxic metals and metalloids such as As, Cd, Cu, Pb and Zn released to the environment (Esshaimi et al., 2012). Similarly, Lee et al. (2005) reported soil and water contamination in the vicinity of the Songcheon Au-Ag mine in South Korea with significant consequent impacts and Soltani et al. (2017) reported soil contamination at GoI-E-Gohar iron ore site in Iran. Similar types of problems were reported from the Bolivian Andes (Pavilonis et al., 2017), the Almaden mining district in Spain (Garcia-Ordiales et al., 2017), the Iberian Pyrite Belt in Portuguese (Ferreira da Silva et al., 2015), the Daduk Au-Ag-Pb-Zn mine area in Korea (Lee et al., 2001), Pb-Zn mining area in the NE Province of China (Zhou et al., 2010), the El-Avenue stream in Spain (Zornoza et al., 2012), and the Bole-Bamboi district of Ghana (Cobbina et al., 2013). Australia is not immune from this problem as similar kinds of issues were reported from the Drake mining area in New South Wales (Clark et al., 2001), Central Queensland (Duivenvoorden et al., 2017), the Boddington gold deposit in western Australia (Lintern and Anand, 2017), Boolaro, Port Kembla, Cowra and the Sydney Basin (Kanchenko and Sing, 2006) and from Central Victoria (Sultan, 2006, 2007; Pearce et al., 2010, 2012; Martin et al., 2014, 2017a, b). Moreover, a higher incidence of cancer was observed in the Central Victorian region of Australia, which was thought to be related to As exposure from legacy mining activities, illustrating that increased metal concentrations may have significant human health consequences (Pearce et al., 2010, 2012).

Similar problems have now been recognised in wider context and society is becoming much more aware of contamination as serious environmental issue and are cognizant of the fact that these potentially toxic metals and metalloids in the soil can affect community health and impact on ecosystems and their significant persistency can create a long-term problem (Fergusson, 1990; Smith et al., 1998; Hinwood et al., 2003; Murray et al., 2004; Smolders et al., 2009; Zhou et al., 2010; Hu et al., 2016; Oorts et al., 2016; Zeng et al., 2017). For example, As is linked with several deleterious health effects in humans such as skin lesion, cardiovascular disease, renal and respiratory disorders, hearing loss, developmental abnormalities and a range of cancers (Chen et al., 1996; IARC, 2004; Centeno et al., 2007; Celik et al., 2008; ATSDR, 2011). Excessive intake of Pb, Cd, Cu and Hg are also reported to cause negative impacts on human health such as low intelligent quotient, kidney damage, skeletal deformities, gastrointestinal effects, brain and nerve system effects by entering the food chain or by the inhalation of dust from contaminated surface soils (Tristan et al., 2000; Smedley and Kinniburg, 2002; Craw et al., 2003; Young, 2005; Mazumdar, 2008; ADWG, 2011; ATSDR, 2011; Cobbina et al., 2011, 2013; Del-Razo et al., 2011; NTP, 2012; Zhang et al., 2012). Concern has focussed particularly on children as their immature body systems and different behaviour patterns put them at increased risk (Rieuwerts et al., 2000). Elevated metal levels also have inhibitory effects on plant growth, enzymatic activity, stromata functions, photosynthesis, accumulation of nutrients and other minerals and also damage to root systems has been observed (Johansson, 1998; Oorts et al., 2016). As a consequence of these issues, regulatory authorities have established risk based soil and water screening levels and guideline values for potentially toxic metals (CEC, 1986; USEPA, 1996; WHO, 1996; ANZECC, 2000; DEC, 2010; ATSDR, 2011; NEPM, 2013), a knowledge of which is essential in the advised management of human and ecosystem health and agriculture, and for long-term land-use planning.

Soil screening values are presented as generic quality standards that can be used to regulate soil contamination and to make informed risk assessment (Carlon et al., 2007). The Australian Federal Government and several Australian States have established appropriate soil screening values for various purposes such as health investigation levels (HILs) and ecological investigation levels (EILs). The focus of such health monitoring activities are residential properties with garden soil access and limited soil access, public lands, schools and parks and commercial and industrial areas (DEC, 2010; NEPM, 2011). For the purpose of this current investigation, the relevant median soil metal concentrations levels in this study were compared with the quoted average Australian and Victorian top soil metal concentrations data (Caritat and de Cooper, 2011a, 2011b, 2016), the health investigation levels set by the National Environmental Protection Measures (NEPM, 2013), and the Department of Environment and Conservation of the State of Western Australia (DEC, 2010).

Although many studies have been published on metal contamination from active and legacy mining areas (Clark et al., 2001; Lee et al., 2001; Lee et al., 2005; Zhou et al., 2010; Esshaimi et al., 2012; Zornoza et al., 2012; Cobbina et al., 2013; Pearce et al., 2012) we assert that site-specific investigations are required. This is absolutely important because each site is unique in respect of their metal concentrations, mixtures and characteristics, which can also vary with time and context, thus a broader set of specific case histories are essential to enable more efficient land-use planning. The current study, and an appreciation of the associated health risks are important as the study area (legacy mine site) is adjacent not only to residential areas, but also to a state forest, which acts as a catchment area for potable water resources. Surface water runoff, wind activity and the possibility of wild fire or even the controlled burns can remobilize the metal concentrations from the study site, which increases the level of health concern (Melendez-Perez et al., 2014; Abraham et al., 2017a, b). In this scenario, the overall objectives of the study were to: (i) determine the spatial distribution of As and nine related metals (Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn) (herein after referred as metals) in the surface soils of a legacy gold mining site close to the township of Maldon, in Central Victoria, Australia. All of these metals were chosen for investigation because they are potentially toxic to the human health and deleterious to ecosystems (ii) evaluate the contamination status of soils in this area when compared with the Australian and Victorian top soil averages (Caritat and de Cooper, 2011a, 2011b, 2016), the health investigation levels set by NEPM (2011) and DEC (2010) in Western Australia, and (iii) assess the ecological risk of these metal levels by comparing the analytical results with advised ecological investigation levels (EIL) published by DEC (2010). Although the study area is relatively small, we suggest that it is indicative of the large landscapes with extensive evidence of soil disturbance, mining and related waste disposal. The implications of human and ecosystem contamination and risk from such unrehabilitated legacy mine sites are extremely large as more than a million legacy mine sites exist across the globe (UNEP, 2001). The potential for these sites to affect the environment and humans for many generations is of particular concern and thus the addressing of rehabilitation of these sites, even long after mine closure, is seen as a priority.

2. Materials and methods

2.1. Characteristics of the study area

Maldon, a legacy mining township is located 140 km NW of the city of Melbourne and 40 km SW of the City of Greater Bendigo in the state of Victoria, Australia. Mining operations in Maldon produced more than 56 t of gold from more than 20 reefs during the historical mining period (Mason and Webb, 1953; Cherry and Wilkinson, 1994). The legacy mining activities include both the driving of adits and shafts together with an open cut mining to access the sulphide bearing ore, which has resulted in the accumulation of mine waste materials of many kinds on the surface. Throughout the Maldon township, relics of mining can be seen and these include adits, shafts, mullock heaps (heap of mine waste materials) and crushed rock fragments with majority of quartz particles. An eight hectare historical mining site located east of the Union Hill mine and west and south of the Stump Street was selected for the current study (Fig. 1). The site is a public land accessible to all and also falls in the State forest, even though, close to residential areas. The study area experience cold wet winters (7.5–20.5 °C) and warm dry summers (16.4–40.3 °C) (Taylor et al., 2000; BoM, 2017) and the annual average rainfall is 540 mm (BoM, 2017).

The location is clearly within the town boundaries and is openly accessible to the public. A creek line that runs in an easterly direction, passes along the middle of the study area. The northern half of the study area slopes slightly towards south and the southern half slopes slightly towards the north, consequently directing all rainfall runoff to the creek. This public land has disturbed overburden with burrows, soil heaps and scattered quartz fragments, which are multiple relics of the legacy gold mining activities. The presence of moderate to highly disturbed surface soils from goldrush mining activities that occurred more than a century ago makes the study area unique for evaluating legacy gold mining impacts on the environment. Although the site is relatively compact, it evidences many of the characteristics of large legacy landscapes, showing extensive surface soil disturbance, remnant mining structural features, and areas used for uncontrolled disposal of waste materials.

2.2. Soil sampling and analysis

Surface soil samples are the focus of this study as they are the most relevant sites for allowing windborne contaminant transport, human exposure to metal and metalloid concentrations, and direct contact with precipitation and surface water runoff (Schaider et al., 2007). To examine the metal concentrations in the surface soils, a total of 18 soil samples (<3 cm depth) were collected using the STAR sampling method with established trace metal clean technique procedures (Ritson et al., 1999; Taylor et al., 2000). After removing the vegetation debris and large rock particles by hand, approximately 1 kg of bulk surface soil samples were collected from an area of 900 cm^2 (30 × 30 cm) from each of the 18 sampling

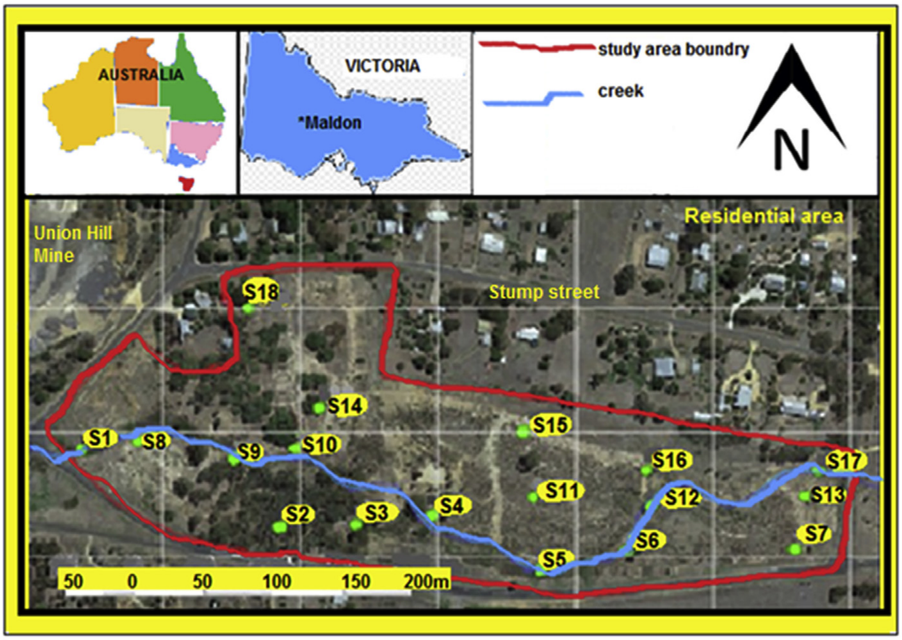

Fig. 1. Showing the Maldon study area, Victoria, Australia (area inside redline) with soil sampling stations and proximity to housing indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

stations. Soil samples were placed in labelled polyethylene containers and transported to the Federation University Australia soil laboratory. In the laboratory, soil samples were placed in aluminium containers and oven dried (at 60 °C) for 24 h. The oven dried samples were hand crushed (after removing residual rock pieces) and were passed through 2 mm wire mesh sieve, and < 2 mm particles were placed in a tightly sealed labelled polyethylene containers for analysis. Significant physicochemical characteristics of soil such as pH (US-EPA 9045D) and EC (US-EPA 9050A) were determined using standard analytical procedures and soil organic matter (SOM) and carbonate content (both as percentages) were determined using the gravimetric/ loss on ignition (LoI) method (Rayment and Lyons, 2014).

Metal concentrations were determined by Ultra-Trace Level Methods using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) with Aqua Regia Digestion method (Gunten et al., 2017; Santoro et al., 2017). The aqua regia method involve con HNO3 and HCl (1:3 proportion) performed in 250 mL of glass beaker covered with a watch glass. Oven dried and < 2 mm sieved sample were milled, and 0.5 g was used for metal analysis, after removing the organic matter. A well-mixed sample of 0.5 g was digested in 12 mL of aqua regia on a hot plate for 3 h at 110 ° C. After evaporation and at near dryness, the sample was diluted with 20 mL of 2% HNO3 and transferred into a 100 mL volumetric flask after filtering through a Whatman no. 42 paper. This has diluted to 100 mL with DDW (deuterium depleted water) and allowed to cool. The resulting solution was diluted with deionized water, mixed and analysed by ICP-AES (Chen and Ma, 2001; Santoro et al., 2017). Following this analysis, the results were reviewed for high concentration of Hg and diluted accordingly. Samples are then analysed by ICP-MS for the remaining suite of elements and the results are corrected for inter-element spectral interference.

2.3. Australian background values

Because contaminated soils can pose a threat to human and ecosystems health through direct exposure such as dermal contact, ingestion and inhalation of soil particles, or through indirect exposure such as inhalation of airborne contaminated dust, making contamination assessment is an unavoidable and essential task (DEC, 2010). The purpose of such site assessment activity is to reveal the human health and ecological risks inherent in the area associated with the suspected presence of site contamination, and thus to inform any remediation or management plan to ensure the site is subsequently fit for the current or proposed land use (NEPM, 2011). In such works, the assessment levels and distribution of soil contamination, which also includes the status of the contaminants carried out are put in comparison with background metal values. Therefore, a vital step in commenting on the metal contamination in an area, is the establishment of a reference value or background metal value in the soils of an area (Qingjie et al., 2008; Ghaleno et al., 2015; Soliman et al., 2015). In this respect, two methods are widely accepted. The first is the use of average crustal values known as the local base line, by analysing comparable local soil, which has been unaffected by anthropogenic activity (Zhou et al., 2010; Esshaimi et al., 2012). In the Maldon study area, it is a challenging task to find uncontaminated soil, as the area has number of legacy mine sites and tonnes of mine waste materials (Sultan, 2006), and because the mine waste materials are more than a century old, the mining wastes may have spread to more pristine areas by way of runoff and wind activities. Therefore, the second method, which is comparison with Victorian background and threshold soil values has been used, and this includes information contained in Australian legislations such as the National Environmental Protection Measures (NEPM) and the Department of Environment and Conservation of State of Western Australia (DEC) were incorporated (DEC, 2010; NEPM, 2013). The average metal concentrations in Australian soils, are given in Table 1 in comparison with average crustal values.

2.4. Australian guidelines

The National Environmental Protection Measures (NEPM) are national guidelines, which provide a frame work for the use in investigation and screening of levels of soil and groundwater contamination in Australia, based on the matrix of human and ecosystems health (NEPM, 2011, 2013). According to NEPM, investigation levels and screening levels are the concentrations of a contaminant above which further appropriate investigation and evaluation will be required, and these provide a basis for Tier 1 risk assessment. Among the number of investigation levels mentioned in the NEPM report, health investigations levels (HILs) of major and trace metals, including As have been selected for this study to compare the soil analysis data (NEPM, 2011).

In a similar manner to the NEPM, the Department of Environment and Conservation (DEC) of the State of Western Australia, also lists generic assessment levels to provide guidance to determine whether a site is potentially contaminated and to decide whether further investigation is required. The HILs adopted by DEC are primarily based on the health based soil investigation levels presented in NEPM (DEC, 2010) and these HILs assess the human health risk of a broad range of metals and organic substances through all relevant pathways of exposure. In addition to these HILs, ecological investigation levels (EILs) also have been established by DEC for a broad range of metals and organic substances, and are conveniently applicable for assessing risk to terrestrial ecosystems.

For comparison purpose, the health investigation levels (HILs) of NEPM and DEC and ecological investigation levels (EILs) of DEC for selected metals are depicted in Table 2. In both cases, the HILs are conventionally derived and are designed to protect human health under a number of soil contaminant circumstances including normal human susceptibilities. They are derived in relation to four generic land-use categories as follows:

- HIL A, Standard residential property, with garden and accessible soil (home grown produce <10% fruit and vegetable) intake (but no poultry). This category includes children's day care centres, preschools and primary schools;
- HIL B/D, Residential property with minimal opportunities for soil access. This includes dwellings with fully and permanently paved yard space such as high-rise buildings and flats;
- HIL C/E, Includes developed open space such as parks, playgrounds, playing fields sports ovals, secondary schools and footpaths. It does not include undeveloped public open space which should be subject to a site-specific assessment where appropriate.
- HIL D/F, Commercial/ industrial properties including premises such as shops, offices, factories and industrial sites (NEPM, 2013).

The ecological investigation levels (EIL) for soils mentioned in the assessment levels of DEC are sourced from NEPM based on the environmental investigation levels listed in the Australian and New Zealand Guidelines for the assessment and management of contaminated site (ANZECC/NHMRC, 1992), from Moen et al. (1986) and also from the Bayside clean-up criteria provided by Environmental Protection Authority Victoria (EPA-VIC, 1990) (DEC, 2010).

Table 1
Average metal concentrations (mg kg^{-1}) in the top soils of the State of Victoria and across Australia, compared with upper continental crust of Australia and world.

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Victorian soil average (mg kg^{-1})	5	0.1	10	42	19	0.03	409	20	13	45
Australian soil average (mg kg^{-1})	3	0.07	9	42	17	0.03	390	17	11	38
Australian continental crust (mg kg^{-1})	1.6	0.04		24	12	0.01		12	7.4	26
Upper continental crust -World (mg kg^{-1})	5.7	0.06		73	27	0.05		34	10	75

Source: Caritat and de Cooper (2011a, 2011b, 2016).

Table 2
Comparison of health investigation levels (HILs) of NEPM and DEC include ecological investigation levels (EILs) of DEC for selected metals (DEC, 2010; NEPM, 2013) (all the values are in mg kg^{-1}).

Metals	NEPM Res-A	DEC Res-A	NEPM Res-B	DEC Res-D	NEPM-C Recrnl	DEC–E Recrnl	NEPM-D Indust	DEC–F Indust	EILs
As	100	100	500	400	300	200	3000	500	20
Cd	20	20	150	80	90	40	900	100	3
Co	100	100	600	400	300	200	4000	500	50
Cr(III)		120000		480000		240000		600000	400
Cr(VI)	100	100	500	400	300	200	3600	500	1
Cu	6000	1000	30000	4000	17000	2000	240000	5000	100
Hg	40	15	120	60	80	30	730	75	1
MeHg	10	10	30	40	13	20	180	50	
Mn	3800	1500	14000	6000	19000	3000	60000	7500	500
Ni	400	600	1200	2400	1200	600	6000	3000	60
Pb	300	300	1200	1200	600	600	1500	1500	600
Zn	7400	7000	60000	28000	30000	14000	400000	35000	200

(Note: Res-A: Residential A – standard residential with garden accessible soil, which include children's day care centres, pre-schools and primary schools; Res-B/D: Residential B/D– Residential with minimum opportunities for soil access including dwellings with fully or permanently paved yard space such as high rise apartment and flats; C/E Recrnl: Recreational– open places such as parks, play grounds, public lands, schools and foot paths; D/F Indust: Industrial and commercial places include shops, offices, factories etc.).

2.5. *Statistical analysis*

IBM SPSS (version 23) software was used for the statistical data analysis. Descriptive analysis such as minimum, maximum, median, percentiles and interquartile range (IQR), which reflects the discrete distribution of various metal concentrations, were determined. Spearman rank correlation was also applied to determine the relationship between the physicochemical properties of the soil and the metal concentrations in the soil. Surfer (version 12) software was used to draw the spatial distribution map of metals.

3. Results and discussion

Metals in the soils of legacy mine sites generally have complex relationships, and it is known that numerous factors control their relative abundance. This includes, but is not limited to, metal concentration in the parent rocks, extent of weathering and soil formation, anthropogenic activities include intensity and types of mining, duration of the mining, types of metal processing and distance to the processing site, topography of the area, and climate (Wei and Yang, 2010; Krishna et al., 2013). This variation is obviously visible in the study area and the spatial distribution maps helps to identify metal hotspots (Fan and Wang, 2017; Sucharova et al., 2012). The spatial distribution of Hg and As, are depicted in Fig. 2 and the other metals are provided as supplementary materials (Fig. S1). The maps highlighted the fact that As and Hg are concentrated mostly at the west and north-west part of the study area, which is thought to be due to the presence of a normal surface soil formed from mine waste materials. A peak in values of As and Hg are also found on the southern side of the site (adjacent to the creek).

The study area consists of soil heaps, mining depressions, creek and disturbed surface soils. The metal concentrations in the normal surface soil samples, samples collected in creek and close to the creek, mining depressions and soil heap were compared to understand the distribution. Most of the metals shown their highest concentrations in the creek and close to the creek and in mining depressions, and lowest in the normal soil surface and in soil heap, which include Cr, Cu and Mn. Some metals shown highest concentrations only in creek and lowest in surface soils and soil heap such as As, Cd, Co and Pb. Hg shown highest levels in surface soils, but lowest concentration found in depressions and soil heap, whereas highest concentrations of Zn found in depressions and low to moderate concentrations were found in surface soils and in creeks. Ni shows an average concentrations in creek, in surface soils and in depressions, but lowest concentrations found in soil heap.

The metal concentrations from the study area were plotted as box plot in comparison with Victorian soil average (Fig. 3). Among the 10 metals analysed Mn displayed the highest median concentration (190 mg kg^{-1}), followed by Zn (94 mg kg^{-1}) and As (85 mg kg^{-1}) and the lowest concentration was observed for Cd (0.11 mg kg^{-1}). The order of concentration from highest to lowest levels are: Mn > Zn > As > Cr > Pb > Cu > Ni > Co > Hg > Cd has observed in the study area. When considering the extreme minima, Cd showed the lowest concentration (0.03 mgkg^{-1}), whereas Mn showed the highest (85 mg kg^{-1}). Similarly, Cd showed the lowest maximum of 0.37 mg kg^{-1} and Mn showed the highest maximum of 560 mg kg^{-1}. The Spearman rank correlation of metals with soil physicochemical characteristics are depicted as Table 3.

3.1. *Metal comparison with background and guideline values*

In the study area, the median Mn concentration (190 mg kg^{-1}) being lower than the Victorian and Australian top soil averages (409 and 390 mg kg^{-1} respectively) and well below the HILs and only one station value exceeded EIL of 500 mg kg^{-1}. Mn concentration showed significant very strong correlation with As, significant strong correlation with Cd, Co, Zn, Pb and Ni and moderate correlation with Cu, Hg and Cr, which is similar to the previous findings (Li et al., 2003; Sultan, 2007). It is suspected that Mn oxides may have strong specific adsorption characteristics for various other metals such as Cd, Co, Zn and Pb and thus serve as a concentrating

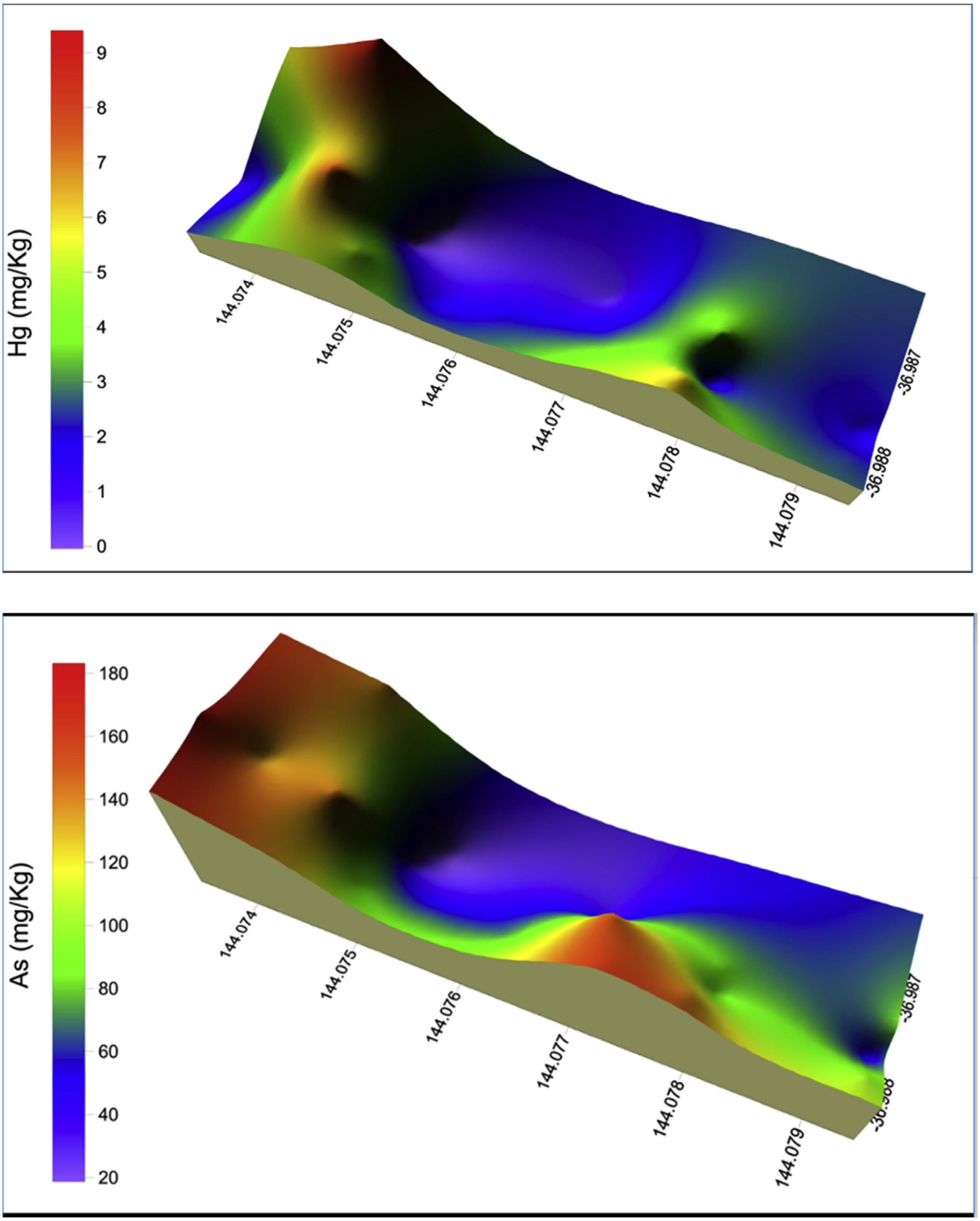

Fig. 2. Spatial distribution map of Hg and As in soils.

sink (McKenzie, 1980).

Zn is generally found to be the most commonly occurring and mobile metal in the rock, soil, water and plants (Kiikkila, 2003), and it has been observed that its mobility and availability depends on low pH conditions, the presence of P, Ca, Al, Mn and Fe oxides, and the amount of organic matter in the soil (Kiikkila, 2003; Kumpiene et al., 2008). The median Zn concentration in the study area is 94 mg kg^{-1}, which exceeded (by a factor of two) the Australian and Victorian top soil averages (38 and 45 mg kg^{-1}), indicating the disruptive presence of mining activities. However, all sampling station levels are below the HILs and except three stations (S1, S9 and S11), all are below EILs. The elevated levels are observed in the samples collected close to the creek indicating the metal mobility through rainfall runoff and considered to be from sphalerite (ZnS), which is normally associated with gold deposits in the region (Sultan, 2007). Zn showed highly significant correlation with Cd and Ni, and significant strong correlation with, As, Co, Cu, Cr, Mn and Pb, and moderate correlation with Hg.

The median As concentration (85 mg kg^{-1}) in the study area is 28 times higher than the Australian top soil average (3 mg kg^{-1})

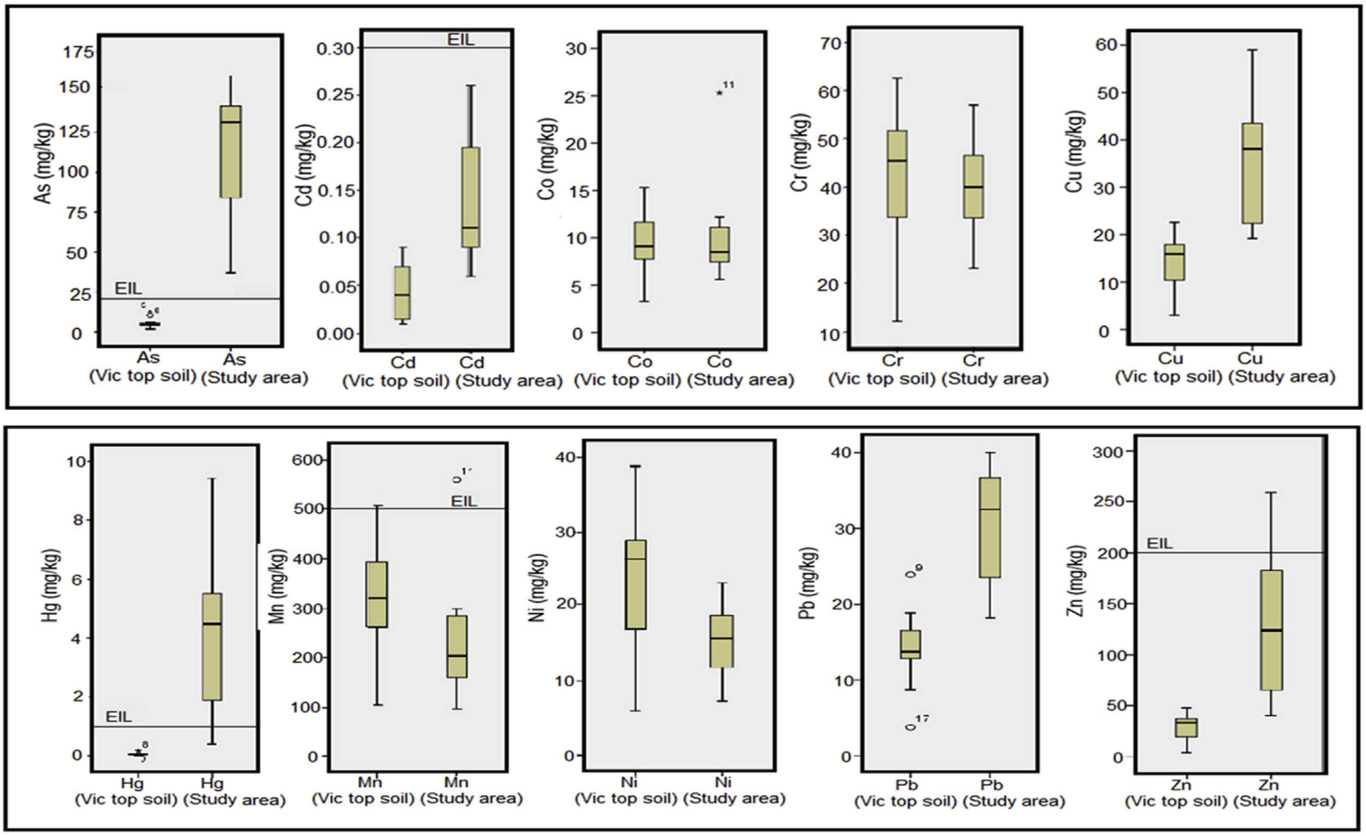

Fig. 3. As and selected metal concentrations (mg kg^{-1}) in the study area compared with Victorian top soil average and Ecological Investigation Levels (EIL) (NB: EIL depicted in As, Cd, Hg, Mn and Zn only, other metals it is above the maximum scale).

Table 3
Spearman rank correlation matrix for the physicochemical soil properties and metal concentration in the soil.

	pH	EC	SOM	Carb	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
pH	1	−0.48	0.42	0.04	0.32	0.37	**0.61****	**0.54***	0.38	−0.02	0.35	**0.62****	−0.04	0.46
EC		1	0.28	0.37	−0.23	−0.10	−0.03	−0.02	0.14	−0.08	0.04	−0.08	−0.03	−0.21
SOM			1	0.37	0.10	**0.53***	0.38	0.44	**0.51***	−0.03	0.36	**0.50***	0.28	0.49
Carb				1	0.33	0.43	0.46	**0.57***	0.48	0.13	0.45	**0.50***	0.48	0.40
As					1	**0.74****	**0.65****	0.48	**0.60****	**0.63****	**0.80****	**0.53***	**0.77****	**0.76****
Cd						1	**0.70****	**0.66****	**0.72****	0.46	**0.73****	**0.75****	**0.75****	**0.98****
Co							1	**0.86****	**0.76****	0.25	**0.73****	**0.94****	0.3	**0.76****
Cr								1	**0.77****	0.04	0.47	**0.95****	0.32	**0.72****
Cu									1	0.37	**0.57***	**0.79****	0.46	**0.74****
Hg										1	0.49	0.12	**0.51***	0.43
Mn											1	**0.61****	**0.62****	**0.71****
Ni												1	0.32	**0.81****
Pb													1	**0.67****
Zn														1

NB: (1) * - correlation is significant at the 0.05 level (2 tailed); (2) ** - significant at the 0.01 level (2 tailed).

and 17 times higher than the Victorian top soil average of (5 mg kg^{-1}). In the study area, eight stations (S1, S5, S6, S7, S8, S9, S11 and S18) exceeded the HILs of NEPM and DEC for Residential area with garden accessible soils (100 mg kg^{-1}), but all values are below other HILs, including the industrial and commercial categories (DEC, 2010; NEPM, 2013). All sampling stations showed that the As values exceeded the ecological investigation level of 20 mg kg^{-1} (except S14), indicating the possible risk to the terrestrial and aquatic ecosystems. Much of Central Victoria, including the Maldon study area, host mineralised zones within the Ordovician shales, and are accompanied by arsenopyrite (FeAsS) and other As bearing sulphides such as iron pyrites (FeS_2), pyrrhotite (FeS), chalcopyrite (CuFeS2), sphalerite (ZnS) and galena (PbS) (Taylor et al., 2000; Smith et al., 2002; Sultan 2006, 2007). As concentrations displayed very strong significant correlation with Mn, strong significant correlation with Pb, Zn, Cd, Co, Hg, and Cu, and moderate correlation with Ni and Cr. Studies have shown that the spatial As distribution is linked to sulphide location and redistribution in processing and transportation of ores during the mining activities (Sultan, 2007).

The Australian and the Victorian average background concentration of Cr in the top soil is 42 mg kg^{-1}. Even though the median Cr concentration (38 mg kg^{-1}) is below state and national average, seven sampling stations (S1, S3, S4, S5, S8, S9, and S11) exceeded it.

All Cr values are well below the HILs of NEPM, DEC and EIL (DEC, 2010; NEPM, 2013) indicating no contamination status. Cr displayed very strong significant correlation with Ni and Co, significantly strong correlation with Cu, Zn and Cd, and moderate correlation with As and Mn.

The median Pb concentration in the study area (30 mg kg^{-1}), include all sampling station Pb levels (except S10), exceeded the Australian and Victorian top soils averages (11 and 13 mg kg^{-1} respectively). All the sampling station values are well below all kinds of HILs and EIL. The majority of high Pb concentrations samples (above 30 mg kg^{-1}) were collected close to the creek indicating its mobility towards the aquatic ecosystem, most probably associated with rainfall runoff. Pb displayed significantly strong correlations with As, Cd, Zn and Mn, and moderate correlation with Cu and Hg. It is suspected that the Pb might have been derived from galena (PbS), which is commonly associated with gold mineralization (Philips and Hughes, 1996).

All sampling stations Cu values include median (30 mg kg^{-1}) is found to exceed the Australian (except S13) and Victorian (except S13 and S14) top soil averages (17 and 19 mg kg^{-1}) (Caritat and de Cooper, 2011a, 2011b), and all Cu concentrations are well below all HILs and EIL. Higher concentrations of Cu content in the soil samples may be due to the presence of Cu sulphides such as chalcopyrite ($CuFeS_2$) associated with gold deposits in Central Victoria (Canavan and Bull, 1988). Increase in ash, carbonate, clays and phosphates in the soil reduce the mobility of Cu and the mobility is strongly pH dependent, where it increases with decreasing pH (Vander de slot et al., 1997; Kabata-Pendias, 2004, 2010). Cu showed significant strong correlation with Ni, Cr, Co, Zn, Cd and As, and moderate correlation with Pb.

In the study area, the median Ni concentration (13 mg kg^{-1}) is found to below the Australian and Victorian top soil averages of 17 and 20 mg kg^{-1} (Caritat and de Cooper, 2011a, 2011b). The Ni levels in seven sampling stations (S1, S2, S4, S5, S8, S9 and S11) exceeded the Australian top soil average and just two stations (S1 and S11) exceeded the Victorian top soil value. All results are far below all the health investigation levels of NEPM and DEC and EIL. Therefore, Ni is not considered as a contaminant in the study area. The highest concentrations (23 mg kg^{-1}) occurred in the sample collected close to the creek bank (S1), and thus demonstrated the mobility towards the aquatic system. Ni showed very strong significant correlation with Cr, Co and Zn, strong significant correlation with Cu, Cd and Mn and moderate correlation with As.

Among the 18 sampling stations, six stations (S1, S2, S5, S8, S9 and S11) Co levels are above the Australian background topsoil level (9 mg kg^{-1}) and five station (S1, S5, S8, S9 and S11) levels are above the Victorian top soil average of 10 mg kg^{-1}, but median (8 mg kg^{-1}) is below both averages (Caritat and de Cooper, 2011a, 2011b). That none of the sampling stations exceeded the HILs and EIL indicates that Co is a non-contaminant in the study area. Co had mentioned highly significant correlation with Ni and Cr, and significant strong correlation with Cu, Zn, Mn, Cd and As.

Hg is a very toxic metal, even in very low concentrations, and the background Hg concentration in the Australian and Victorian top soils is reported as 0.03 mg kg^{-1} (Diomides, 2005; Caritat and de Cooper, 2011a, 2011b). In the study area, Hg concentration ranged from 0.1 to 9 mg kg^{-1} (median, 2 mg kg^{-1}) and all sample values exceeded the Australian and Victorian top soil averages. When comparing with various types of health investigation levels contained within NEPM and DEC, the observed concentrations are well below limits, but in 14 stations, the Hg levels are above the EIL creating worrying health concerns (DEC, 2010). Hg concentrations have shown a significant strong correlation only with As, but moderate correlation with Pb, Mn, Zn and Cd. The lack of Hg correlation with other metals indicates the origin of Hg is not associated with other metals, indicating strongly that the origin is associated with gold processing.

Cd is a rare, but widely dispersed metal, which occurs in the environment in association with Zn, Pb and Cu ores (Birke et al., 2016). Cd is found to have lowest concentrations in the soils of the study area, which ranged from 0.03 to 0.37 mg kg^{-1} with median of 0.1 mg kg^{-1}. The Cd concentrations at 14 stations, include median are above the Australian background concentrations (0.07 mg kg^{-1}), and 11 stations are above Victorian top soil average (0.1 mg kg^{-1}). All Cd concentrations are well below all kinds of HILs and EIL. Therefore, Cd is not considered as contaminant in the study area. Cd shown highly significant strong correlation with Zn and significantly strong correlation with Ni, Pb, As, Mn, Cu, Co and Cr, and moderate correlation with Hg.

Presence of contaminants in each sampling stations and the corresponding guidelines are presented in Table 4. Based on this assessment, it is found that Hg and As are considered as more frequent potential contaminants in the study area.

3.2. Physicochemical properties

Besides the metal concentrations in the surface soil, the physicochemical properties such as soil pH, electrical conductivity (EC), soil organic matter (SOM) and carbonate content (both as percentages) were reported (Fig. 4), and their correlation analysis (Spearman rank correlation) were included in Table 3.

All the soil samples have an acidic pH ranging from 3.6 to 5.6 with an average of 4.5, most probably associated with the weathering of sulphide minerals such as pyrite (FeS_2), arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and galena (PbS_2). It was found that pH has significant strong correlation only with Ni ($r = 0.62$, $p < 0.01$), and Co ($r = 0.61$, $p < 0.01$), and moderate correlation only with Cr ($r = 0.54$, $p < 0.05$) and Zn ($r = 0.46$). The EC values ranges from 95 to 970 μS cm^{-1} with an average of 435 μS cm^{-1}, which is considered to be low, and thus in the Australian context is not considered environmentally problematic. EC does not have significant correlation with any of the analysed metals. The soil organic matter (SOM) content ranges from 4% to 42% with an average of 12% and carbonate content ranges from 0.78% to 2.44% (average of 1.5%). The SOM does not show significant strong or very strong correlation with any of the metals, but has a moderate correlation with Cd ($r = 0.53$, $p < 0.05$), Cu ($r = 0.51$, $p < 0.05$) and Ni ($r = 0.50$, $p < 0.05$). Similarly, carbonate also not have any significant strong and very strong correlation with any of the metals except a moderate correlation with Cr ($r = 0.57$, $p < 0.05$) and Ni ($r = 0.50$, $p < 0.05$). However metals themselves show strong and very strong correlations (Table 3)

4. Conclusions

The objective of the study was to identify the concentrations of As and nine selected metals (Cd, Co, Cr, Cu, Mn, Hg, Ni, Pb and Zn) in the soils of a legacy mine site in Maldon, Victoria, Australia. The investigation of metal concentrations in the soil was carried out by analysing the soil samples using ICP-AES and ICP-MS. In the area, concentrations of As (185 mg kg^{-1}), Cd (0.4 mg kg^{-1}), Co (25 mg kg^{-1}), Cr (57 mg kg^{-1}), Cu (59 mg kg^{-1}), Hg (9 mg kg^{-1}), Mn (560 mg kg^{-1}), Ni (23 mg kg^{-1}), Pb (76 mg kg^{-1}) and Zn (328 mg kg^{-1}) were observed, among them Hg and As are considered as elevated. The soil analysis results were compared with Australian and Victorian top soil averages, together with health investigation levels set by NEPM and DEC and also with EIL limits. The results of the investigation demonstrated contamination by As and Hg only and these higher concentrations were consistent with an origin associated with gold mining and processing. The

Table 4
Presence of contaminant metals in each sampling station above associated guidelines (ecological investigation levels (EIL) and health investigation levels (HIL)).

Contamination based on	S1	S2	S3	S4	S5	S6	S7	S8	S9
EILs	As, Zn	As, Hg	As, Hg	As, Hg	As, Hg	As, Hg	As, Hg	As, Hg	As, Hg, Zn
HILs	As				As	As	As	As	As
Contamination based on	**S10**	**S11**	**S12**	**S13**	**S14**	**S15**	**S16**	**S17**	**S18**
EILs	As	As, Hg, Mn, Zn	As, Hg	As, Hg		As	As, Hg	As, Hg	As, Hg
HILs		As							As

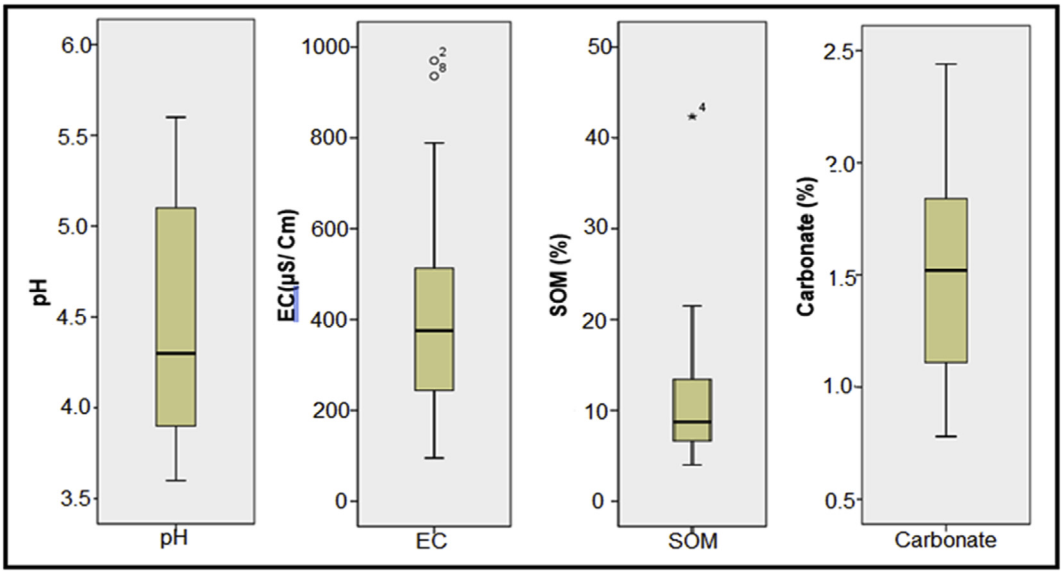

Fig. 4. Box plot showing pH, electrical conductivity (EC), soil organic matter (SOM) and carbonate contents of the surface soil in the Maldon study area, Central Victoria, Australia.

elevated concentrations of Hg and As in the soils of the Maldon study area imply their extremely elevated contaminant levels and significantly high ecological risk, which is of create particular concern due to the potential impacts of these metals on human and ecosystems health. The study area is openly accessible to all and is adjacent to a residential area and the rainfall runoff and wind activity can carry contaminants to the downstream water resources. This is highly significant as the forest catchment provides potable water resources to surrounding communities. Moreover, climate fluctuation and the subsequent increase in rainfall and forest fire, including controlled use of fire for vegetation and forest fire management may mobilize metals into the aquatic ecosystems which service to heightens the significance of these findings.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2017.10.150.

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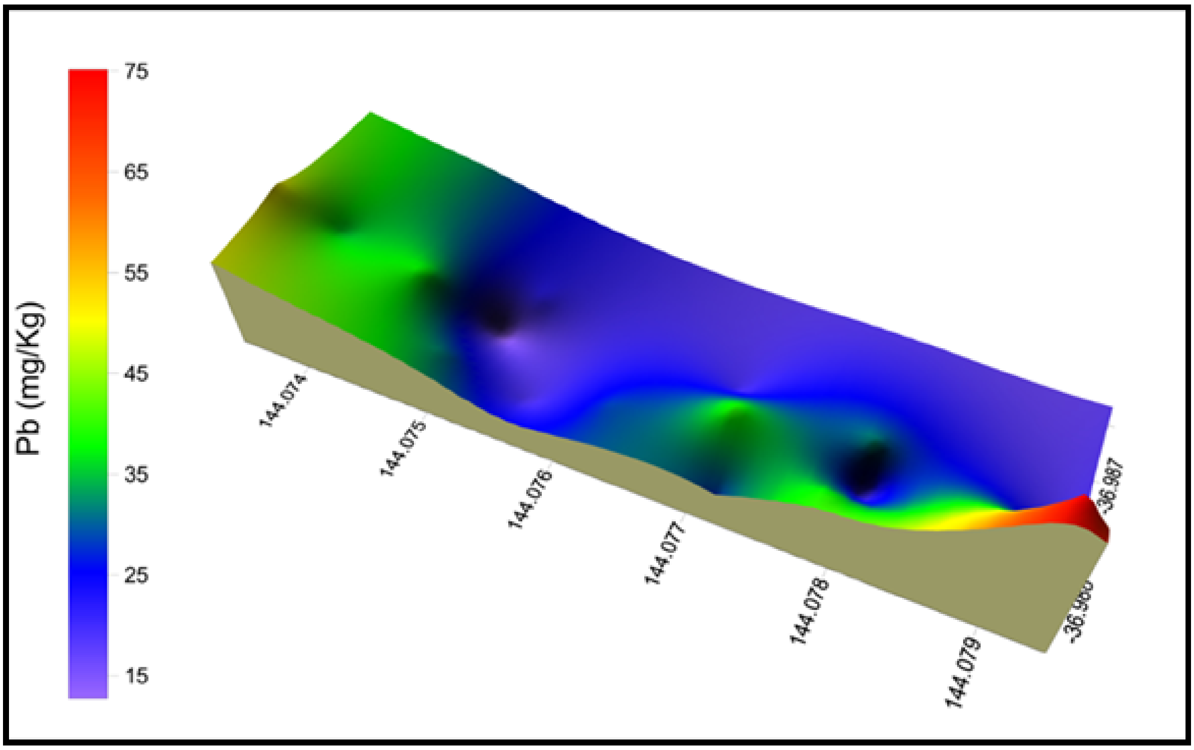
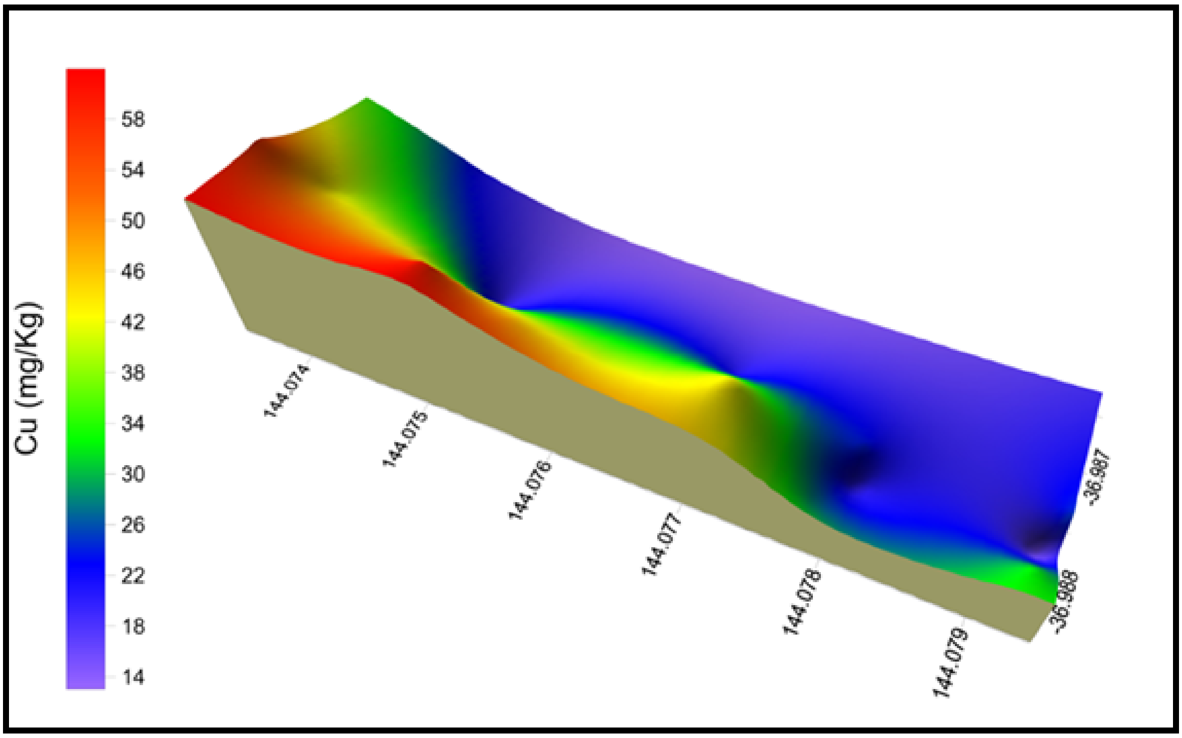

Pb (mg/Kg)
75
65
55
45
35
25
15
144.074
144.075
144.076
144.077
144.078
144.079
-36.987
-36.988


Cu (mg/Kg)
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54
50
46
42
38
34
30
26
22
18
14
144.074
144.075
144.076
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144.078
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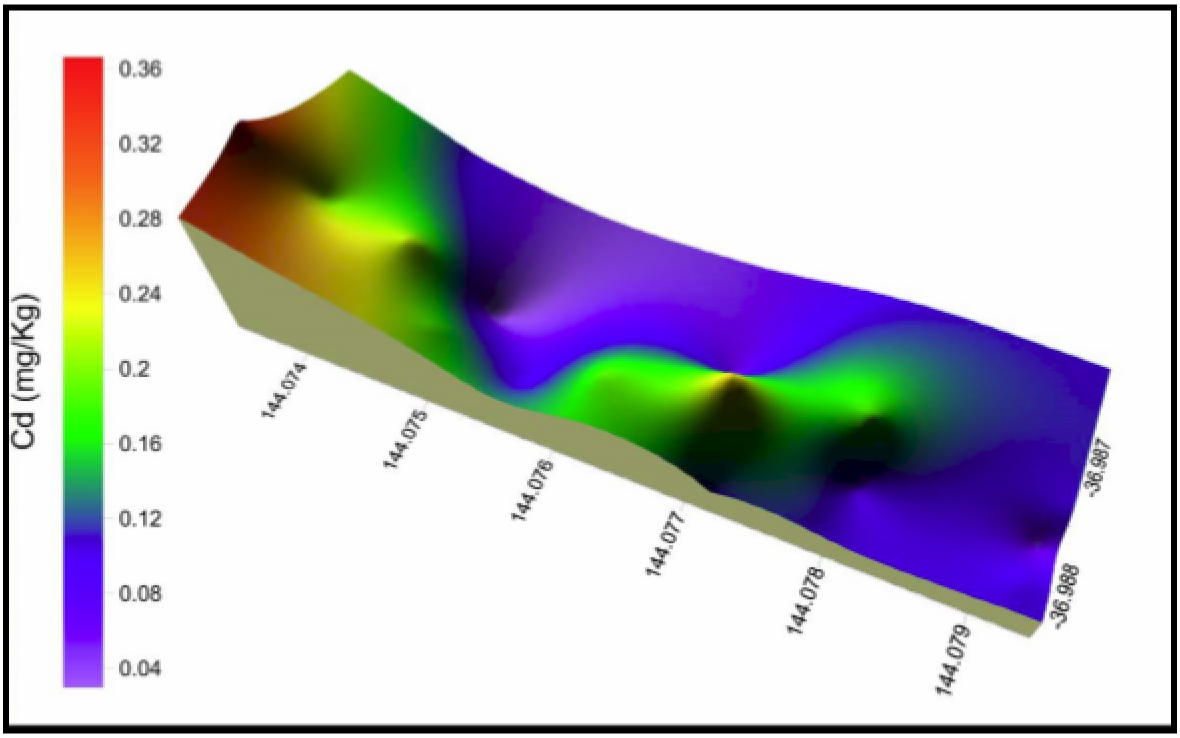
-36.988


Cd (mg/Kg)
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0.24
0.2
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0.12
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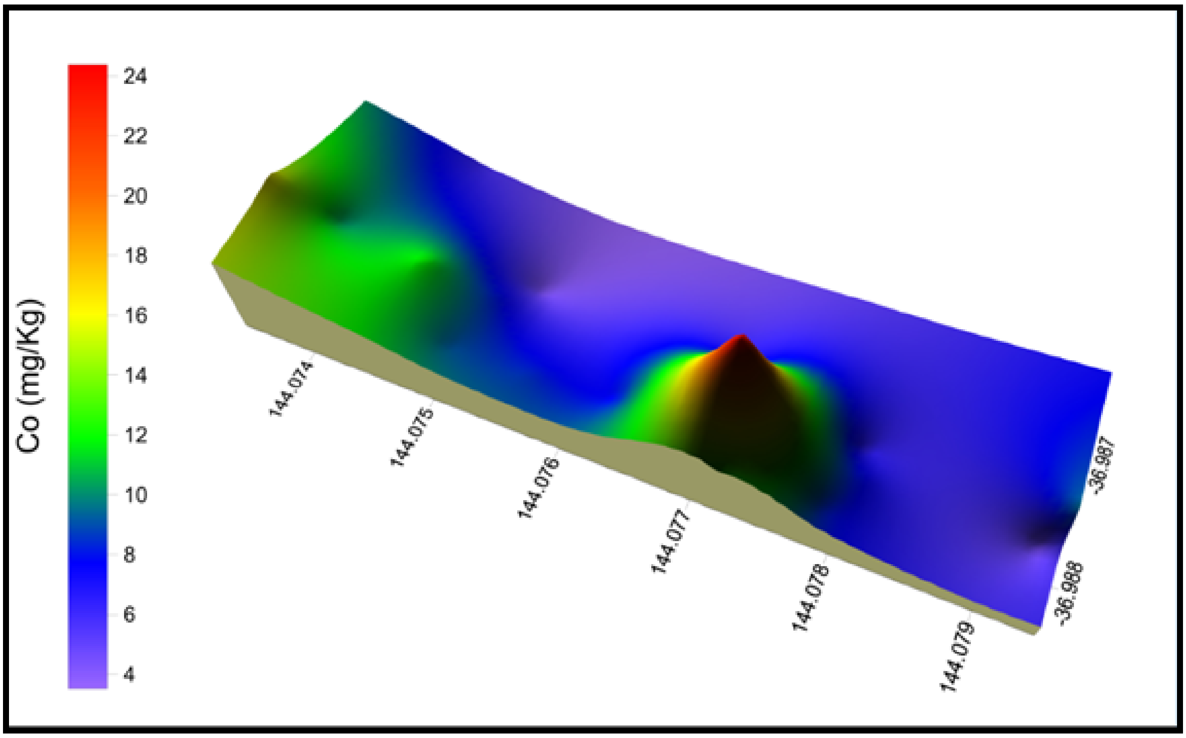
Co (mg/Kg)
24
22
20
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14
12
10
8
6
4
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144.075
144.076
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144.079
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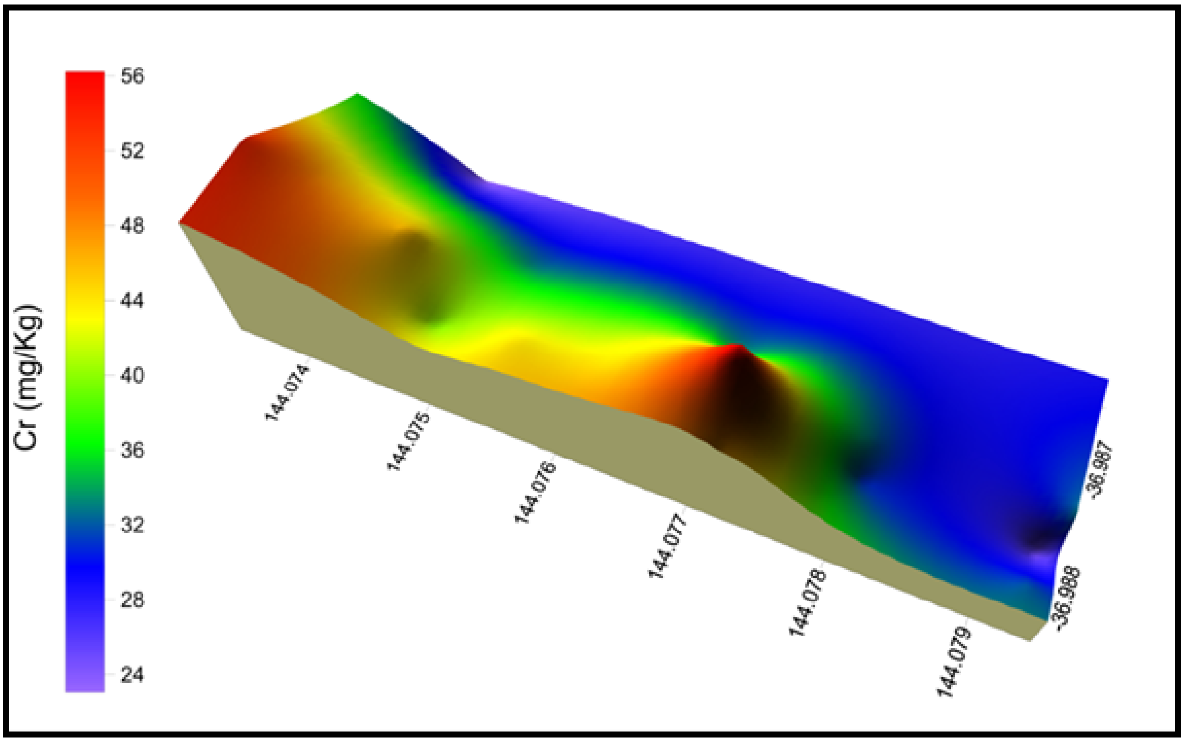
Cr (mg/Kg)
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52
48
44
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36
32
28
24
144.074
144.075
144.076
144.077
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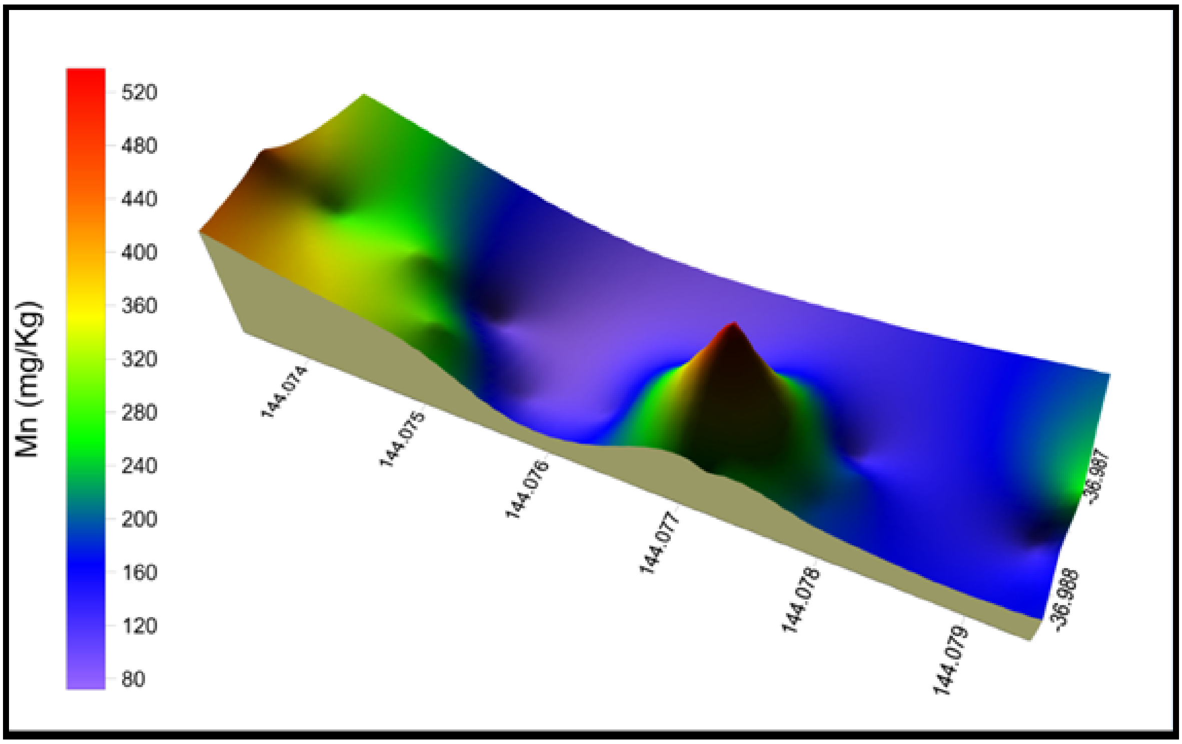
144.079
-36.987
-36.988


Mn (mg/Kg)
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440
400
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280
240
200
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120
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144.074
144.075
144.076
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144.078
144.079
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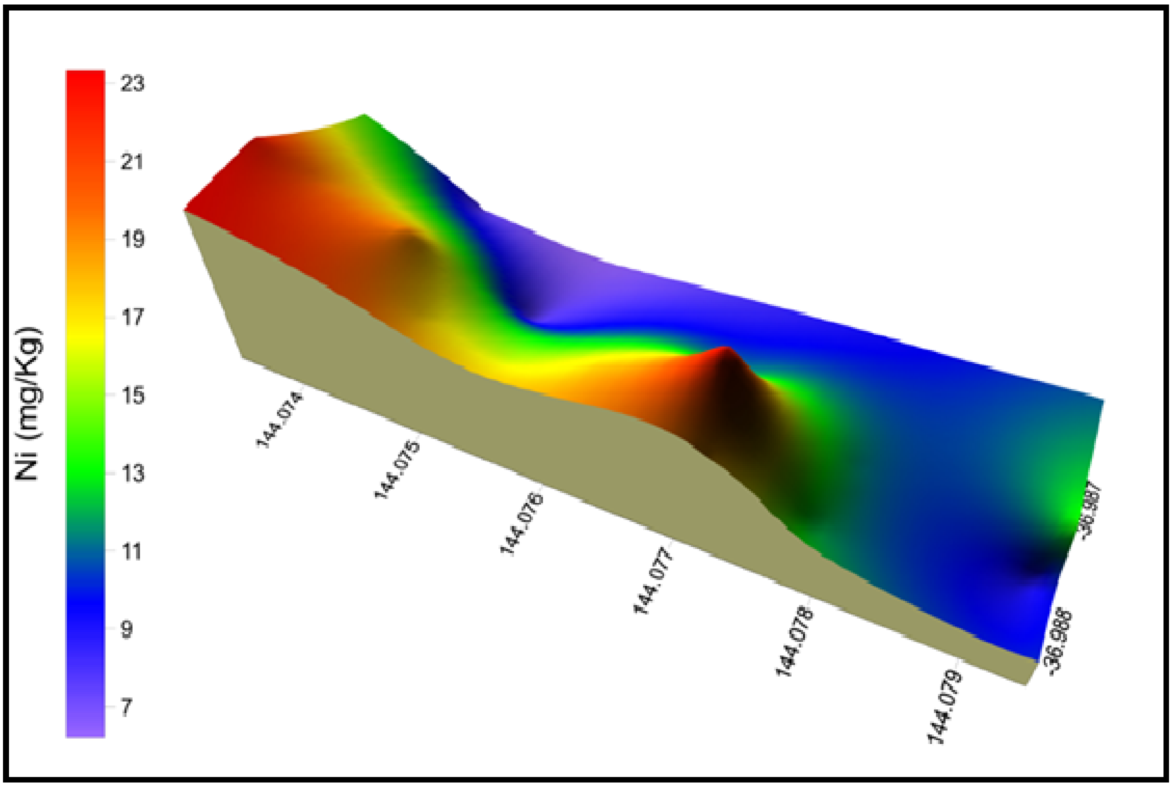

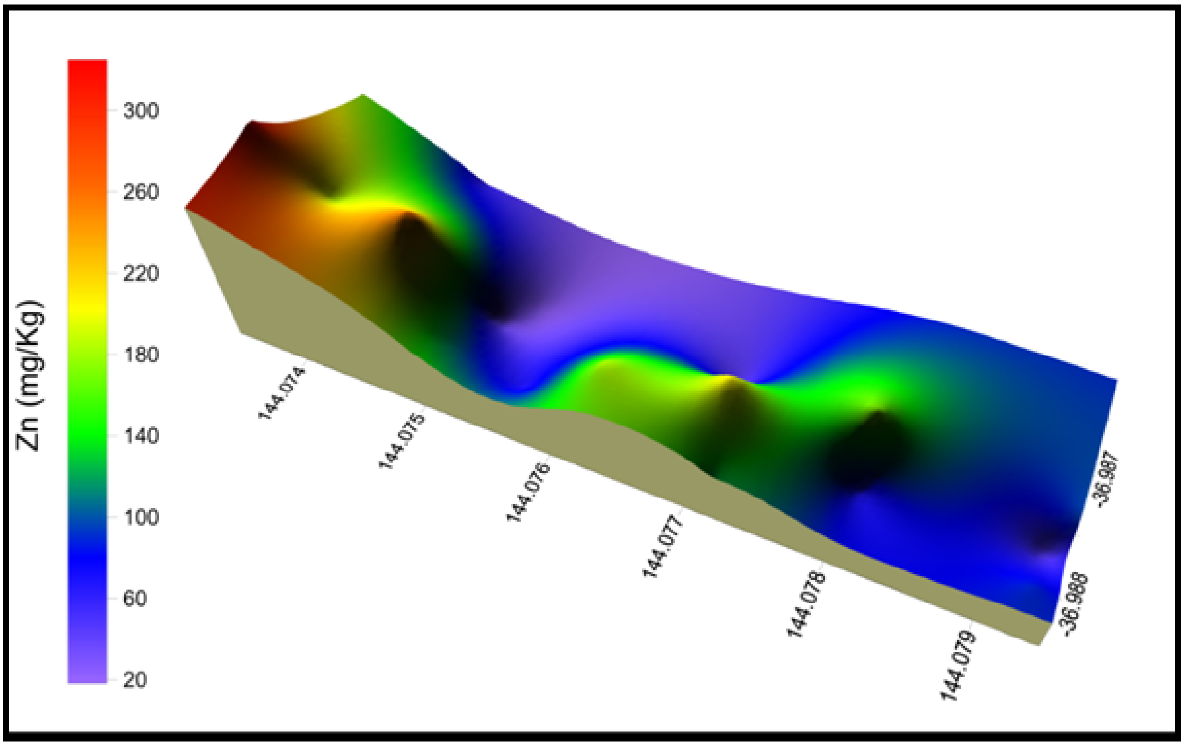

Fig. S1. Spatial distribution map of Pb, Cu, Cd, Cr, Co, Mn, Ni and Zn in the Maldon study area, Central Victoria, Australia.

Table S1. Descriptive statistical analysis of metal analysis data (mg kg^{-1}) such as minimum, maximum, range, median, percentiles (25th, 50th, 75th and 90th) and interquartile range (IQR).

Statistical Parameters	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Minimum	19	0.03	4	23	14	0.10	85	7	12	22
Maximum	185	0.37	25	57	59	9	560	23	76	328
Range	166	0.34	21	34	45	9	475	16	64	4
Median	85	0.11	8	38	30	2	191	13	30	94
Percentiles										
25th	63	0.07	6	33	20	1	116	11	19	51
50th	85	0.11	8	38	30	2	191	13	30	94
75th	141	0.19	10	46	44	5	284	19	38	185
90th	163	0.27	17	54	57	8	470	23	54	266
IQR	78	0.13	5	14	23	4	167	8	19	135

Table S2. Geographical locations of the 18 sampling stations.

Sample ID	Latitude	Longitude	Elevation(m)
S1	-36.9876	144.0734167	362
S2	-36.9881167	144.07505	360
S3	-36.9880833	144.0756667	355
S4	-36.988	144.0762833	359
S5	-36.9883667	144.0771833	358
S6	-36.9882167	144.0778833	357
S7	-36.9881667	144.07925	355
S8	-36.9875333	144.0738667	362
S9	-36.9876333	144.07465	362
S10	-36.98755	144.07515	358
S11	-36.98785	144.0771	361
S12	-36.9878833	144.0780667	354
S13	-36.9877833	144.0793167	354
S14	-36.98725	144.0753333	364
S15	-36.9873833	144.077	362
S16	-36.9876333	144.0780167	357
S17	-36.9876	144.0794167	353
S18	-36.9864167	144.07445	366

Chapter- 5

Application of pollution indices in soil metal contamination assessment–Maldon legacy mine site, Central Victoria, Australia

Application of Pollution Indices in Soil Metal Contamination Assessment - Maldon Legacy Mine Site, Central Victoria, Australia

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Abstract

Metal contamination and pollution in soil, water and air is of significant concern due to the potential health impacts to humans with transference into the human body through ingestion, inhalation and dermal contact. The objective of the study is to assess the current status of soil metal contamination in a legacy mine site in Central Victoria, Australia by the applications of several pollution indices and the subsequent ecological risk assessment by Potential Ecological Risk Index (PERI). Soil sample collection, metal analysis and assessment with Geo-accumulation Index (I*geo*), and Contamination Factor (CF) revealed that the study area is contaminated with Hg and As, which is supported by Pollution Index (PI), Integrated Pollution Index (IPI) and Pollution Load Index (PLI). Moreover, the Nemerow Integrated Pollution Index (NIPI) highlighted that the study area is highly polluted with Hg, As, Pb and Zn, and moderately with Cu and the enrichment factor indicated severe enrichment with As. The Potential Ecological Risk Assessment, demonstrated that the entire study area is at significantly high ecological risk by the metals in the following order Hg > As > Cd > Pb > Cu > Ni > Zn > Cr. This metal contamination status and the subsequent information provide significant insight for site characterization, preparing appropriate land and water management strategies, at the legacy mining sites globally.

Key Words: Arsenic, Environmental management, Historical mine sites, Soil pollution, Potentially toxic elements

1. Introduction

Major and trace metals in the environment are of concern due to potential toxicity, bioaccumulation and non-degradable characteristics over a long time periods, which may negatively impact human and ecosystems health (Gong et al. 2000, 2008; Mohamed et al. 2014; Soliman et al. 2015). Elevated major and trace metal concentrations in the soil environment is associated with both natural and anthropogenic activities (Adriano 1986; Yammine et al. 2010; Murrogo-Negrete et al. 2017). Among the anthropogenic activities, metal mining and processing are significant, specifically legacy mining activities, due to the lack of enforced environmental regulations during mine operation and at closure. Moreover, even after the mine closure, waste materials act as a continuous source of toxic metal contamination (Krishna et al. 2013). For example, Osher et al. (2006) reported the Cd, Cu, Pb and Zn contamination in the sediments in the Egypt Bay at the Hancock County in Maine, USA is coming from the upland historical Cu mine which operated during 1877–1855. In China, Zhou et al. (2010) investigated the metal contamination in a Pb-Zn mining and Zn smelting area in the Liaoning Province and reported that the soil was severely polluted with Cd and Pb and at moderate level by Cu and Zn. Similarly, contamination assessment in the Nuggihalli mining area in South India by Krishna et al. (2013) found that the soils were contaminated by metals from the Cr mining, which create a serious health risks to humans. Contamination reported in Korean coastal sediments with Cu, Zn, Cd and Hg are significant, specifically at the industrial coastal area (Ra et al. 2013). In another study, Lee et al. (2001) reported the elevated concentrations of Cd, Cu, Pb and Zn in mine tailings, associated with the Daduk Au-Ag-Pb-Zn mine in Korea, which extended up to more than 3 km downstream from the mine. A largest metal survey in the 1980s on urban dust and soils in Great Brittan revealed that the place Derbyshire shown highest metal concentration, due to the presence of legacy mine sites (Cullbard et al. 1988). Moreover, Cd pollution and ecological risk has been evaluated in a coal gangue dump in the Jilin Province in north east China (Jiang et al. 2014) and in the Mediterranean Sea area of Egypt (Soliman et al. 2015). All these studies highlights the global extend of major and trace element contamination from the legacy mining areas and the significant impacts.

Major and trace element contamination assessment is a significant step in the evaluation of a contaminated site. Various soil and sediment contamination assessment methods are reported and include contamination factor (CF), pollution index (PI), pollution load index PLI), geo-accumulation index (I*geo*), enrichment factor (EF), potential ecological risk index (PERI) and many more to investigate the metal contamination status of an area (Chen et al. 2005; Zhou et al. 2010; Guan et al. 2014; Rabee et al. 2011; Zhiyuan et al. 2011; Yang et al. 2011; Mohamed et al. 2014; Fan and Wang 2017). Despite being reported, some researchers criticised these indices saying that which is not fruitful to provide actual contamination magnitude (Reimann and Caritat 2000, 2005). These critics suggest that soil metal data where compared with background average or existing threshold levels is enough to evaluate the contamination. Direct comparison to background metal levels may be sufficient to identify metal contamination, but it is insufficient for complete evaluation and a magnitude value is necessary for evaluation purpose, specifically comparison between various sites and in land management context. This is also valuable for site characterization and determining if further investigation is required.

A large number of studies have been conducted across the world, which applied various pollution indices in assessing the metal contamination in soil. To illustrate this, Nazzal et al. (2013) assessed the metal contamination in the urban road side dust collected from selected highways of Greater Toronto, Canada, using I*geo*, revealed that the road side dust extremely contaminated with Cu and Zn and strongly to extremely contaminated with Ni and Pb. In Poland, Loska et al. (2004) assessed the selected metals contamination in farming soils at Suszec Commune, not far away from industrial areas, using I*geo*, EF, and CF and reported the presence of elevated concentration of Cd, Pb, As, Sb and Hg. Similarly, Nowrouzi and Pourkhabbaz (2014) assessed the metal contamination in surface sediments of Hara Biosphere in Iran using I*geo* and EF reported that the sediments are moderately contaminated with Cd. Related study from Korean coastal sediments using I*geo*, EF, and PLI reported that the eastern, western and southern coastal sediments were moderately contaminated with Cu, Zn, As, Cd, Pb and Hg (Ra et al. 2013). Parallel to this, Yaqin et al. (2008) applied I*geo* to assess the metal contamination status of soils in 15 Cities in China and Chen et al. (2005) applied PI and IPI to assess metal pollution in the surface soils of urban Parks in Beijing, China. Besides this, metal pollution in the soils around a Pb-

Zn smelter in Baoji City in China were assessed with I*geo*, EF and Eri and found that the degree of contamination was high at the surface soils, compared with soil in depths (Fan and Wang 2017).

Environmental contamination and pollution by major and trace elements caused by mining and metal processing is a global issue, but still requires further attention as each site is unique and temporal variations of metal concentrations continue. This is also significant in legacy mining areas as most of the legacy mining sites are un-rehabilitated. Central Victoria in Australia is legacy gold mining region, where mining started in 1850. Even though, major mining activities ceased in the beginning of last century, some mines are active in the present time. Extensive amount of mine waste materials stored in number of places in the region create contamination of soil, water and air with major and trace metals (Sultan 2006, 2007; Martin et al. 2014) In this scenario, the objective of the current study is to evaluate the metal contamination status of one of the Maldon legacy mine site in Central Victoria in Australia by analysing the soil samples and by computing the degree of contamination with indices include I*geo*, CF, PI, IPI, PLI, EF and PERI (Yongming et al. 2006; Abrahim and Parker 2008; Jiang et al. 2014; Nowrouzi and Pourkhabbaz 2014; Zhuang and Gao 2014; Aiman et al. 2016; Mazurek et al. 2017). This contamination assessment is highly significant as the legacy mine site is located close to a residential area and surface water were distributed as potable water to the local communities.

2. Materials and Methods

2.1 Characteristics of the study area

Maldon, is a historical mining town located 140 km SW of the City of Melbourne in Australia (Fig.1) and has been the centre of gold mining and processing since 1850s (Mason and Webb 1953; Cherry and Wilkinson 1994). Cold wet winters (7.5–20.5 ºC) and warm dry summers (16.4–40.3 ºC) are the normal climate pattern in the area (Taylor et al. 2000; BoM 2017) with annual average rainfall of 540 mm (BoM 2017). Throughout the Maldon township relics of mining can be seen and includes adits and shafts and open cut sites to access the sulphide bearing gold ore. Mining and the subsequent ore processing resulted in the accumulation of enormous quantities of overburden materials, crushed rock fragments and mine tailings rich in potentially toxic metals. A 20 acres of legacy mining affected public landscape, located east of the Union Hill mine were selected for the contamination assessment study. Though the study area is relatively small, it represents large Central Victorian regional landscape, with enormous number of legacy gold mining sites.

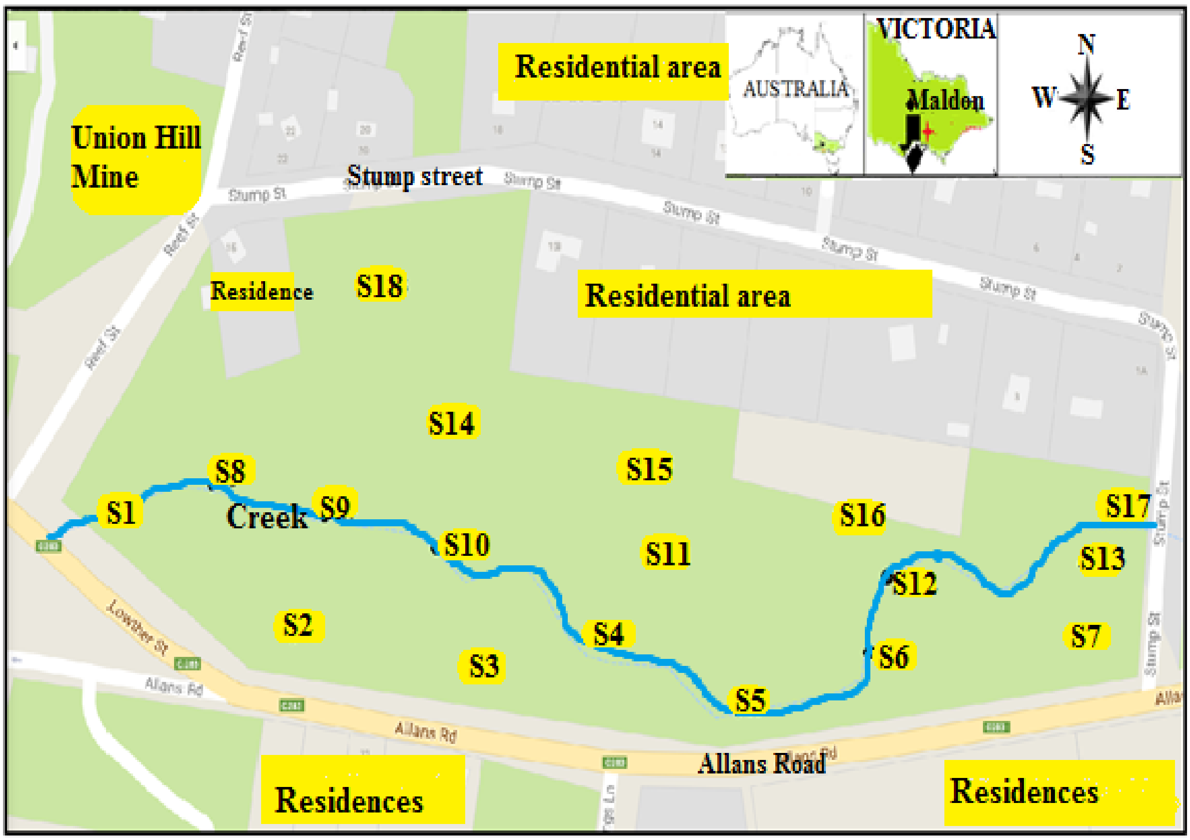

Fig.1. Showing the Maldon study area with soil sampling stations (S1 to S18).

2.2 Soil sampling and analysis

In the study area, surface soil samples are significant in the contamination assessment as it may mostly affected by mining and gold processing, natural geological process such as rainfall and subsequent runoff and wind activities (Schaider et al. 2007). Moreover surface soil has the potentiality to provide significant impacts to human and ecosystems health due to the potential for mobility and exposure. For the metal analysis and the subsequent contamination assessment, 18 surface soil samples (< 3 cm depth) were collected from the study area with STAR sampling method. Approximately 1 kg of soil samples were collected from each sampling stations from an area of 900 cm^2 (30 cm x 30 cm) and transported to the Federation University

Australia laboratory. In the laboratory, oven dried samples (24 hrs at 60 ºC) were crushed and sieved through 2 mm wire mesh sieve and < 2 mm samples were placed in a tightly sealed poly ethylene containers for laboratory analysis. Soil metal concentrations were determined in a NATA accredited laboratory by Ultra-Trace Level Methods using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) with Aqua Regia Digestion (GEO-AR01).

2.3 Soil Pollution Indices

The assessment of soil metal enrichment and distribution, includes their status of contamination or pollution were carried out using a variety of most commonly reported indices: index of geo-accumulation (I*geo*), contamination factor (CF), pollution load index (PLI), pollution index (PI), Integrated Pollution Index (IPI), Nemerow integrated pollution index (NIPI) and enrichment factor (EF) (Chen et al. 2005; Abrahim and Parker 2008; Rabee et al. 2011; Esshaimi et al. 2012; Ra et al. 2013). The above indices are suitable to assess single contaminant of concern, but in reality, multiple contaminates usually accumulate together in need of a combined assessment method, such as PERI (potential ecological risk index). Application of more than one index may support to ensure and compare the degree of contamination.

An important phase in evaluating the metal contamination in the study area is the establishment of a reference metal value or background metal value (Qingjie et al. 2008; Ghaleno et al. 2015; Soliman et al. 2015). Either the use of average crustal values or the local base line values by analysing comparable local soil unaffected by anthropogenic activity is considered to be optimum (Zhou et al. 2010; Esshaimi et al. 2012). In the Maldon study area, it is a challenge to locate the uncontaminated soil as the area has number of legacy mine sites and tonnes of mine waste materials (Sultan 2006, 2007; Pearce et al. 2010, 2012; Martin et al. 2014, 2016, 2017). Therefore, average concentrations of metals in the Victorian top soil established by Geoscience Australia has been adopted (Caritat and Cooper 2011a, b, 2016) (Table 1).

Table 1. Average metal concentrations in the top soils of the State of Victoria and entire Australia compared with upper continental crust of Australia and world (Caritat and Cooper 2011a, b, 2016).

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Victorian soil average (mg kg^{-1})	5	0.1	10	42	19	0.03	409	20	13	45
Australian soil average (mg kg^{-1})	3	0.07	9	42	17	0.03	390	17	11	38
Australian continental crust (mg kg^{-1})	1.6	0.04		24	12	0.01		12	7.4	26
Upper continental crust -World (mg kg^{-1})	5.7	0.06		73	27	0.05		34	10	75

2.3.1 Geo-accumulation Index (I*geo*)

Geo-accumulation index (I*geo*) is a common approach to determine and define the metal contamination in soil and sediments, which is proposed by Muller in 1969 (Banat et al., 2005). Since then, this matrix has been extensively used as a quantitative indicator of metal contamination all around the world (Yaqin et al. 2008; Qingjie et al. 2008; Likuku et al. 2013; Ra et al. 2013; Ghaleno et al. 2015). I*geo* assesses the metal contamination by comparing the current and pre-industrial concentration of metals in the study area (Muller 1981) using the following equation:

$$Igeo = \log_2 (C_n / k\,B_n)$$

Where C_n is the concentration of metals in the soil sample, B_n is the background value of the same metal in the soil in the study area or on the earth's crust and k is the background matrix correction factor due to the lithogenic effects and is considered as 1.5 in normal soil samples (Stofers et al. 1986). The method assesses the degree of metal contamination / pollution in terms of seven enrichment classes based on the increasing numerical values of the index (Table 2). A number of studies have reported the degree of contamination in soils and sediments with I*geo* (Abrahim and Parker

2008; Zou et al. 2010; Rabee et al. 2011; Ghaleno et al. 2015; Olatunde et al. 2015; Murrugo-Negrete et al. 2017).

2.3.2 Contamination Factor (CF)

According to Muller (1969) contamination factor (CF) is obtained by dividing the concentration of each metal in the soil (C_m) by the baseline or background value in the unpolluted soil (C_{bg}).

$$CF = (C_m / C_{bg})$$

The contaminant levels have been classified based on the intensities on a scale ranging from 1 to 6 (Table 2). Many studies report the degree of contamination with CF (Qingjie et al. 2008; Rabee et al. 2011; Esshaimi et al. 2012; Mohamed et al. 2014; Olatunde et al. 2015; Murrugo-Negrete et al. 2017)

Table 2. Geo-accumulation Index (I*geo*) classes and Contamination Factor (CF) levels with respect to soil contamination (Muller, 1981).

Class	Value of I*geo*	Soil Quality		Value of CF	Soil Quality
0	<0	Uncontaminated			
1	0 – 1	Uncontaminated to moderately contaminated		1	None to medium
2	1 – 2	Moderately contaminated		2	Medium
3	2 – 3	Moderately to heavily contaminated		3	Medium to high
4	3 – 4	Heavily contaminated		4	High
5	4 – 5	Heavily to extremely contaminated		5	High to very high
6	>5	Extremely contaminated		6	Very high

2.3.3 Pollution Load Index (PLI)

Pollution Load Index (PLI) was developed by Tomlinson et al. (1980) and provides a mechanism for assessing the levels of metal contamination in the site and a number of studies adopted this method for contamination assessment (Rabee et al. 2011; Mohamed et al. 2014; Ghaleno et al. 2015; Aiman et al. 2016). It is also called Metal Pollution Index (MPI) (Aiman et al. 2016). Many studies were applied PLI to assess the site contamination around the world. This index is a quick tool to assess the contamination in a particular location or to compare the contamination status of different places (Rabee et al. 2011; Esshaimi et al. 2012; Mohammed et al. 2014; Ghaleno et al. 2015). It is the product of n contamination factor (CF) (Usero et al. 2000).

$PLI = (CF1 \times CF2 \times CF3 \times \ldots\ldots\ldots \times CFn)^{1/n}$

where, n is the number of metals. Here PLI < 1 indicates no contamination / pollution, whereas PLI > 1 indicates contamination / pollution.

2.3.4 Pollution Index (PI)

Pollution index (PI) is a powerful computational method for processing, analysing and conveying raw environmental information to decision makers, environmental managers, scientist, engineers and the public (Caeiro et al. 2005). PI is calculated in the same way as CF, however it requires the mean value of five (minimum) samples for analysis.

$PI = Cn/Bn$

Where Cn is the mean of metal concentration of the samples ($n \geq 5$) and Bn is the concentrations of metals in the reference soil. The result is classified in a different way than I*geo*: $PI \leq 1$ - low level contamination / pollution; $1 < PI \leq 3$ - middle level contamination / pollution; $PI > 3$ - high level contamination / pollution.

2.3.5 Integrated Pollution Index (IPI)

Integrated Pollution Index (IPI) is defined as the mean value of the pollution index (PI) of an element (Faiz et al. 2009). It is classified as: $IPI \leq 1$ - low level contamination / pollution; $1 < IPI \leq 2$ - middle level contamination / pollution and $IPI > 2$ - high level contamination / pollution.

2.3.6 Nemerow integrated pollution index (NIPI)

The calculation of NIPI is based on PI and defined in the following way (Yang et al., 2010, 2011, 2014).

$NIPI = \sqrt{(PI^2_{iave} + PI^2_{max})/2}$ where $PI = Ci/Si$

PI is the ratio of measured concentration of each metal (Ci) in the study area to that of background value (Si). The PI^2_{max} is the maximum PI value of each metal and PI^2_{iave} is the mean PI value. The NIPI is considered as non-pollution when it is < 0.7. It is considered as low level pollution when 1 < IPI ≤ 2, moderation pollution, when 2< NIPI ≤ 3 and high level pollution when NIPI > 3 (Yang et al. 2010; 2011)

2.3.7 Enrichment factor (EF)

Enrichment factor (EF) evaluate the contamination levels by standardization of a metal against a reference metal such as Al, Fe, Mn, Ti, Rb etc. in the soil (Zahra et al. 2014). A reference metal in the EF study should be a stable metal in the soil, which is characterised by absence of vertical mobility and degradation (Yongming et al. 2006; Barbieri 2016). Ideally, it should exist as fine particles and its concentration not affected by anthropogenic activities (Loska et al. 2003; Zahra et al. 2014). Since the study area is a legacy gold mining area, anthropogenic mobility of other metals (except Mn) are possible. Moreover, the geochemistry of Fe is similar to that of many other metals in the oxic and anoxic environment (Yongming et al. 2006; Aiman et al. 2016). Therefore, this study adopted Mn as the reference element. EF is computed based on the following formula (Buat-Menard and Chesselet 1979).

$$EF = \frac{C_n \text{ (sample)} / C_{ref} \text{ (sample)}}{B_n \text{ (background)} / B_{ref} \text{ (background)}}$$

Where C_n (sample) is the concentration of the examined metal in the soil; C_{ref} (sample) is the concentration of the reference metal in the study area; B_n (background) is the concentration of examined element in the background (country/ region); and B_{ref} (background) is the concentration of reference metal in the region. For classification purpose EF has been divided into seven groups (Ra et al. 2013; Fan and Wang 2017). $EF < 1$ is considered as no enrichment, $1 \leq EF < 3$ is minor enrichment, $3 \leq EF < 5$ is moderate enrichment, $5 \leq EF < 10$ is moderately severe enrichment, $10 \leq EF < 25$ severe enrichment, $25 \leq EF < 50$ very severe enrichment and $EF > 50$ extremely severe enrichment.

2.3.8 Potential Ecological Risk Index

The Potential Ecological Risk Index (PERI) was proposed by Hakanson (1980). This method introduced a toxic response factor for a given substance and thus can be used to evaluate the combined pollution risk to an ecological system. This method comprehensively considers the synergy, toxic level, metal concentration and ecological sensitivity of the metals (Singh et al. 2012; Douay et al. 2013). The equation used to calculate the index include three basic components: degree of contamination (C_D), toxic response factor (T_R) and potential ecological risk factor (E_R) (Jiang et al. 2014). It reflects the toxicity level of the metals in the study area and it is calculated with the following formula:

$$C_F = C_M / C_R$$

$$E_{RI} = T_{BF} \times C_F$$

$$RI = \sum_{i-1}^{m} E_{RI}$$

Where C_M is the measured concentration of metals in each sampling station, C_R is the reference value (background concentration), E_{RI} is the potential ecological risk index of a single metal, T_{BF} is the biological toxic factor of a single metal (Zn = 1; Cr = 2; Cu = Pb = Ni = 5, As = 10; Cd = 30 and Hg = 40.5) (Hakanson 1980; Jiang et al. 2014) and RI is the comprehensive potential ecological risk index. This method not only considers the metal level in the soils, but also associates ecological and environmental effects with toxicology (Qiu 2010). Based on the method, the E_{RI} and RI have been classified as in Table 3.

Table 3. Classes of ecological risk coefficient (Eir) and risk index (RI).

Er value	Soil quality	RI value	Soil quality
< 40	low ecological risk	< 150	low ecological risk
40 – 80	moderate ecological risk	150 – 300	moderate ecological risk
80 - 160	appreciable eco risk	300 – 600	high ecological risk
160 – 320	high ecological risk	> 600	significantly high ecological risk
> 320	serious ecological risk		

3. Results and Discussion

The descriptive statistics of metal analysis such as minimum, maximum, range, median, and interquartile range were given in Table 4 and logarithmic metal concentrations were plotted as box plots (Fig. 2). The statistical analysis revealed that Mn and Cd are extremes when we consider minima, maxima, range, median variance and IQR with Mn located at the highest side and Cd at the lowest side. The median concentration of Mn in the Maldon study area is 191 mg kg^{-1} with a minimum value of 85 mg kg^{-1} and with a maximum of 560 mg kg^{-1}. Zn is the second highest metal (median 94 mg kg^{-1}) with a minimum of 22 mg kg^{-1} and maximum of 328 mg kg^{-1}. This is followed by As (85 mg kg^{-1}), Cr (38 mg kg^{-1}), Pb (30 mg kg^{-1}), Cu (30 mg kg^{-1}), Ni (13 mg kg^{-1}), Co (8 mg kg^{-1}), Hg (2 mg kg^{-1}) and Cd (0.1 mg kg^{-1}) (based on the median).

Table 4. Descriptive statistics of metal analysis data from the Maldon Study area, Victoria, Australia.

Statistical Parameters	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Minimum	19	0.03	4	23	14	0.10	85	7	12	22
Maximum	185	0.37	25	57	59	9	560	23	76	328
Range	166	0.34	21	34	45	9	475	16	64	4
Median	85	0.11	8	38	30	2	191	13	30	94
IQR	78	0.13	5	14	23	4	167	8	19	135

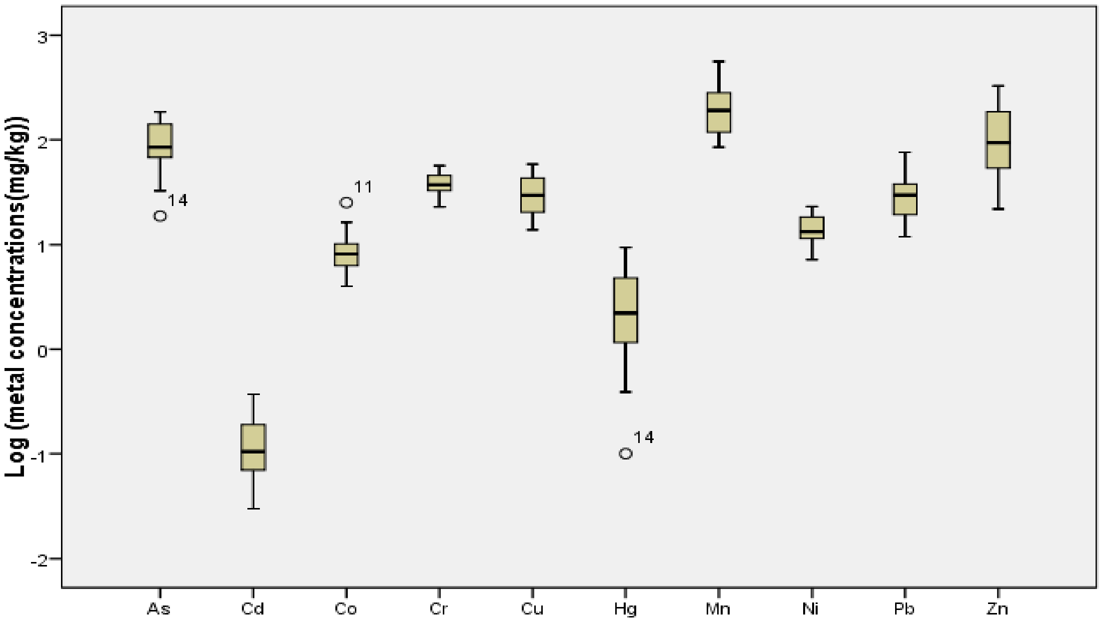

Fig. 2. Distribution of analysed metals in the study area in logarithmic scale. (NB: open circles denote outliers with corresponding station id).

3.1 Evaluation of the Geo-accumulation Index (I*geo*)

The range and mean of the geo-accumulation index of all the analysed metals are given in Table 5 and plotted in Fig. 3 and 4.

Table 5. Range and mean of the geo-accumulation index (I*geo*) of the metals and the corresponding soil quality from Maldon, Victoria, Australia.

Metals	Geo-accumulation factor (I*geo*)		Soil Quality based on the mean value
	Range	Mean	
As	1.3 to 4.6	3.5	Heavily contaminated
Cd	-2.3 to 1.3	-0.3	Uncontaminated
Co	-1.9 to 0.8	-0.08	Uncontaminated
Cr	-1.5 to -0.1	-0.7	Uncontaminated
Cu	-1.03 to 1.04	0.08	Uncontaminated to moderately contaminated
Hg	1.2 to 7.7	5.4	Extremely contaminated
Mn	-2.9 to -0.13	-1.7	Uncontaminated
Ni	-2.05 to -0.3	-1.1	Uncontaminated
Pb	-0.6 to 2.07	0.7	Uncontaminated to moderately contaminated
Zn	-1.6 to 2.3	0.5	Uncontaminated to moderately contaminated

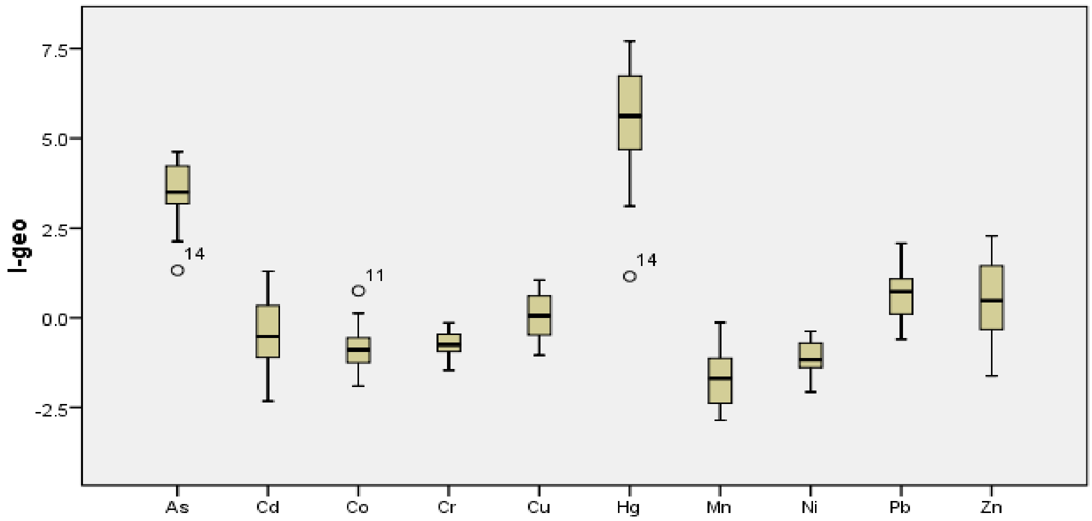

Fig. 3. Distribution of geo-accumulation index (I*geo*) of metals from the study area (Note the contamination status of Hg and As) (NB: open circles denote outliers with corresponding station id).

Of the 18 sampling stations, the Geo-accumulation index identifies that Hg and As are the main contaminating metal in all the 18 sampling stations. The contamination of other selected metals are not deemed significant in the study area. The I*geo* values of Hg varied between 1.2 and 7.7 with a mean value of 5.4. Twelve sampling stations (S2, S3, S4, S5, S6, S7, S8, S9, S11, S16, S17 and S18) (66.6%) highlighted the I*geo* value of above 5, which represents the highest classification range (extremely contaminated) according to Muller (1981). Three sampling stations (S1, S12 and S13) (27.8%) returned an I*geo* value in between 4 and 5 (heavily to extremely contaminated), two stations (S10 and S15) (11.1%) values are in between 3 and 4 (heavily contaminated), and one station (S14) value falls between 1 and 2 (5.5%) moderately contaminated. Therefore, according to I*geo* the entire study area is contaminated (moderately to above extremely) with Hg.

The second main contaminant is As with an I*geo* in between 1.3 to 4.6 with a mean value of 3.5. Seven sampling stations (S1, S5, S6, S8, S9, S11 and S18) (38.8%) showed the I*geo* value in between 4 and 5 (heavily to extremely contaminated) and seven sampling stations (S2, S3, S4, S7, S12, S16 and S17) (38.8%) showed the value in between 3 and 4 (heavily contaminated). Three sampling stations (S10, S13 and S15) (16.6%) showed the value in between 2 and 3, which represents moderately to heavily contaminated and one station (S14) (5.5%) showed I*geo* in between 1 and 2, denoted moderately contaminated.

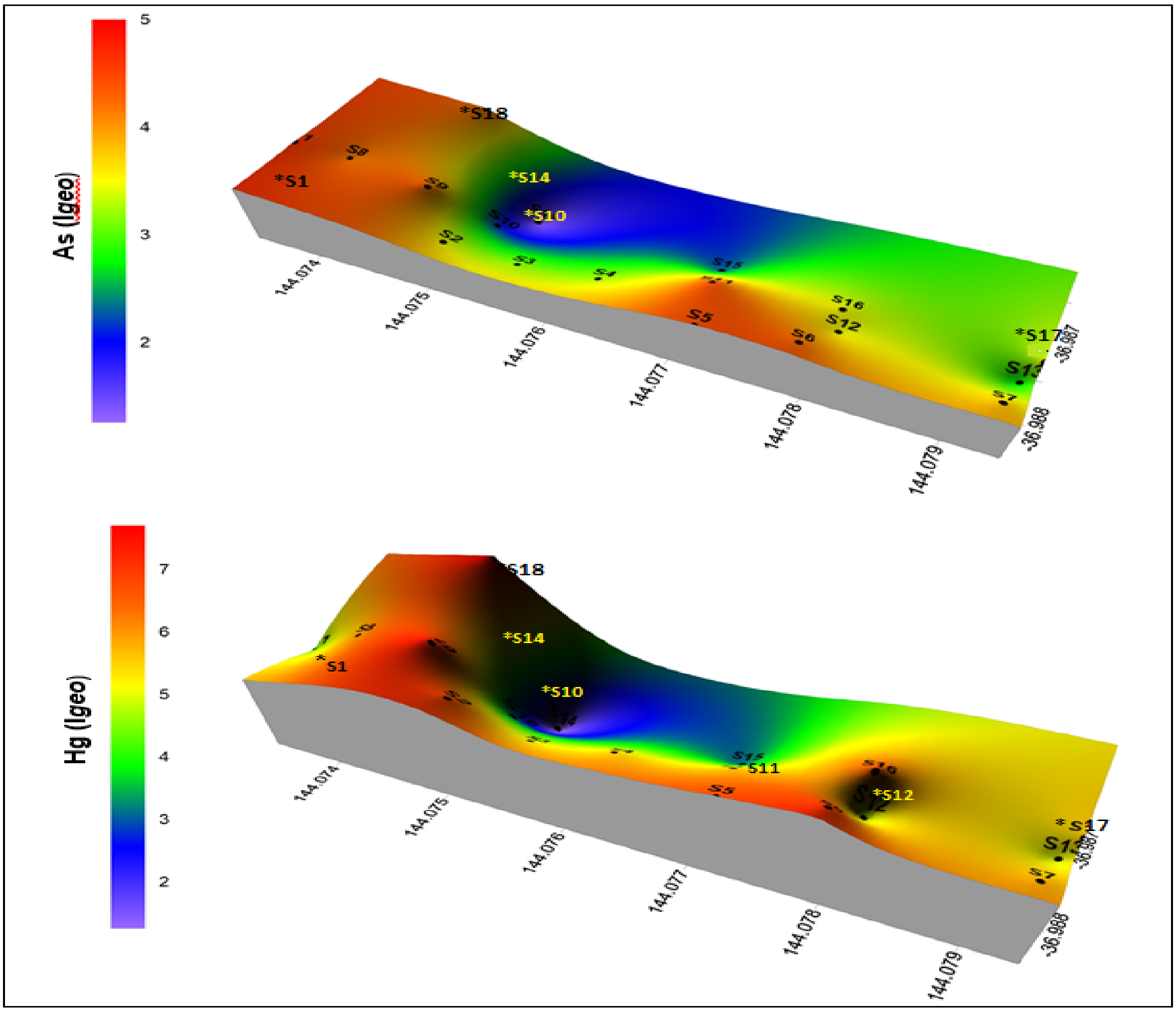

Fig.4. 3D map showing the geo-accumulation index (I*geo*) of As and Hg study area.

The I*geo* values of Pb in the study area ranged from -0.6 to 2.1 (mean 0.7). One sampling station (S7) (5.5%) displayed moderate to heavily contamination (between 2 and 3), four sampling stations (S1, S6, S9 and S11) (22%) displayed moderate contamination (between 1 and 2), 12 stations (S2, S3, S4, S5, S8, S12, S13, S14, S15, S16, S17 and S18) (66%) showed range in between uncontaminated to moderately contaminated (between 0 and 1), and the rest one station (S10) (5.5%) not shown any contamination with Pb. The I*geo* of Zn ranged from -1.6 to 2.3 (mean 0.5). One sampling station showed (S1) (5.5%) moderate to heavily contamination, five sampling stations (S4, S8, S9, S10 and S16) (28%) showed moderate contamination, and five stations (S2, S5, S6, S7 and S17) (28%) showed uncontaminated to moderately contaminated with Zn. Other sampling stations did not register as contaminated with Zn. One station (S1) (5.5%) showed moderate contamination with Cd and six stations (S2, S4, S8, S9, S11 and S16) (33%) falls in the range uncontaminated to moderately contaminated. The remaining stations are not affected by Cd contamination. Two sampling stations (S1 and S2) (11%) highlighted moderate contamination with Cu and seven stations (S3, S4, S5, S7, S8, S9 andS11) (39%) displayed I*geo* in the range of 0 to 1 (uncontaminated to moderately contaminated) with Cu and the other stations are not affected. Only one station (S1) affected by Co (uncontaminated to moderately contaminated) and none of the sampling stations are affected by Cr, Mn and Ni.

3.2 Evaluation of Contamination Factor (CF)

The minimum, maximum and mean of the CF and the contaminant levels of each analysed metals in the study area is mentioned in Table 6 and as box plots depicted in Fig. 5. Among the number of metals analysed, Hg showed the highest mean CF (102), followed by As (19.5) and Mn showed the lowest (0.5). The CF of Hg varies from 3.3 to 314 with mean value of 102, demonstrated that all the sampling sites (except S14) have above high contamination. As varies from 3.8 to 37 (mean of 19.5) also indicates above high contamination in all the sites except S14. The CF of Zn ranged from 0.5 to 7.3 (mean of 2.7), which represents none to very high contamination. With Pb concentration, only one sampling station (s7) (5.5%) showed very high contamination, but another one station (S1) (5.5%) has high contamination. Three stations (S6, S9 and S11) (17 %) showed medium to high contamination, six stations (S2, S4, S5, S8, S16 and S18) (33.3%) showed medium contaminations and the remaining station highlighted no to medium contamination.

With regards to Zn, one sampling station (S1) (5.5%) showed very high contamination and another one (S9) (5.5%) showed high to very high contamination, three stations (S4, S8 and S11) (17%) showed high contamination, one station (S16) (5.5%) showed medium to high contamination and the remaining stations showed none to medium and medium contamination. CF factor of Cd varies from 0.3 to 3.7 (average 1.4). In the study area, S1 showed high contamination (5.5%) with Cd, one stations (S11) (5.5%) showed medium to high contamination, four stations (S4, S8, S9 and S16)

(22%) showed medium level of contamination and the rest sampling stations showed none to medium contamination with Cd. The CF of Cu ranged from 0.7 to 3.1 with the mean of 1.7. Two sampling station (S1 and S2) (11%) showed medium to high contamination, six stations (S3, S4, S5, S8, S9 and S11) (33%) showed medium level of contamination and the remaining showed none to medium contamination with Cu. Co showed medium contamination in one station (S11) (5.5%), whereas Cr, Mn and Ni showed only minor contamination.

Table 6. Minimum, maximum and mean of the CF and the corresponding contamination levels

Metals	Minima	Maxima	Mean	Contamination level
As	3.8	36.9	19.5	Very high
Cd	0.3	3.7	1.4	None to medium
Co	0.4	2.5	0.9	None
Cr	0.6	1.4	0.9	None
Cu	0.7	3.1	1.7	None to medium
Hg	3.3	314	102	Very high
Mn	0.2	1.4	0.5	None
Ni	0.4	1.2	0.7	None
Pb	0.9	6.1	2.5	Medium
Zn	0.5	7.3	2.7	Medium

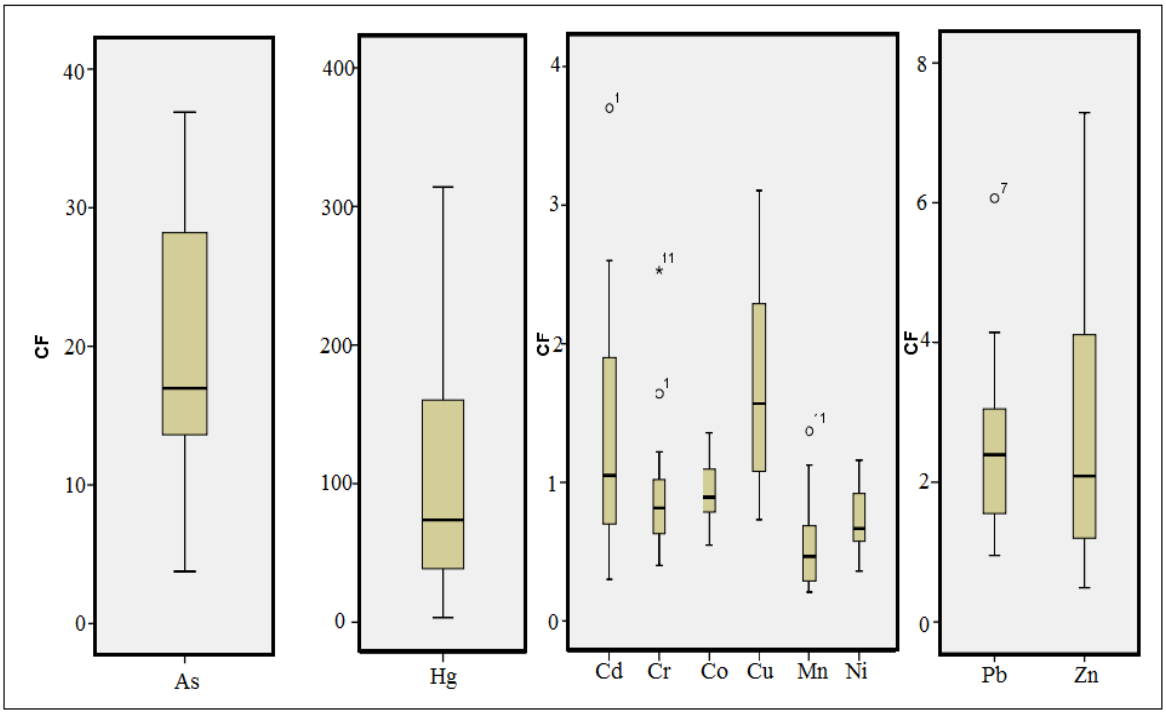

Fig. 5. Box plots showing the Contamination Factor of metals (NB: open circles denote outliers with corresponding station number).

3.3 Evaluation of Pollution Load Index (PLI)

The value of the Pollution Load Index (PLI) was found to be generally greater than 1 in all the sampling stations (except S14 (0.8)), with values ranging from 1.10 to 4 (Fig.6 and Table 7). Sampling stations S1, S2, S5, S8, S9 and S11 demonstrate high level of contamination compared to other stations.

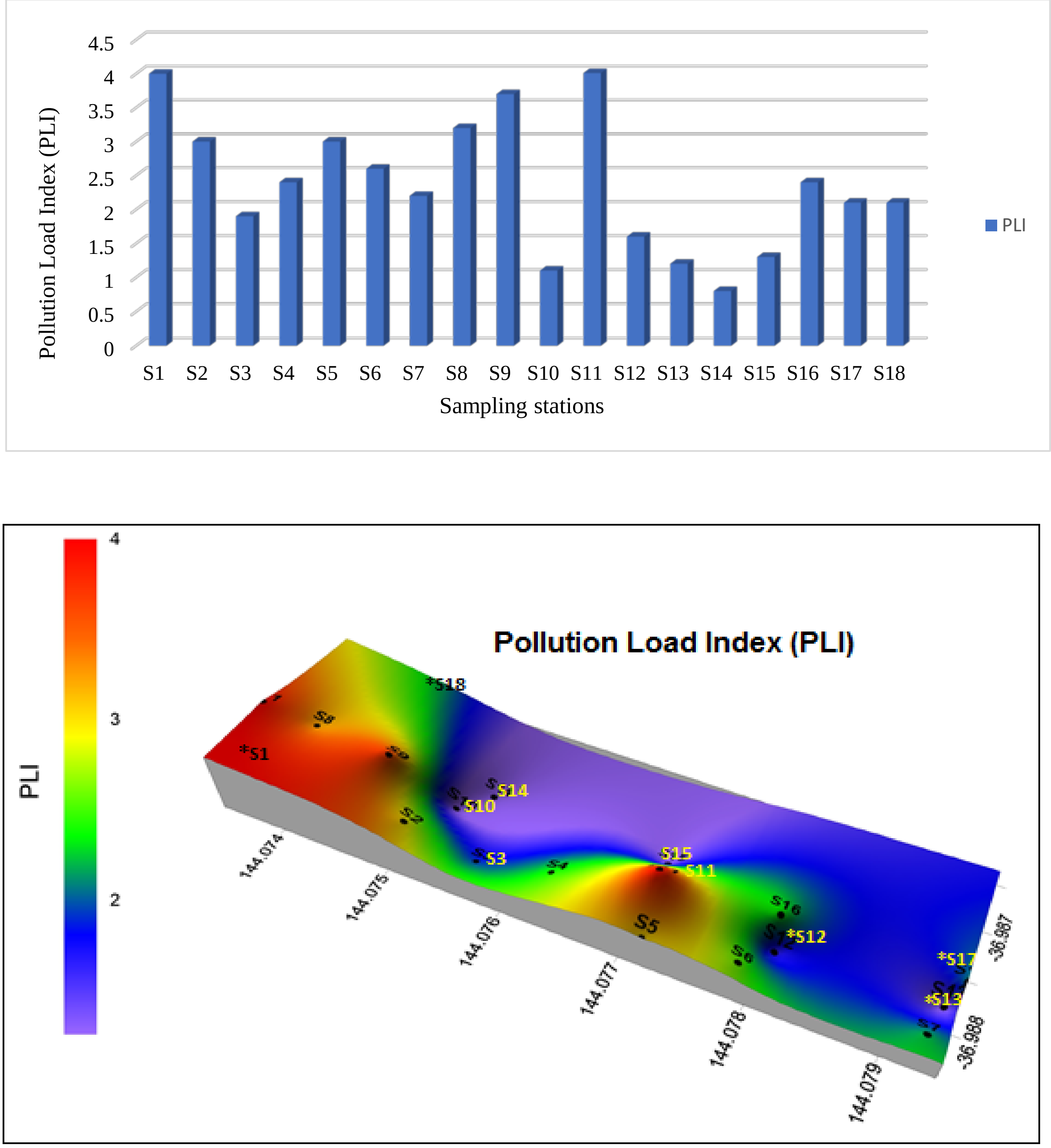

Fig. 6. Pollution Load Index (PLI) computed in each sampling stations as bar graph (top) and as 3D map (bottom).

Table 7. Contamination Factor and Pollution Load Index in each sampling station.

Sampling station	As CF	Cd CF	Co CD	Cr CF	Cu CF	Hg CF	Mn CF	Ni CF	Pb CF	Zn CF	PLI
S1	36.9	3.7	1.6	1.3	3	32.7	1.1	1.1	4.1	7.3	4
S2	16.9	1.8	0.9	1	3.1	163.3	0.7	0.9	2.5	2.8	3
S3	13.6	0.9	0.8	1	2.5	53	0.2	0.8	1.5	1.5	1.9
S4	14.2	1.9	0.8	1	2.1	66.7	0.3	0.9	2.3	4.1	2.4
S5	32.1	1	1.2	1	2.3	160.3	0.6	0.9	2.2	2.8	3
S6	28.2	1.1	0.8	0.9	1.4	204.3	0.5	0.6	3.1	2	2.6
S7	20.6	1	0.5	0.8	1.7	83	0.4	0.5	6.1	2	2.2
S8	26.2	2	1	1.1	2.2	94.3	0.7	1	2.8	4.1	3.2
S9	28.3	2.2	1.2	1.1	2	254.3	0.7	1	3.0	5.8	3.7
S10	6.5	0.3	0.8	0.9	1	13	0.2	0.7	1	0.8	1.1
S11	30.5	2.6	2.5	1.4	2.3	73	1.4	1.2	3.2	4.7	4
S12	16.6	0.7	0.8	0.7	1	38.7	0.5	0.6	1.5	1.4	1.6
S13	9.3	0.5	0.4	0.6	0.7	43.7	0.3	0.4	1.6	0.8	1.2
S14	3.8	0.3	0.4	0.8	0.9	3.3	0.2	0.4	1.7	0.5	0.8
S15	7.4	0.6	0.7	0.8	1.1	13	0.3	0.6	1.5	0.9	1.3
S16	17.0	1.9	0.6	0.8	1.3	149.3	0.3	0.6	2.6	4	2.4
S17	16.6	1.1	1	0.8	1.3	74.7	0.6	0.7	1.6	2.2	2.1
S18	27.1	0.9	0.6	0.5	1.1	314	0.5	0.4	2.6	1.2	2.1

3.4 Evaluation of the Pollution Index (PI)

The minimum, maximum and mean of the PI is depicted in Table 8. The Pollution Index of Hg ranges from 30 to 159 with an average of 93 and represents the highest contaminated metal followed by As, which varies from 10.8 to 27 with an average of 19. Zn is the next most contaminated metal, which ranges from 1.5 to 3.7 (average of 2.6). Based on the average PI value the study area demonstrated high level contamination with Hg and As, middle level contamination with Cd, Cu, Pb and Zn and low level contamination with Co, Cr, Mn and Ni.

Table 8. Minimum, Maximum and mean of Pollution index (PI).

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Minimum	10.8	0.8	0.6	0.7	1	34.3	0.3	0.5	1.8	1.5
Maximum	27	2	1.3	1	2.6	159	0.7	0.92	3.5	3.7
Mean	18.6	1.3	0.95	0.94	1.7	92.8	0.5	0.7	2.5	2.6

3.5 Evaluation of the Integrated Pollution Index

In the study area, Hg shows highest Integrated Pollution Index (IPI) of 93, followed by As (19) and both are considered as high level contaminants in the study area as their IPI value is > 2. Pb (2.5) and Zn (2.6) are also consider as high level contaminants, whereas other metals such as Cd (1.3) and Cu (1.7), demonstrated middle level contamination and the remaining four metals Co (0.9), Cr (0.9), Mn (0.5) and Ni (0.7) displayed only low level contamination (Fig. 7)

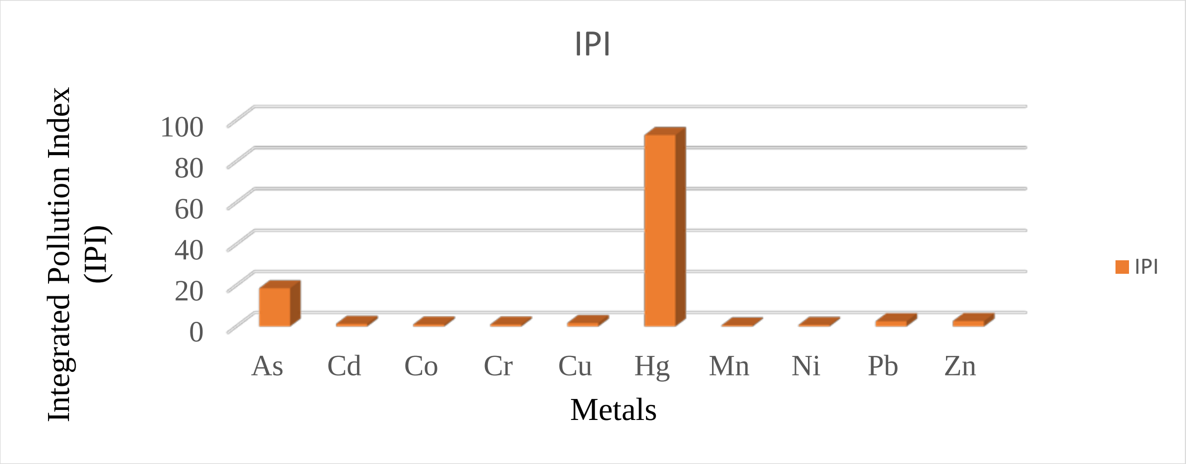

Fig. 7. Showing the level of Integrated Pollution Index in the Maldon study area, Victoria, Australia.

3.6 Evaluation of Nemerow integrated pollution index (NIPI)

The NIPI value of metals in the Maldon study area ranged from 0.61 to 130.4 with Mn showing the minimum and Hg showing the maximum value. According to NIPI the study area is highly polluted with Hg (130.4), As (23.2), Zn (3.2) and Pb (3.03), moderately polluted with Cu (2.2). The low level contaminants in the area are Cd (1.6), Co (1.1), Cr (1.02) and Ni (0.83) and Mn showing no contamination as the values is less than 0.7 (Table 9).

Table 9. Showing the NIPI value of metals in the study area.

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
NIPI	23.2	1.6	1.12	1.02	2.2	130.35	0.61	0.83	3.03	3.19

3.7 Evaluation of the Enrichment Factor (EF)

The enrichment factor (EF) of each metal has been computed by taking Mn as the reference element and the minimum, maximum and the mean values include enrichment levels were mentioned in Table 10. Based on the mean value, only As showing very severe enrichment, whereas moderate enrichment shown by Cu, Pb and Zn. Co, Cr and Ni shown only minor enrichment and Cd and Hg shown no enrichment at all.

Table 10. Showing the enrichment level of each metal in the study area.

Metals	Minimum	Maximum	Mean	Enrichment levels based on mean
As	17.6	60.56	40.32	Very severe enrichment
Cd	0.00013	0.0007	0.0002	No enrichment
Co	1.37	4.64	2.4	Minor enrichment
Cr	1.04	4.58	2.27	Minor enrichment
Cu	1.94	12.31	4.54	Moderate enrichment
Hg	0.00015	0.0063	0.002	No enrichment
Ni	0.7	3.28	1.61	Minor enrichment
Pb	2.38	15.89	5.71	Moderate enrichment
Zn	2.24	15.15	5.4	Moderate enrichment

3.8 Evaluation of Potential Ecological Risk Index (PERI)

The results of the evaluation of the potential ecological risk factor (E_{RI}) and the potential ecological risk index (RI) are summarised in Table 11. The order of potential ecological risk coefficients of (E_{RI}) metals in soils of the Maldon study area is Hg > As > Cd > Pb > Cu > Ni > Zn > Cr. The mean potential ecological risk coefficients of Hg is (4128) > 320, which belongs to the serious ecological risk and As belongs to the high ecological risk category, whereas, Cd belongs to moderate risk and other metals falls in the low risk category. This clearly demonstrates the overall site contamination issue linked to the presence of Hg and As. The Risk Index (RI) values demonstrated that all the sampling stations (except S14) are at significantly high ecological risk category and hence the entire study area (Fig. 8 and 9)

Table 11. Evaluation of the potential risk of metal contamination in soil from Maldon study area (SHER – Significantly high ecological risk, and MER – Moderate ecological risk).

Sampling stations	E_{RI}								RI	Risk grade
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn		
S1	369	111	2.6	15	1323	5.7	20.7	7.3	1854.4	SHER
S2	169	54	1.9	15.7	6615	4.3	12.5	2.8	6875.4	SHER
S3	136	27	2.1	12.6	2147	3.9	7.3	1.5	2337.1	SHER
S4	142	57	2.1	10.8	2700	4.4	11.4	4.1	2932	SHER
S5	321	30	2.2	11.6	6494	4.6	11.2	2.8	6876.9	SHER
S6	282	33	1.7	7.3	8276	3.1	15.7	2	8620.3	SHER
S7	206	30	1.5	8.6	3362	2.4	30.3	2	3642.3	SHER
S8	262	60	2.3	11.4	3821	4.9	14.1	4.1	4179.3	SHER
S9	283	66	2.2	10.1	10301	4.8	15.2	5.8	10687.6	SHER
S10	66	9	1.8	5.2	527	3.3	4.8	0.8	616.9	SHER
S11	305	78	2.7	11.6	2957	5.8	16	4.7	3380.3	SHER
S12	166	21	1.5	5.1	1566	2.9	7.6	1.4	1771.7	SHER
S13	93	15	1.1	3.7	1769	2.2	7.8	0.8	1892.5	SHER
S14	38	9	1.6	4.8	135	1.9	8.4	0.5	198.8	MER
S15	74	18	1.6	5.5	527	3	7.6	0.9	636.7	SHER
S16	170	57	1.6	6.4	6048	2.9	13.1	4	6303.3	SHER
S17	166	33	1.6	6.7	3024	3.4	8.1	2.2	3244.9	SHER
S18	271	27	1.1	5.5	12717	1.8	13	1.2	13037.6	SHER
Mean	196	41	1.9	8.8	4128	3.6	12.5	2.7	4393.7	SHER

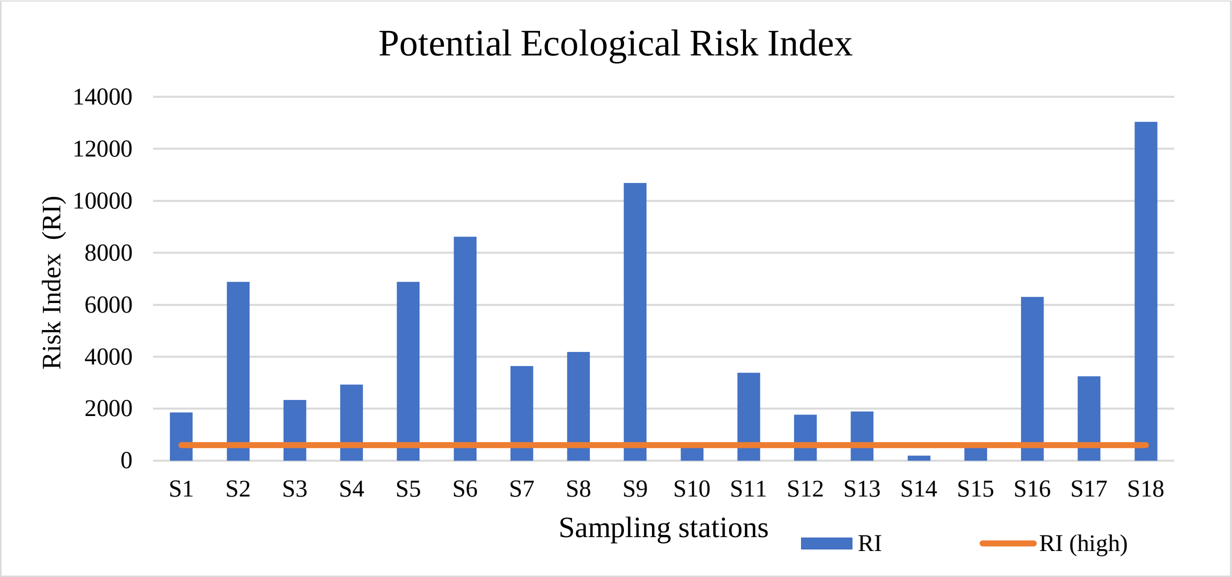

Fig. 8. Potential ecological risk index at each sampling stations (RI high at 600; the values exceeded 600 are considered as significantly high ecological risk).

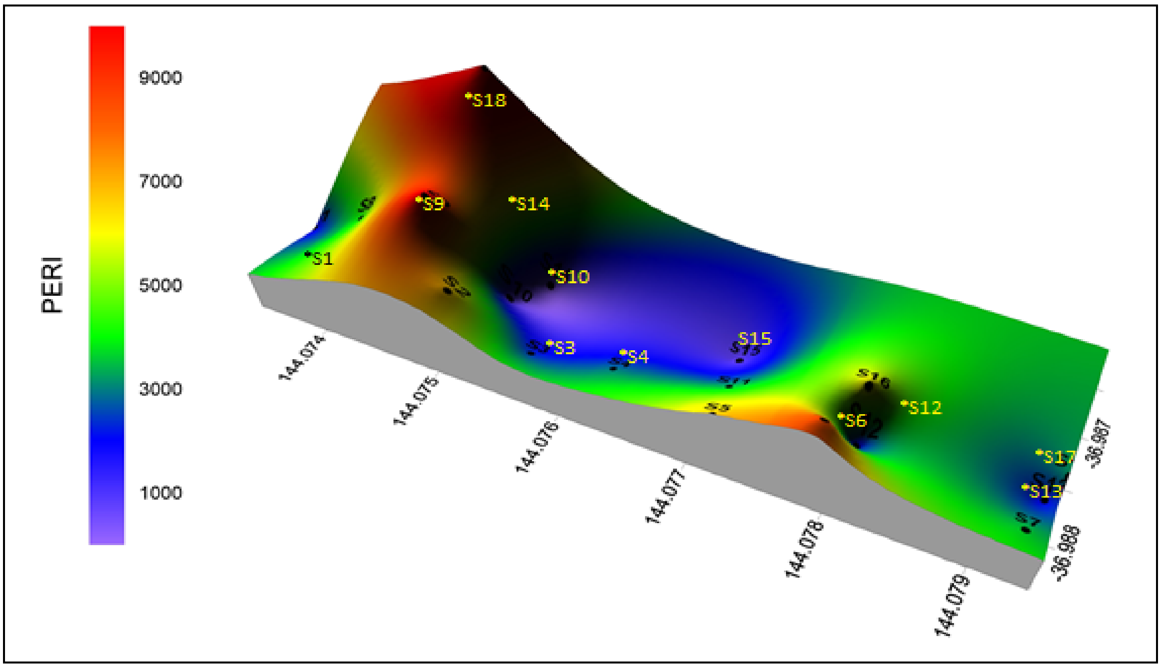

Fig. 9. 3D map showing the Potential ecological risk index (PERI).

4. Conclusion

This work presents the metal contamination assessment in the soils of the Maldon legacy mine site in Central Victoria Australia by collecting and analysing soil samples. The metal analyses results demonstrated that Mn has the highest median concentration in the study area followed by Zn and Cd is the lowest with the metals in the following order Mn> Zn> As> Cr> Pb> Cu> Ni> Co> Hg> Cd. The results were assessed with Contamination Factor (CF), Geo-accumulation index (I*geo*), Pollution Load Index (PLI), Pollution Index (PI), Integrated Pollution Index (IPI), and Nemerow Integrated Pollution Index (NIPI). The geo-accumulation index and contamination factor assessment revealed that the study area is extremely and heavily contaminated by Hg and As respectively. The Pollution Load Index revealed that the entire study area (except S13, S14 and S15) is highly contaminated and the Pollution Index (PI) displayed that the study area is highly polluted with Hg and As and moderately contaminated with, Pb, Zn, Cd and Cu. Integrated Pollution Index also shown the presence of high level contamination by Hg and As. In general, it is considered that the entire study area is extremely contaminated with Hg and As and moderately contaminated with Zn and Pb. Other metals are not considered as problematic in this legacy mine site. In addition to the applications of above indices, the ecological risk of the metal contamination was assessed with Potential Ecological Risk Index (PERI) method and found that the entire study area (except S14 sampling station) provide significantly high ecological risk and S14 acts as moderate ecological risk. The presence of elevated concentrations of Hg and As are of high concern due to the potential health impacts of these metals to the human health. This is highly significant as the study area is located close to the residential areas and the possible surface water contamination during precipitation and subsequent runoff and through the wind activity. The study highly recommend that the human health risk should be seriously considered and follow up action should be taken at the earliest. The study shows that contamination indices are valuable tools in determining the contamination assessment, which will be useful for decision makers, land use managers, environmental planners and local governments. These tools are also helpful in determining if further investigations required.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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Chapter- 6

Controlled burn and immediate mobilization of potentially toxic elements in soil from a legacy mine site in Central Victoria, Australia

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Controlled burn and immediate mobilization of potentially toxic elements in soil, from a legacy mine site in Central Victoria, Australia

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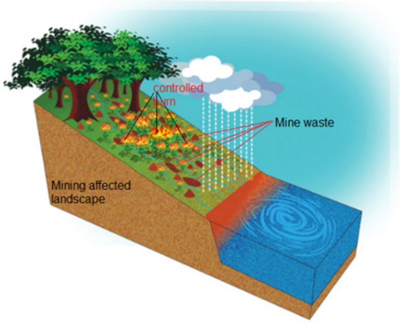
HIGHLIGHTS

- Legacy gold mining sites have elevated potentially toxic element (PTE) concentrations.
- PTEs are sequestered in the soil organic matter and vegetation, limiting its mobility.
- Controlled burns remobilized PTEs such as Zn, Mn, Cd & Hg.
- Liberated PTE mobilized to soil, and may be to air & water environment.
- Controlled burns should be carefully considered as a forest management strategy.

GRAPHICAL ABSTRACT



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ABSTRACT

Conducting controlled burns in fire prone areas is an efficient and economic method for forest management, and provides relief from the incidence of high severity wild fires and the consequent damage to human property and ecosystems. However, similar to wild fires, controlled burns also affect many of the physical and biogeochemical properties of the forest soil and may facilitate remobilization of potentially toxic elements (PTEs) sequestered in vegetation and soil organic matter. The objective of the current study is to investigate the mobilization of PTEs, in Central Victorian forest soils in Australia after a controlled burn. Surface soil samples were collected two days before and after the controlled burn to determine the concentration of PTEs and to examine the physicochemical properties. Results show that As, Cd, Mn, Ni and Zn concentrations increased 1.1, 1.6, 1.7, 1.1 and 1.9 times respectively in the post-burn environment, whereas the concentrations of Hg, Cr and Pb decreased to 0.7, 0.9 and 0.9 times respectively, highlighting considerable PTE mobility during and after a controlled burn. Whilst these results do not identify very strong correlations between physicochemical properties of soil and PTEs in the pre- and post-burn environments, PTEs themselves demonstrated very strong and significant correlations. The mobilization of As, Hg and other toxic elements raise potential health concerns as the number of controlled burns are projected to increase in response to climate change. Due to this increased level of PTE release and remobilization, the use of any kinds of controlled burn must be carefully considered before being used as a forest management strategy in mining-affected landscapes which include areas with high PTE concentrations.

1. Introduction

Potentially toxic elements (PTEs) such as As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn, contribute to contamination in soil and aquatic

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environments, and this is of great concern due to the immediate risks to human and ecosystems health and the perceived persistency of these elements in the environment (Tijani et al., 2005; Zhuang et al., 2014; Soliman et al., 2015). Gold and other metal mining activities may contribute to significant PTE contamination in many rural areas (Sultan, 2006, 2007; Taylor et al., 2010; Pearce et al., 2012; Krishna et al., 2013). Mining, milling and grinding operations, which result in concentrations of fine ore materials, together with the subsequent disposal of tailings and mine and mill waste water, are a source of water, soil and air contamination in the vicinity of the mine site (Schaider et al., 2007; Navarro et al., 2008; Esshaimi et al., 2012; Doronila et al., 2014). This is particularly significant in legacy mine sites, where environmental regulations were neither enforced during active mining, nor at the time of mine closure. For example, Central Victoria, in Australia has a long history of gold mining since 1850 (McDonald and Powell, 2008) and has significantly contributed to the economy with the region producing more than 2500 t of gold (EER, 2015). However, mine closure left tonnes of mine waste materials rich in PTEs in the surface soils with resultant contamination of soils, water, air, and plants (Sultan, 2006, 2007; Pearce et al., 2010, 2012; Martin et al., 2014, 2016). Recent studies have reported As absorption by adults, specifically children living close to these abandoned sites in Central Victorian soils, are of growing concern (Pearce et al., 2010, 2012; Martin et al., 2013, 2014). Furthermore, most of these mine waste materials are located in forest areas, and are un-rehabilitated, leaving them prone to mechanical dispersion, which may increase their mobility and bioavailability.

Forest ecosystems generally absorb PTEs from natural and anthropogenic activities as most have an affinity for soil organic matter (SOM). This is particularly the case for Hg, Cu and Pb (Wei and Yang, 2010; Shcherbov, 2012; UNEP, 2013), and the rate of absorption depends on the amount of SOM, the fixation to clay minerals, local adsorption and desorption processes and their correlation with Al and Fe hydroxides and Mn oxides (Sipos et al., 2005; Kabata-Pendias, 2004, 2010; Reis et al., 2015). After entering forest ecosystems, PTEs may concentrate in the organic layers of the soil, sequester in sediments, form compounds with SOM and may be absorbed by plants and hence become immobile in the system (Grigal, 2003; Hernandez et al., 2003; Biswas et al., 2007; Obrist et al., 2008; Friedli et al., 2009; Shcherbov, 2012). Grigal (2003) reported that 90% of the Hg in the forest ecosystem is found to be associated with SOM in the forest floor, and in addition to Hg, other PTEs such as Cr, Cu and Pb are also found to be strongly bound in the system, whereas, Cd, Co, Mn, Ni and Zn are weakly bound (Tipping, 1998; Lawlor and Tipping, 2003). When forest fire, either as a wild or controlled burn occurs, combustion of the vegetation and SOM causes soil property alterations, which can release the sequestered elements from the system and become labile and will be able to remobilize, mostly through ash and smoke (Odigie and Flegal, 2011, 2014). This is particularly significant in the Central Victoria region of Australia, as the region is prone to wild fires due to weather patterns and types of dense vegetation and controlled burns are regularly applied in the region as a standard fire-risk reduction strategy.

Controlled or prescribed burning is the deliberate application of fire to forest fuels or agricultural lands, mainly in autumn or spring (but may also be applied in late winter) under stipulated settings to ensure such that well-defined targets are achieved (Wade et al., 1989). Preparation for agriculture and tree restoration, control of weeds and insects populations, wildlife habitat management, maintenance of biodiversity, fuel level reduction and other land management practices are usually the intention of careful application of controlled burns (Fernandez and Botelho, 2003). In general, controlled burns are of low to moderate intensity, and consume most of the forest floor layers and understory vegetation, with no or little damage to the canopy trees (Úbeda et al., 2005). The burn reduces the occurrence of a subsequent wildfire, or can reduce its intensity, by reducing the fuel loads both vertically and horizontally, which directly improve the fire control measures (Hatten et al., 2005). Therefore, controlled burning is considered to be a valuable tool in forest protection and wildfire mitigation (Fernandez and Botelho, 2003; Certini, 2005; Castellinou et al., 2010) and is practised in the fire prone forest landscapes in many countries in Europe, North and South America and Australia.

Fire intensity equates to the release of thermal energy as a result of the physical combustion process, and is defined as the measure of time averaged energy flux (Keeley, 2009). Severity is the response of an ecosystem to fire, which is gauged by the product of fire intensity and residence time (Certini, 2005; Neary et al., 2005; Keeley, 2009). Physically fire intensity is quantified using temperature, flame height, duration of fire, and the emission of pyrogenic gases (Lentile et al., 2006). It is mostly controlled by fuel (vegetation) types and density, moisture content in the fuel, weather pattern, topography and other local factors (DeBano et al., 1998). Intensity can be measured by measuring the fire temperature using thermocouples or can be inferred from the observation of flame length and fire spread rate (Smith and Wooster, 2005; Dennison, 2006). Fire severity provides information about how fire intensity affects ecosystems and is sometimes used wrongly as a synonym for fire intensity (Certini, 2005; Keeley, 2009). Fire severity measures are based on number of methodologies, and among them, observation of ash colour is significant (Úbeda et al., 2009; Pereira et al., 2011). Another relevant term is 'burn severity', which sometimes is mistakenly used for fire severity. Burn severity identifies the impact of fire on soil and plants when the fire is extinguished, and is related to the post-fire phase. Further fire-related information is available in a number of studies (Certini, 2005; Neary et al., 2005; Lentile et al., 2006; De Santis and Chuvieco, 2007; Murphy et al., 2008; Safford et al., 2008; Keeley, 2009; Parsons et al., 2010; Mataix-Solera et al., 2011).

The intrinsic character of any kind of forest fire is the complex process of heat release during biomass combustion (Bento-Gonçalves et al., 2012). The burning biomass and ash can transfer heat to the soil surface, and it may reach up to 30 cm depth in the case of high severity wild fires (DeBano, 2000). As a result, fire can change the physicochemical, mineralogical and biological properties of the forest soil and surface materials (Certini, 2005; Verma and Jayakumar, 2012). However, most of these alterations are ephemeral, such as pH and electrical conductivity (EC) (Arocena and Opio, 2003), with only a few being perpetual (Certini, 2005), and all alternations depend on fire severity (Dzwonko et al., 2015). Similar to wildfires, controlled burns also affect soil properties, but, often to a limited extent (Arocena and Opio, 2003; Castro et al., 2011; Pereira et al., 2011; Melendez-Perez et al., 2014). Fire typically increases pH values and EC of the soil, makes significant alterations in SOM levels, decreases soil permeability and porosity, resulting in the reduction of hydraulic conductivity and causing considerable loss in nutrient levels (Certini, 2005; Verma and Jayakumar, 2012). With these soil property alterations, many authors reported that wild fire is able to release PTEs (metals) from plants and soil organic matter from their sequestered phase (Odigie and Flegal, 2011, 2014; Burton et al., 2016; Kristensen et al., 2014; Odigie et al., 2016). For example, Ignatavicius et al. (2006) reported an increase in concentrations of Pb, Cu, and Zn (21 to 74%) in Lithuanian river waters (August–September 2002) one month after a series of 497 forest and peat bog fires in the region. Similarly, remobilization of Fe, Mn and Hg after the 2009 Station Fire in Los Angeles, USA was observed (Burton et al., 2016). In conjunction with this, Kristensen et al. (2014) reported the remobilization of natural and industrial Pb (4 to 23 mg kg^{-1}) after three wild-fires in Australia (the Tostaree Fire in Victoria, at Red Hill and the Kelmscott Fire in Western Australia). In addition to this, Odigie et al. (2016) linked the occurrence of PTEs in the sediments of the Lake Thomson in Chile with forest fires which occurred in mid 1900s. Though these studies were directed to establish the consequence of wild fire on PTE mobility, there is a general lack of research in the global literature on the effects of controlled burns in PTE mobility, specifically on legacy mining landscapes.

Forest fire and subsequent PTE mobilization is particularly pertinent to legacy mining areas because of the presence of an extensive volume of tailings and other mine waste materials with elevated PTE concentrations. Many such mining affected landscapes are located in forest regions, as in Central Victoria, which are prone to frequent and uncontrolled wild fires and their incidence and severity are predicted to increase because of climate change effects, which may require more controlled burns (Hennessy et al., 2005; Westerling et al., 2006). Given that fires are able to mobilize PTEs from SOM and vegetation, the objective of the current study is to (i) determine the mobility of 10 PTEs (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn) which are toxic to human health and ecosystems, in the surface soils of a legacy mine site (Maldon) in the Central Victorian region of Australia, after a controlled burn, and (ii) to assess the change in soil physicochemical characteristics immediately after fire. Assessing the mobility of PTEs in any legacy mine site after a controlled burn is necessary as the excess PTE concentrations can influence animals, and plants as well as human health (Hindwood et al., 2003; Kelly et al., 2006; Nunes et al., 2017). This is particularly significant in the study area as it is adjacent to a residential area and the Central Victorian forest catchment provides potable water resources to a number of local communities. The outcome of this study will be useful for environmental scientists and land managers in reviewing the potential for contamination after a controlled burn, and the result will provide guidance to post-fire watershed management practices in terms of water quality, which will be useful for water distribution managers. Results will also be useful for local, state and national authorities and environmental agencies to assist better environment and fire management practices within legacy mining landscapes. In addition, this work may also assist un-rehabilitated mine site management in other fire prone states or countries. Although it is recognised that the study area is relatively small, the mobilization of PTEs during or after any kind of forest fire (including controlled burns) is significant because more than a million un-rehabilitated legacy mine sites exist across the globe, and many of them are in fire prone forest areas (UNEP, 2001).

2. Materials and methods

2.1. Description of the study area

Maldon, a legacy gold mining area, is located 145 km NW of the city of Melbourne and 40 km SW of the City of Greater Bendigo, where small scale mining was started in 1853 and subsequently, production moved to larger mining companies. Mining was stopped in 1926 due to difficulties encountered in the mining process. In this historical mining period, the Maldon area produced more than 56 t of gold from a number of mining sites (Cherry and Wilkinson, 1994), and was the eighth largest City in the State of Victoria in Australia (Egold, 2017). Early gold extraction techniques used cradle and gold pan to separate the gold from alluvium, but later moved to puddling, quarts reef mining, deep lead mining and various forms of sluicing (Egold, 2017). Among these approaches, quartz reef mining was the most widely practiced, requiring construction and operation of crushing mills and stamping batteries. Today, constructed adits, shafts and open cut mining trenches used to access the sulphide bearing ore, can be seen in Maldon as mining remnants (Cherry and Wilkinson, 1994; Maldon, 2017). The mining resulted in the accumulation of tonnes of mine waste materials of many kinds on the surface, often seen as mullock heaps. A specific mine site located east of the Union Hill mine and west and south of the Stump Street was selected for the controlled burn influenced PTE mobility study (Fig. 1). It comprises 20 acres of land which falls under the jurisdiction of public land (State forest) and is adjacent to number of residences.

The study area experiences cold wet winters (7.5–20.5 °C) and warm dry summers (16.4–40.3 °C) (Taylor and Alley, 2001; BoM, 2017), with an annual average rainfall of 540 mm (BoM, 2017). The major vegetation in the area is a mix of native and introduced species including *Ulex europaeus* (Gorse), *Cassinia arcuta* (Chinese shrub), *Juncus acutus* (Shirp), *Asphodelus fistulosus* (Onida), *Acacia pycnantha*, and *Eucalyptus radiata*.

A creek line runs in an easterly direction, passing along the middle of the study area. The northern half of the study area slopes slightly towards the south, and the southern half slopes (slightly) towards north, thus directing all the runoff to the creek. In this public land, disturbed overburden with burrows, soil heaps, and scattered quartz fragments demonstrate legacy gold mining activities. The occurrence of moderate-to-highly disturbed (by legacy mining) soils, together with more than a century's accretion of old mining waste materials in the area, makes it ideal for evaluating legacy mining impacts on the environment. The study area is notable as it is adjacent to residential areas (Fig. 1) and has a creek running through middle of this public land

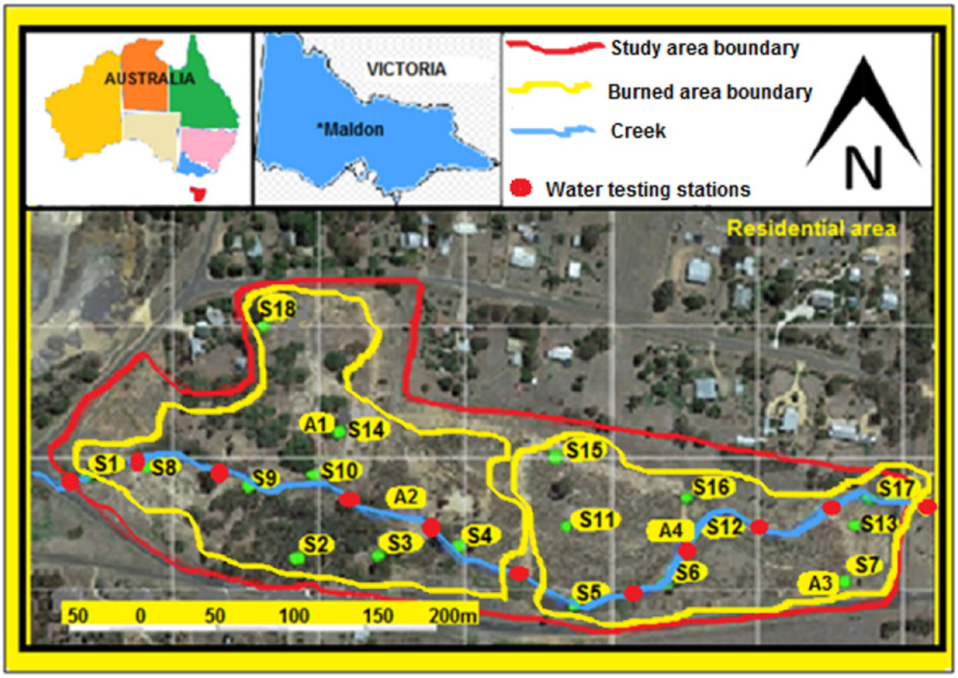

Fig. 1. Location of the study area with soil sampling (S1 to S18), ash sampling (A1 to A4) and water testing (red spot along the creek) stations. Proximity to housing is noted. >80% of the study area has been affected by controlled burns.

that could carry contaminants 1.6 km to downstream residential areas and 8 km to a small water body and 30 km to a large reservoir (McCay reservoir).

2.2. Controlled burn, soil sampling and analysis

Forest floor material, also called detritus, is a substantial segment of the forest ecosystem, and is mainly composed of organic matter, mixture of minerals, biogenic substance and water soluble organic compounds, which act as a potential reservoir of toxic elements (Shcherbov, 2012). In the Maldon study area, significant growth of an invasive species Gorse (*Ulex europaeus*) is the major vegetation, and controlled burning is a standard fire risk reduction and weed management strategy. The investigated burn was carried out by the State Department of Environment Land Water and Planning (DELWP) and Parks Victoria fire crews on 20th August 2015 (Fig. 2), which was the end of the winter season. The day was calm and sunny with wind moving in a SW direction. The fire was started around 10:00 am by the Parks Victoria fire crews, at the western part of the study area and moved to east. Immediately after ignition, the fire grew rapidly due to the presence of a significant fuel load (Fig. 2) and the smoke moved in a SW direction. Approximately one and a half hour was more than enough to burn the majority of the forest floor fuel load. While the seemingly intense fire lasted for only several minutes in one location and subsided normally, slow burning of plant materials was observed up to three days after ignition. The fire burned most of the shrub type vegetation (<2 m in height), including Chinese shrub (*Cassinia arcuta*), Onida (*Asphodelus fistulosus*), and also the ground cover litter (Fig. 3). More than 80% of the study area was affected by the fire, as it was completely covered by vegetation and litter as a result of there being no history of any kind of fire in the area (information from DELP). There were high quantities of ash observed in some pockets in the burned area, where thick vegetation, particularly tree branches, were burnt. In some spots, it was grey in colour, indicating the moderate to high fire severity (Úbeda et al., 2009). The fire left all canopies of the eucalyptus radiate untouched, but consumed some of the barks and roots, and all of the shrubs were completely burned (Fig. 3).

Surface soil and ash samples are important in this study as they bear relevant products of the fire event, and can be mobilized by precipitation and subsequent surface runoff, wind-borne transport, and can cause negative impacts on human and other animals (Schaider et al., 2007). Furthermore, the majority of the PTEs in the forest ecosystem are concentrated in the organic layers of the soil in the forest floor, since they have an affinity for soil organic matter (SOM) (Hernandez et al., 2003; Shcherbov, 2012). To examine the PTEs mobility in the surface soils after the controlled burn, 18 surface soil samples (not >3 cm deep) were collected two days before the burn and 18 samples were collected two days after the burn from the same sampling stations (S1 to S18: Fig. 1), using the STAR sampling method with trace metal clean technique procedures (Ritson et al., 1999; Soto-Jimenez et al., 2006; Taylor et al., 2010; Odigie and Flegal, 2011). In addition to the soil samples, four ash samples (A1 to A4, Fig. 1) were also collected, having a maximum of approximately 200 g from each site.

Fig. 2. Controlled burn conducting in the Maldon study area (Victoria, Australia) on 20th August 2015.

In most of the sampling stations, post-burn soil samples represent a mix of both soil and ash particles. After removing the debris and rock particles, approximately 1 kg of bulk surface soil samples were collected within an area of 1600 cm^2 (40 cm × 40 cm) from each station, two days before the burn and two days after the burn. The pre-burn and post-burn sampling stations were selected as close as possible (not 5–10 cm). Soon after collection, at each sampling station (S1 to S18) the soil samples (also ash) were carefully transferred to clean, dry and labelled polyethylene containers and carried to the Federation University Australia soil and water laboratory. Samples were placed in an oven (Memmert GMBH-D 8540) at 60 °C for 24 h. After removing the rock pieces, oven dried samples were hand crushed and sieved through a 2 mm stainless steel sieve. The pre-burn and post-burn sieved samples (<2 mm) were stored in air-tight polyethylene containers until all analyses were completed. Soil pH and EC were determined with standard analytical procedures (US-EPA 9045D & 9050A respectively) using a pH meter (WP-80) and an EC meter (Hanna HI-8633) (Rayment and Lyons, 2014). SOM and carbonate content (both as percentages) were determined with Loss on Ignition (LOI) method using a muffle furnace (Eurothem 2132) (Rayment and Lyons, 2014). The pH and EC of creek water sample were measured at 11 stations along the creek (W1 to W11 Fig. 1) with an Horiba multi-parameter water quality meter (IC-U51-2M), two days before the burn and two days after the burn. Ash samples were also collected from four different stations (A1 to A4) (Fig.1) and analysed for PTE concentrations and physicochemical properties. 10 g of soil and ash samples were used for pH and EC analysis and <2 g were used for soil organic matter and carbonate content analysis.

PTE concentrations in soil and ash were determined by Ultra-Trace Level Methods, using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) with Aqua Regia Digestion (GEO-AR01) in a NATA (National Association of Testing Authorities) accredited laboratory (Accreditation No. 825). Dried and sieved soil samples were milled using stainless steel bowls and a milled sample of 0.5 g was used for PTE analysis. The soil samples were digested with aqua regia in a graphite heating block and allowed to cool. The resulting solution was diluted with deionized water, thoroughly mixed and analysed by ICP-AES. Immediately after this analysis, the results were revised for elevated concentration of Hg and diluted appropriately. These diluted and mixed samples were then analysed by ICP-MS for the remaining potentially toxic elements and the results were corrected for inter-element spectral interference (Santoro et al., 2017). A similar analysis scheme was also conducted for ash samples with a similar amount (0.5 g) of samples.

2.3. Data analysis

The data were statistically analysed using SPSS (version 23) and R (version 3.4.1) software(s). Some descriptive statistics (minimum, maximum, range, median, percentiles (10th, 25th, 50th, 75th and 90th) and interquartile range (IQR)) of the soil properties such as pH, EC, SOM, carbonate content and PTE analysis were applied to the pre-fire and post-fire results.

Pre-burn soil sample data from the study area such as physicochemical properties including pH, EC, SOM, carbonate content and PTE concentrations were compared with corresponding post-burn sample data in order to establish the influence of controlled burn on the concentrations of PTEs in the soil and the physicochemical properties of the soil. Moreover, the pH and EC of creek water flowing through the middle of the study area were also compared. The Wilcoxon matched pair test was conducted to the pre-burn and the corresponding post-burn

Fig. 3. Showing a part of the study area before (left), during (middle) and after (right) the controlled burn.

data to verify if statistically significant differences existed between them, including water pH and EC. Spearman rank correlation coefficients were determined to obtain the relationships between the pre- and post-burn physicochemical properties of the soil and the corresponding concentrations of PTE in the soil/ash environment include relationship between the PTE themselves.

3. Results and discussion

3.1. Physicochemical characteristics of soil

The descriptive statistics included minimum, maximum, range, median, percentiles and interquartile range (IQR) of physicochemical properties of soil and water in two sampling periods (BF and AF) were depicted in Table 1. The post-burn soil samples demonstrated significantly higher pH ($p < 0.05$), EC ($p < 0.01$), and SOM ($p = 0.07$) compared with pre-burn soil samples with difference in values amounting to a factor of 1.2, 2.2, and 1.4 respectively. However, the carbonate content showed only minor variations in the pre- and post-burn environment. In the case of creek water, at individual locations, pH may showed up to 3 units post-burn difference, however the median pH for all sampling stations calculated before and after the controlled burn show no statistically significant difference. Conversely, the median EC value of water samples showed significant ($p < 0.0001$) increase after the burn, with a difference up to 100 μS cm^{-1} being was observed.

3.1.1. Soil pH

The soil pH and its relationship with PTEs in soils have been noted by many authors, and it is generally agreed that pH is generally related to PTE mobility (Bergkvist et al., 1989; Violante et al., 2010), speciation (Drever, 1988), solubility and uptake by plants (Adriano, 1986; Breulmann et al., 2002). The solubility and mobility of PTEs increased with lowering the soil pH, but this change has been shown to decrease the organophyllic characteristics of some PTEs (Drever, 1988).

The pre-burn and post-burn pH distribution is depicted in Fig. 4(a). In the post-burn soil environment, the soil acidity is slightly reduced compared to the pre-burn environment and the pH becomes slightly basic. Among the 18 sample stations, 12 stations (67%) showed increase

Table 1
Descriptive statistics (minimum, maximum, range, median, percentiles and interquartile range (IQR)) of pH, EC (μS cm^{-1}), SOM (%) and carbonate content (Carb %) of soils and pH and EC (μS cm^{-1}) of water samples, both from the pre-burn (before fire –BF) and post-burn (after fire – AF) environment ($N = 18$).

Soil

	pH-BF	pH-AF	EC-BF (μS cm^{-1})	EC-AF (μS cm^{-1})	SOM-BF (%)	SOM-AF (%)	Carb-BF (%)	Carb-AF (%)
Minimum	3.6	3.8	95	174	4	3	0.8	0.6
Maximum	5.6	8.6	970	2800	42	33	2.4	2.4
Range	2.0	4.8	875	2626	38	31	1.7	1.9
Median	4.3	4.8	376	863	9	15	1.5	1.4
Percentiles								
10th	3.8	4.0	200	253	5	4	0.8	0.6
25th	3.9	4.3	238	423	7	9	1.1	1
50th	4.3	4.8	376	863	9	15	1.5	1.4
75th	5.1	6.4	553	1249	14	26	1.9	1.7
90th	5.3	8.1	939	2170	24	29	2.4	2.1
IQR	1.2	2.1	316	826	7	17.5	0.8	0.7

Creek water

	pH-BF	pH-AF	EC-BF (μS cm^{-1})	EC-AF (μS cm^{-1})
Minimum	6.8	6.1	63	67
Maximum	9.1	11.0	172	275
Range	2.6	4.9	109	208
Median	7.7	7.8	123	170
Percentiles				
10th	6.9	6.3	69	75
25th	7.2	7.2	98	124
50th	7.7	7.8	123	170
75th	8.4	8.4	157	225
90th	9.0	10.5	171	266
IQR	1.2	1.2	59	101

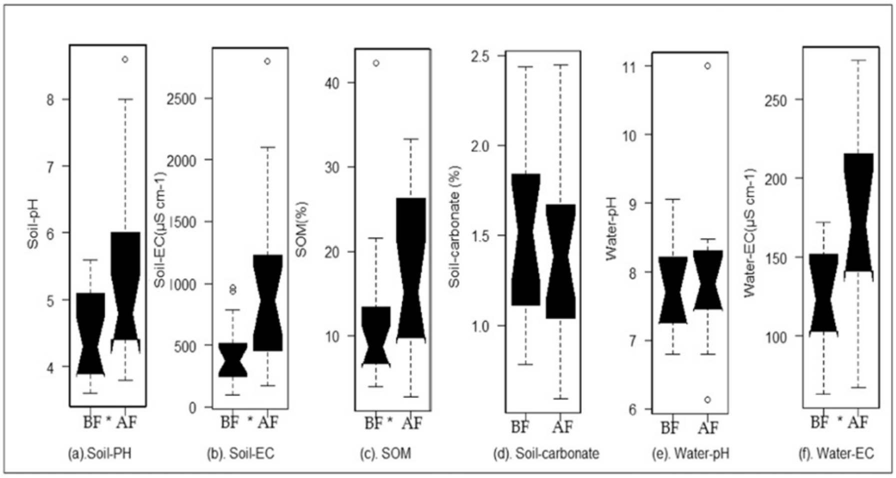

Fig. 4. Notched box plot showing (a) soil-pH, (b) soil-electrical conductivity (EC), (c) soil organic matter (SOM), (d) soil carbonate content, (e) water-pH and (f) water-EC observed before (BF) and after (AF) the controlled burn (NB: o represents outliers).

in pH value and 5 stations (28%) showed reduction in pH and one station (5%) showed no change in pH after the controlled burn. The highest pH variation observed is 3.7, followed by 3.5 and the lowest is 0.3 and no variation observed at sampling station S3. In two stations, post-burn pH increased to 7.6 and in one station pH increased to 8.6.

This increase in pH is observed at sampling stations where high amounts of ash were deposited during the burn due to the local increase in fuel load. It is thought that the increase in pH is mainly due to the release of large amounts of oxides, hydroxides, carbonates and cations through ash and the reduction in the production of organic acids as have been mentioned in other studies (Ulery et al., 1993; Khanna et al., 1994; Ulery et al., 1995; Certini, 2005; Goforth et al., 2005; Verma and Jayakumar, 2012). In similar works in other laboratories (Sever et al., 2001; Badía and Marti, 2003; Marcos et al., 2007) and field studies (Arocena and Opio, 2003; Úbeda et al., 2005; Campos et al., 2016) including controlled burn studies (Deluca and Zouhar, 2000; Arocena and Opio, 2003; Úbeda et al., 2005), there were also reported increase in soil pH after fire. This post-burn increase in soil pH is reported as ephemeral, as it has the tendency to step back to the pre-burn levels, after several months, although this has taken several years in some environment (Ulery et al., 1993, 1995; Kim et al., 2003; Certini, 2005; Jovanovic et al., 2011).

3.1.2. Electrical conductivity (EC)

In the case of EC (Fig. 4(b)), thirteen sample stations (72%) showed increase in EC values, and five stations (28%) showed decrease after the burn. The highest EC variation observed is 2011 µS cm^{-1}, followed by 2005 µS cm^{-1} and 1026 µS cm^{-1} and the lowest is 28 µS cm^{-1}. In a similar mechanism to pH change, the increase in post-fire soil EC is linked to the combustion of vegetation, SOM and the associated deposition of ash, which release of high amounts of oxides, hydroxides, cations and carbonates (Ulery et al., 1993; Khanna et al., 1994; Ulery et al., 1995; Certini, 2005; Verma and Jayakumar, 2012). Similar to pH, EC is also considered as ephemeral in nature as it has the tendency to step back to the pre-fire levels, over time (Ulery et al., 1993, 1995; Kim et al., 2003; Certini, 2005; Granged et al., 2011). Among the 18 sample stations, 7 stations displayed both increase in pH and EC, possibly due to the increase in fuel load, intense burn and the resulting addition of ash.

3.1.3. Soil organic matter (SOM)

The influence of forest fire on SOM is highly dependent on the intensity and types of fire, nature of fuels, soil moisture and many other factors so that generalised trends cannot be predicted (González-Pérez et al., 2004; Verma and Jayakumar, 2012). Low severity controlled burns result in a small change in the SOM, whereas a high severity fire consume most of the organic matter (Johnson, 1992; Castro et al., 2011; Verma and Jayakumar, 2012). The SOM content in the study area (Fig. 4(c)) was measured using loss on ignition method and is reported as percentage (%). In the study area, 12 stations (67%) showed increase in SOM content after burn, whereas, 6 stations showed (33%) reduction in SOM. The increase may be due to the remains of burned organic matter from plants in the form of ash, while the reduction may be due to the removal of existing SOM by volatilisation. The highest variation observed is 24.44 followed by 24.43 and 19.8% and the lowest variation observed is 0.4%. Similar to pH and EC, the post-burn SOM increase is also ephemeral in nature, as it reduces with time due to the mobilization of ash (Hernández et al., 1997; Kim et al., 2003; Granged et al., 2011). In the pre-burn and post-burn environment, the highest SOM values were detected in samples collected close to the creek.

3.1.4. Carbonate content in soil

The measurement of carbonate (Carb) content expressed as % in the soil showed only minor variations before and after the burn (Fig. 4(d)). In the study area, 8 stations (44%) highlighted an increase and 10 stations (56%) highlighted decrease in carbonate content after the controlled burn. The highest variation observed between pre-burn and post-burn samples was 1.3% followed by 0.9% and the least variation observed was 0.11%.

The physicochemical properties of the surface soil is altered by the process of controlled burn such as organic matter combustion, heating and ash deposition (Certini, 2005; Verma and Jayakumar, 2012) and hence such changes are expected in the Maldon study area after the controlled burn. The data analysis clearly indicate that increase has observed in the soil pH, EC and OM in the post-burn environment (2 days after fire) compared to the pre-burn environment (2 days before burn) as noted by many authors (Hernandez et al., 2003; Certini, 2005; Quintana et al., 2007; Boerner et al., 2009; Verma and Jayakumar, 2012), but the carbonate content showed a reduction in the median value in the post-burn environment. The fire related pH and EC alterations (mainly increases) are mostly attributed to the combustion of forest fuels (plant materials including leaf litter), organic matter and the associated ash deposition (Ulery et al., 1993, 1995; Verma and Jayakumar, 2012; Campos et al., 2016).

3.2. Creek water pH and EC

When considering the median value of the creek water pH, there is no difference observed, however, individual testing stations showed increase of up to three units in pH value. Among the 11 water sampling stations, nine stations (82%) displayed an increase in pH.

When comparing the median EC value of the Creek water, the post-burn results displayed 38% increase, in such a way that all sampling stations displayed increased EC from 4 to 103 μS cm^{-1}. The increase in water pH and EC (Fig. 4(e) and (f)) is most probably attributed to ash particles during and after fire, which have high concentrations of cations, oxides, hydroxides and carbonates (Ulery et al., 1993, 1995; Goforth et al., 2005; Verma and Jayakumar, 2012). Similar outcomes were observed by Costa et al. (2014) with an increase in water pH and EC after fire, which were influenced by the transportation of ash and nutrients from the burned slope to the water resources. This immediate increase in water pH and EC is considered to be due to the mobility of ash through wind activity (in the absence of rainfall).

3.3. Physicochemical characteristics of ash

Ash is the solid material residue deposited on the soil surface from biomass burning, which consists of charcoal, charred organic material and residual mineral matter (Bodi et al., 2011; Pereira et al., 2014), and can deliver scientific information about fire influence on landscape. The ash presents as patches of white, grey and black colour and provides information about organic matter loss and fire severity (Blank and Zamudio, 1998; Keeley, 2009). Black ash contains a higher amount of charred organic materials and corresponds to a low to moderate fire severity, whereas, grey and white ash corresponds to high fire severity (Pereira et al., 2014). The major chemical constituents found in ash are Ca, K, Mg and P (Gabet and Bookter, 2011), and when blended with water the resulting slurry has a high pH value (Ulery et al., 1993). The pH, EC, organic matter (OM) and carbonate content of four ash samples collected just after the controlled burn are summarised in Table 2. The ash samples demonstrated high alkalinity with pH ranges from 9.1 to 11.4, and the EC ranges from 1173 to 28,500 μS cm^{-1}. The elevated pH and EC values of ash (compared with soils) are attributed to the formation of oxides, hydroxides and carbonates during the fire and the increase in amount of mineralised nutrients in ash (Ulery et al., 1995; Certini, 2005; Úbeda et al., 2009; Pereira et al., 2011; Verma and Jayakumar, 2012; Bodí et al., 2014). The OM ranged from 1.11% to 39.83% and the carbonate ranges from 10.37% to 37.77%.

The variations in ash properties are due to the amount of fuel burned, types of fuels, moisture content in the fuels, and fire severity in each sampling stations. The high pH value of ash 1 sample include a high carbonate content and grey colour demonstrated that this ash was produced at high temperature with high fire severity (Etiegni and Campbell, 1991; Ulery and Graham, 1993; Henig-Sever et al., 2001; Goforth et al., 2005; Pereira et al., 2008). The high OM content in ash 2 and its dark colour may be due to the incomplete combustion of vegetation (Goforth et al., 2005; Bodí et al., 2014). Similar to the case of soil, it is reported that ash pH, EC and OM also show ephemeral characteristics (Ulery et al., 1993; Campos et al., 2016).

3.4. Potentially toxic elements in pre-burn and post-burn soils

In the forest ecosystem, soil surface is considered the most affected area during forest fire (Mandal and Sengupta, 2006; Odigie and Flegal, 2014; Campos et al., 2015). The extend and severity of this burning affect varies with weather pattern, forest topography, vegetation types and density, fire intensity, maximum temperature reached, soil moisture, amount of ash production, and post-fire climatic conditions (Certini, 2005; Maia et al., 2012; Verma and Jayakumar, 2012).

During any kind of forest fire, combustion of vegetation and soil organic matter, release the associated PTEs and convert them into a labile form, which increase the PTE mobility (Young and Jan, 1977; Certini, 2005; Biswas et al., 2007). During combustion, when the temperature reaches 180 °C, volatilization (slight distillation) of organic compounds begins, and this may continue up to 200 °C. This is followed by volatilization of nutrients, which starts at 200 °C and may continue up to 400 °C (Neary et al., 1999). In general, the influence of fire on organic matter comprises volatilization and charring, resulting in the partial or complete removal of forest floor litter (Simard et al., 2001), but organic matter recovery in the burned area is rapid through the natural and artificial reintroduction of vegetation (Certini, 2005). Fire can remobilize up to 85% of Hg and Pb as airborne components (dust and fly ash), whereas Cu and Co can be enriched in residue formed from the biomass burning (Narodoslawsky and Obernberger, 1996; Nzihou and Stanmore, 2013). This results in elevated concentrations in ash samples and rarity in post-fire soils (Costa et al., 2014; Campos et al., 2016). The elevated concentration of PTEs in ash make it as a primary source of post-fire PTEs, which can be effectively transported to distal areas (include downslope surface water resources) by rainfall runoff and wind activities (Yarmonenko, 2007; Bogacz et al., 2011; Campos et al., 2015, 2016).

When comparing the PTE concentrations in the pre-burn and post-burn soil environment, it has been shown that some of the PTEs have evidenced an increase in concentrations, while others decrease. Both can be considered as PTE mobility, especially if the difference in median values exceeds 10%. The descriptive statistics (minimum, maximum, range, median, percentiles and IQR) of pre-burn and post-burn PTE analysis data are depicted in Table 3 and summarised in Fig. 5. The median concentration of PTEs from highest to lowest in the pre-burn and post-burn samples were found to be in the same order (Mn > Zn > As > Cr > Cu > Pb > Ni > Co > Hg > Cd) and the post-burn concentrations of Zn, Mn, Cd, As, Ni, and Co were higher than their pre-burn concentrations, with values differing up to 7.8, 9.2, 10, 30.2, 3.8 and 3.9 times respectively. The concentrations of Hg, Pb and Cr were less in the post-burn samples, compared with pre-burn samples with values differing up to 2.2, 3.5 and 2 times respectively.

Zn demonstrated an increase in median concentration of 87% in the post-burn soil samples compared to the pre-burn samples. Twelve sampling station (66%) highlighted an increase in Zn concentrations, whereas other stations (44%) highlighted decrease. Zn in soil is more sensitive to soil pH changes than any other toxic element in the soil environment, and its mobility has also been found depend on soil pH (Chirenje et al., 2006).

When comparing the pre-burn and post-burn median Mn concentrations in the soil, the post burn soil showed 72% increase compared with pre-burn soils. Among the 18 sampling stations, 12 samples (66%) displayed increase in post-burn soil Mn concentration, which may be due to the presence of ash content in the soil as most of the Mn is reported to be stored in the plant leaves (Parra et al., 1996; Costa et al., 2014). The decrease in Mn concentration was observed in the sampling stations close to the creek, where leaf litter was comparatively lower compared to other soil samples. The highest Mn variation observed was 794 mg kg^{-1} at S3 and the least variation observed was 1 mg kg^{-1} at S16. The current increase in post-burn Mn concentration is supported by previous studies (Chambers and Attiwill, 1994; Parra et al., 1996; Costa et al., 2014).

Compared to other metals in this investigation, the concentration of Cd in the soil is very much lower. However, according to the median values, there was a 45% increase in Cd observed in the immediate post-burn environment, and it is noted that accumulation of Cd in the soil is related to sorption by SOM, clay mineral fixation and association with Mn oxides, Fe and Al oxides and hydroxides (Sipos et al., 2005; Kabata-Pendias, 2010).

Table 2
pH, EC, OM, carbonate content and colour of ash samples collected after the controlled burn.

Sample	pH	EC (μS cm^{-1})	OM (%)	Carbonate (%)	Colour
Ash1	11.6	1173	1	38	Grey
Ash2	9.1	28,500	40	10	Light grey
Ash3	9.7	2600	19	19	Black
Ash4	9.6	18,900	18	17	black

Table 3
Showing the minimum, maximum, range, median, percentiles and interquartile range (IQR) of pre-burn and post-burn potentially toxic element concentrations (mg kg^{-1}) in the soil.

	As-BF	As-AF	Cd-BF	Cd-AF	Co-BF	Co-AF	Cr-BF	Cr-AF	Cu-BF	Cu-AF
Minimum	19	12	0.03	0.01	4	3	23	15	14	6
Maximum	185	544	0.37	0.7	25	16	57	61	59	90
Range	166	533	0.34	0.69	21	13	34	46	45	84
Median	85	95	0.11	0.16	8	9	38	33	30	29
Percentiles										
10th	31	40	0.03	0.04	4	3	24	16	18	16
25th	63	63	0.07	0.09	6	7	33	29	20	21
50th	85	95	0.11	0.16	8	9	38	33	30	29
75th	141	126	0.19	0.24	11	13	46	41	44	47
90th	163	203	0.27	0.55	17	16	54	54	57	70
IQR	78	63	0.12	0.15	5	6	13	12	24	26

	Hg-BF	Hg-AF	Mn-BF	Mn-AF	Ni-BF	Ni-AF	Pb-BF	Pb-AF	Zn-BF	Zn-AF
Minimum	0.1	0.1	85	70	7	5	12	8	22	12
Maximum	9.4	9.9	560	7000	23	26	76	52	328	611
Range	9.3	9.9	475	6930	16	20	64	45	306	599
Median	2.2	1.6	191	329	13	14	30	25	94	176
Percentiles										
10th	0.4	0.1	89	112	8	6	18	17	33	32
25th	1.1	1.2	116	211	11	12	19	21	51	85
50th	2.2	1.7	191	329	13	14	30	25	94	176
75th	4.8	2.9	284	490	19	22	38	36	186	268
90th	7.8	4.7	470	1501	23	23	54	48	266	526
IQR	3.7	1.7	168	279	8	10	19	15	135	183

The median values demonstrated that in the immediate post-burn soil environment, As increased 11.5% compared to the pre-burn environment. Nine sampling stations (50%) displayed increases in As concentrations and 9 stations (50%) displayed decreases immediately after the burn. The increase in As concentrations in the post-burn environment may be associated with elevated As content in the ash by combustion of vegetation. Local vegetation may have absorbed As from the soil, where it was initially concentrated due to historical mining activities with gold bearing sulphides such as arsenopyrite (FeAsS), iron pyrite (FeS_2), pyrrhotite (FeS), galena (PbS), sphalerite (ZnS) and chalcopyrite ($CuFeS_2$) (Sultan, 2006).

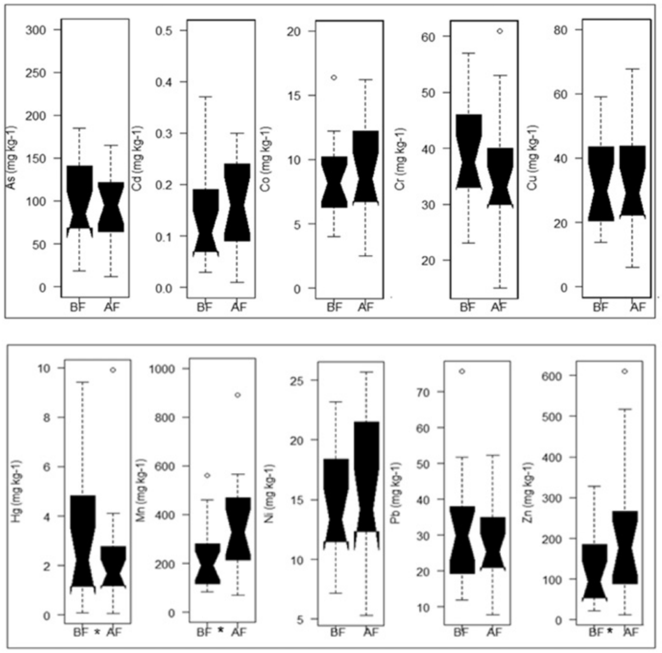

Fig. 5. Notched box plot showing the concentrations (mg kg^{-1}) of potentially toxic elements in the pre- and post-burn soil environment (Note: (i). 'o' denotes outliers, however in some plots outliers are away from figure as it exceeded the scale chosen, for example: As, Cd, Cu and Mn; (ii). "*" highlights the presence of statistically significant difference).

The Ni displayed a small increase (6%) in median concentration in the immediate post-burn environment. Similar to the case of Pb and Cd, Ni distribution and mobility may also depend on SOM, clay mineral and Fe oxides (Kabata-Pendias, 2010).

Regarding the Co concentration in the soil, the median showed only a slight increase (3.7%) in the burned soil as reported in previous studies (Costa et al., 2014; Campos et al., 2016).

When we compare the medians, Hg showed an overall reduction of 27% after the controlled burn with a minimum of 8% and maximum of 97% in the post-fire soils. Low concentrations of total Hg (THg) has been observed in ash samples and post-burn soil samples compared with pre-burn soil samples, and this is considered to be due to Hg volatilization during burning, as reported in previous studies (Biswas et al., 2007, 2008; Mergler et al., 2007; Burke et al., 2010; Melendez-Perez et al., 2014; Campos et al., 2015). The study of Biswas et al. (2007) supported this observation by noting 22–86% decrease in Hg concentration in the soil samples collected immediately after fire (IAF), and they added the observation that Hg mobility primarily depends on fire severity. However, additional studies are required in numerous soil types and numerous environmental circumstances to reconcile the differences between the laboratory and field studies.

In addition to Hg, other three elements have also shown decrease in median concentrations in the immediate post-burn environment: Pb showed 15%, Cr showed 12% and Cu showed only 2%, compared to the pre-burn environment.

The pre- and post-burn concentrations of PTEs in the soils of the 18 sampling stations demonstrated their mobility after the controlled burn. Among the 10 PTEs studied, Zn (87%), Mn (72%), Cd (45%), As (11.5%), Ni (6%) and Co (3.7%) demonstrated increase in their concentrations, whereas Hg (27%), Pb (15.4%), Cr (12%) and Cu (2%) demonstrated decrease in concentrations after the controlled burn. However, the mobility of Co, Ni and Cu are considered as small (as the mobility is found to be <10%). While Cu did not show significantly higher concentration in the post-burn soil, it showed high concentration (145 mg kg^{-1}) in the ash, which is consistent with other studies (Costa et al., 2014; Campos et al., 2016). Though soil pH strongly influences the adsorption, retention and mobility of the PTEs (Hernandez et al., 2003), such an association is not identified in the current post-burn environment. This may be due to the immediate sampling which was done two days after the burn. Though the median levels of all PTEs demonstrated variations in the immediate post-burn environment, only difference in Zn, Mn and Hg levels are statistically significant ($p < 0.05$).

The quantity of PTE released through any kinds of forest fire primarily depends on the accrual and storage levels in the pre-fire environment, topography of the area, soil types and moisture content in the soil, types and amount of fuel, moisture content of fuel, weather pattern, temperature and duration of burning and maximum temperature reached (DeBano et al., 1998; Flannigan and Wotton, 2001; DeBano, 2000; Certini, 2005; Neary et al., 2005; Biswas et al., 2007). For example, in a laboratory study, soil released low amounts of Hg (<10%) when heated at 180 °C for an hour, but four hours of heating at 320 °C released >95% of the THg from the soil (Biswas et al., 2007). Since fire intensity and duration of heating is less in a controlled burns compared to wild fires, it is not severe enough to remobilize most of the PTEs sequestered in forest vegetation and soil organic matter specifically from the lower and middle layers of the forest floor (Nriagu, 1996; Shcherbov, 2012; Sen and Peucker-Ehrenbrink, 2012).

3.5. Potentially toxic elements in ash

The heterogeneous residue left at the soil surface after the forest fire known as ‘ash’, gives a general impression of the forest fire. It is a key component to addressing PTEs mobility on the landscapes, as most of the forest fire ash contains elevated concentration of PTEs (Plumlee et al., 2007; Pereira and Ubeda, 2010; Odigie and Flegal, 2011, 2014). It represents the enduring accumulation and storage of mineral matter in soil organic horizon and of the vegetation in the pre-fire environment, include PTEs and other contaminants (Someshwar, 1996; Johansen et al., 2003; Goforth et al., 2005; Biswas et al., 2007; Campos et al., 2012; Wade et al., 2013; Campos et al., 2015, 2016).

The descriptive statistics of PTE concentration in ash is depicted in Table 4. The ash left after the controlled burn revealed perceptible differences in physicochemical properties and the PTE concentrations compared to post-fire soil. Based on the PTE analysis data it was found that Mn (from 330 to 2790 mg kg^{-1}) achieved the highest concentration and Zn (from 221 to 555 mg kg^{-1}) achieved the second highest concentrations in ash, whereas, Cd (0.02 to 0.22 mg kg^{-1}) and Hg (0.02 to 0.41 mg kg^{-1}) represent the lowest concentrations. The highest Mn concentration in ash is supported by other studies (Costa et al., 2014; Campos et al., 2016). There are appreciable quantities of Cu (56.1 to 207 mg kg^{-1}) and As (20.08 to 260 mg kg^{-1}) also found in ash. It is noteworthy that the As concentration in the ash is elevated so that this presents a vector for As redistribution in the atmosphere, soil and downstream water resources. The median concentration of Mn, Zn, Cu and Ni in ash is found to be higher than their concentration in the soil, whereas, the concentration of As, Cd, Co, Cr, Hg and Pb are found to be higher in soil than in ash. The varying concentrations of PTEs in ash depends upon many natural factors such as meteorological conditions, pre-fire metal concentrations (in the soil, soil organic matter, and in vegetation), age and vegetation density in the forest ecosystems, vegetation parts burned (like bark, leaves and litter), duration of the burning, fire intensity, maximum temperature reached, soil types, and moisture content in the soil (Someshwar, 1996; Pereira et al., 2009; Pereira and Ubeda, 2010; Machado et al., 2015).

Table 4
Concentrations of potentially toxic elements (mg kg^{-1}) in ash.

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Median	23	0.1	9	9	145	0.04	1270	28	5	475
Range	239	0.2	7	4	151	0.4	2460	28.	13	334
IQR	180	0.2	5	3	114	0.3	1990	25	10	277

NB: IQR - interquartile range.

Previous studies revealed the presence of PTEs (Mn, Zn, Cu, Pb, Hg, Cd and As) in ash samples found in forests across the globe (Ferreira et al., 2005; Plumlee et al., 2007; Pereira and Ubeda, 2010; Bogacz et al., 2011; Odigie and Flegal, 2011, 2014; Campos et al., 2016). To illustrate this, Plumlee et al. (2007) reported significantly elevated concentration of PTEs (As up to 140 mg kg^{-1}, Pb up to 344 mg kg^{-1}, Cu 1370 mg kg^{-1} and Zn up to 2800 mg kg^{-1}) in ash samples after the southern California forest fire in USA that persisted for a year following the fire. Similarly, distribution of Co (3–11 mg kg^{-1}), Cu (15–69 mg kg^{-1}), Ni (6–15 mg kg^{-1}), Pb (7–42 mg kg^{-1}) and Zn (65–500 mg kg^{-1}) were observed in ash after the Williams fire in Los Angeles (2012), USA (Odigie and Flegal, 2014) and Kristensen et al. (2014) reported mobilization of natural and industrial Pb in ash samples after three large uncontrolled intense wildfire events (February 2011) in Australia. Many of the metal mobilization studies highlighted Mn as being present in the highest concentration (Parra et al., 1996; Costa et al., 2014; Campos et al., 2016). For example, highest levels of Mn (121–448 mg kg^{-1}) in ash were reported by Costa et al. (2014) after the Marao Mountain forest fire and Campos et al. (2016) reported 57–598 mg kg^{-1} of Mn in ash after the Ermida fire, both in Portugal. The increase in concentration of Mn in ash is linked to combustion of plant leaves as it is a component of the photosynthesis (the water splitting complex) (Kabata-Pendias, 2010; Farzadfar et al., 2017; Shao et al., 2017). Studies emphasised that PTEs formed in ash during fire may be remobilised through post-fire rainfall runoff and wind activities (Smith et al., 2011; Stein et al., 2012; Costa et al., 2014; Campos et al., 2016; Abraham et al., 2017a, 2017b). Thus, forest fires include controlled burns, can be considered as a vector for environmental alterations that may influence human and ecosystems health.

3.6. Relationship of potentially toxic elements in soil and ash with physicochemical characteristics

The relationship between PTE concentrations in pre-burn and post-burn soil (Table 5) and ash (Table 6) with physicochemical characters such as pH, EC, SOM and carbonate contents were assessed with Spearman rank correlation method using R (3.4.1). The results do not identify any statistically significant very strong ($r = 0.80$–1.0) and strong ($r = 0.60$–0.79) correlations between physicochemical properties of soil and PTEs in the pre- and post-burn environments, except pH with Ni and Co, however PTEs themselves shown very strong and strong correlations.

When we consider pH, it showed a strong correlation with Ni ($r = 0.62$) and Co ($r = 0.61$), and a moderate ($r = 0.40$–0.59) correlation with Cr ($r = 0.54$) and Zn ($r = 0.46$) in the pre- and post-burn soils. Similar relation between soil pH with Ni and Co were also reported by Wilde et al. (2004). The soil EC does not show any significant correlation with any of the PTEs in both pre- and post-burn environments, but SOM displayed moderate correlations with Cd ($r = 0.53$), Cu ($r = 0.51$), Ni ($r = 0.50$), Zn ($r = 0.49$) and Cr ($r = 0.44$) in the pre- and post-burn environments. Similar to SOM, carbonate also exhibit moderate correlation with number of PTEs, including Cr ($r = 0.57$), Ni ($r = 0.50$), Cu ($r = 0.48$), Pb ($r = 0.48$), Co ($r = 0.46$), Mn ($r = 0.45$), Cd ($r = 0.43$) and Zn ($r = 0.40$) in both pre- and post-burn soil environments.

The correlations between PTEs (themselves) in the pre- and post-burn soil environments are almost similar in value (Table 5), and the strong and very strong correlations highlight their common origin. The very strong correlation of As with Mn ($r = 0.80$) shows that Mn is a significant element in the soil, which controlling the mobility of arsenate (an abundant form of As), which is also reported by Sultan (2007). The strong correlation of As with Pb ($r = 0.77$) and Zn ($r = 0.76$) revealed their common origin in the Ordovician sedimentary rock during gold mineralization in association with galena (PbS) and sphalerite (ZnS). As also shown strong correlation with Cd ($r = 0.75$), Co ($r = 0.65$), Hg ($r = 0.63$) and Cu ($r = 0.60$) revealed the legacy mining activity. Mn demonstrated strong correlation with Cd ($r = 0.73$), Co (0.73),

Table 5
Spearman rank correlation coefficient between the physicochemical properties of soil and PTEs in the pre-burn (above diagonal elements) and the post-burn (below the diagonal elements) environment.

	pH	EC	SOM	Carb	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
pH		−0.48	0.43	0.04	0.32	0.37	**0.61**	0.54	0.38	0.02	0.35	**0.62**	−0.04	0.46
EC	−0.48		0.28	0.37	−0.23	−0.10	−0.03	−0.02	0.14	−0.08	0.04	−0.08	−0.03	−0.21
SOM	0.43	0.28		0.37	0.10	0.53	0.38	0.44	0.51	−0.03	0.36	0.50	0.28	0.49
Carb	0.04	0.38	0.37		0.32	0.43	0.46	0.57	0.48	0.13	0.45	0.50	0.48	0.40
As	0.32	−0.23	0.10	0.32		**0.75**	**0.65**	0.48	**0.60**	**0.63**	**0.80**	0.53	**0.77**	**0.76**
Cd	0.37	−0.10	0.53	0.43	**0.74**		**0.70**	**0.66**	**0.72**	0.46	**0.73**	**0.75**	**0.75**	**0.98**
Co	**0.61**	−0.03	0.38	0.46	**0.65**	**0.70**		**0.86**	**0.76**	0.25	**0.73**	**0.94**	0.30	**0.76**
Cr	0.54	−0.02	0.44	0.57	0.48	**0.66**	**0.86**		**0.77**	0.04	0.47	**0.95**	0.32	**0.72**
Cu	0.38	0.14	0.51	0.48	**0.60**	**0.72**	**0.76**	**0.77**		0.37	0.58	**0.79**	0.46	**0.74**
Hg	−0.02	−0.08	−0.03	0.13	**0.63**	0.46	0.25	0.04	0.37		0.49	0.12	0.51	0.43
Mn	0.35	0.04	0.36	0.45	**0.80**	**0.73**	**0.73**	0.47	0.57	0.49		**0.61**	**0.62**	**0.71**
Ni	**0.62**	−0.08	0.50	0.50	0.53	**0.75**	**0.94**	**0.95**	**0.79**	0.12	**0.61**		0.32	**0.82**
Pb	−0.04	−0.03	0.28	0.48	**0.77**	**0.75**	0.30	0.32	0.46	0.51	**0.62**	0.32		**0.67**
Zn	0.46	−0.21	0.49	0.40	**0.76**	**0.98**	**0.76**	**0.72**	**0.74**	0.43	**0.71**	**0.81**	**0.67**	

Note: Very strong (r = 0.80–1.0) and strong (r = 0.6–0.79) correlations are in bold.

Zn (0.71), Pb (0.62) and Ni (0.61) considered to be due to the specific absorption capacity of Mn oxides to these elements (Cd, Co, Zn, Pb and Ni).

The physicochemical properties of ash and PTEs in the ash display a number of very strong and strong correlations, and all these significant correlations are highlighted in Table 6 for easy reference. In the ash samples, pH displayed strong positive correlation with Co (r = 0.80) and strong negative correlation with Cu (r = −0.80) and Zn (r = −0.80), however, EC shown strong positive correlation with Cu (r = 0.80) and Zn (r = 0.80) and strong negative correlation with Co (r = −0.80). SOM has very strong correlation with Zn (r = 1.0) and strong negative correlation with Cr (r = −0.74). Carbonate also follow similar kind of very strong positive correlation with Co (r = 0.80) and very strong negative correlation with Cu (r = −0.80) and Zn (r = −0.80).

Previous studies noted that physicochemical characteristics such as pH, EC and OM of soil perform a significant part in the retention and mobilization of PTEs in the soil environment (Chlopecka et al., 1996; Mehes-Smith et al., 2013). In this study, however, no significant very strong correlation was observed between physicochemical parameters of soil and PTEs in the soil (except few strong and a number of moderate and weak relationships), similar to the studies of Wang et al. (2010).

4. Conclusion

Detailed analysis of PTE dynamics relevant to the effects of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn on the environment, is crucial for ecosystem management and sustainability. The overall increase in concentrations of PTEs such as Zn, Mn, Cd, As, Ni and Co, together with changes in physicochemical characteristics of soil including pH, EC and SOM in the post-burn soil environment, highlight that a controlled burn acts as a mobility vector and a source of PTE contamination. In addition, ash formation during fire, and its propensity for mobility influences the PTE concentration in the adjacent soil, water and air environments. Results of this study showed that ash was consistently enriched in PTEs compared to the underlying and adjacent surface soil, signifying that the accumulation of ash on soil and water surfaces can contribute to an increase in PTE concentration in the post-burn environment. The increase in soil pH, EC, SOM and the increase in water pH and EC is also attributed to the presence of ash, which has elevated quantities of oxides, hydroxides, carbonates and many other minerals and nutrients.

The observed decrease in levels of Hg and Pb in the post-burn soil environment, suggests that volatilization of these elements have taken place during fire. This PTE mobility has substantial implications in the environment due to its influence on all aspects of biota from soil microbes to terrestrial and aquatic vertebrates, including humans and ecosystem resilience in general. For example, Hg is of particular concern in the post-burn environment, specifically in wetlands, because the physicochemical and biological conditions are favourable for the formation of methyl Hg (MeHg), which has severe neurological implications for organisms, and may also reach the human consumer. As a consequence, controlled burning, and the resulting PTE mobility, highlights significant concern given the impacts of these toxic elements to human and ecosystem health. This is particularly relevant given that controlled burning is increasingly being used over large areal extents in fire-prone areas, and is also often used in proximity to human settlements as a standard fire risk reduction strategy. Such changes in use and extent of controlled burns will release and remobilize greater volumes of PTEs into the environment, which is of some concern. Therefore, information regarding

Table 6
Spearman rank correlation coefficient between the physicochemical properties of ash and the PTEs in ash.

	pH	EC	OM	Carb	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
pH	1													
EC	−1.0	1												
SOM	**−0.80**	**0.80**	1											
Carb	1.0	−1.0	**−0.80**	1										
As	0.40	−0.40	−0.20	−0.40	1									
Cd	0.20	−0.20	−0.40	0.20	**0.80**	1								
Co	**0.80**	**−0.80**	−0.40	**0.80**	0.00	−0.40	1							
Cr	0.21	−0.21	**−0.74**	0.21	0.11	**0.63**	−0.32	1						
Cu	**−0.80**	**0.80**	0.40	**−0.80**	**−0.80**	−0.40	**−60**	0.11	1					
Hg	0.40	−0.40	−0.20	0.40	**1.0**	**0.80**	0.00	0.11	**−0.80**	1				
Mn	−0.20	0.20	0.40	−0.20	**−0.80**	**−1.0**	0.40	**−0.63**	0.40	**−0.80**	1			
Ni	−0.20	0.20	0.40	−0.20	**−0.80**	**−1.0**	0.40	**−0.63**	0.40	**−0.80**	**1.0**	1		
Pb	0.40	−0.40	−0.20	0.40	**1.00**	**0.80**	0.000	0.11	**−0.80**	**1.00**	**−0.80**	**−0.80**	1	
Zn	**−0.80**	**0.80**	**1.00**	**−0.80**	−0.20	−0.40	−0.40	**−0.74**	0.40	−0.20	0.40	0.40	−0.20	1

Note: Very strong (r = 0.8–1.0) and strong (r = 0.60–0.79) correlations are in bold.

PTEs mobility associated with controlled burning is a significant contribution to managing environmental and ecosystem health and sustainability.

It has been shown that PTE concentrations in post-burn environments are directly linked to their original concentration in the pre-burn environment. This means that if the pre-burn soil has elevated amounts of PTEs, such as found in legacy mine sites or any kinds of mining or industry-affected landscapes, the mobilization of the PTEs will also be elevated during, or after, the controlled burn. As a consequence, the possible local effects of the resulting PTE mobility, with its related health impacts on human and ecosystems, must be carefully examined and due vigilance must be applied before any controlled burns are to be used to provide an effective forest management tool in mining-affected landscapes.

Conflict of interest

The authors declared that they have no conflict of interest.

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Chapter- 7

Effects of prescribed fire and post-fire rainfall on mercury mobilization and subsequent contamination assessment in a legacy mine site in Victoria, Australia

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Effects of prescribed fire and post-fire rainfall on mercury mobilization and subsequent contamination assessment in a legacy mine site in Victoria, Australia

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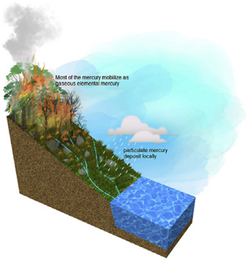
HIGHLIGHTS

- Legacy gold mining sites have elevated Hg concentration.
- Hg sequestered in the soil organic matter and vegetation limiting its mobility.
- Prescribed fires are able to release and remobilize sequestered Hg.
- The liberated Hg mobilized to atmosphere mostly as Hg^0 and the rest as PHg.
- Post-fire rainfall increased the Hg concentration in the soil.

GRAPHICAL ABSTRACT



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ABSTRACT

Prescribed fire conducted in fire-prone areas is a cost-effective choice for forest management, but it also affects many of the physicochemical and bio-geological properties of the forest soil, in a similar manner to wild fires. The aim of this study is to investigate the nature of the mercury mobilization after a prescribed fire and the subsequent temporal changes in concentration. A prescribed fire was conducted in a legacy mine site in Central Victoria, Australia, in late August 2015 and soil sample collection and analyses were carried out two days before and two days after the fire, followed by collection at the end of each season and after an intense rainfall event in September 2016. Results revealed the occurrence of mercury volatilization (8.3–97%) during the fire, and the mercury concentration displayed a significant difference ($p < 0.05$) before and immediately after the fire. Integrated assessment with number of pollution indices has shown that the study site is extremely contaminated with mercury during all the sampling events, and this poses a serious ecological risk due to the health impacts of mercury on human and ecosystems. In times of climate fluctuation with concomitant increase in forest fire (including prescribed fire), and subsequent precipitation and runoff, the potential for an increased amount of mercury being mobilized is of heighted significance. Therefore, it is recommended that prescribed fire should be cautiously considered as a forest management strategy in any mercury affected landscapes.

1. Introduction

Prescribed or controlled fire is the intentional application of fire in forest or agricultural areas in order to achieve specific land management goals. Included in this activities are fuel reduction,

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land preparation prior to agriculture, tree restoration, weed and insect control, wildlife habitat management and biodiversity maintenance, all of which can be enhanced by the application of prescribed fire (Arocena and Opio, 2003; Fernandez and Botelho, 2003; Pereira et al., 2011). Prescribed fire is generally practised in the autumn or spring seasons (and possibly in late winter) depending on the local weather pattern. These fires are usually of low to moderate intensity when compared to the effect of wild fires, and are used to ingest most of the understory vegetation and part of the forest floor layers without detrimental impacts to the tree canopy (Pereira et al., 2011; Úbeda et al., 2005). The combustion reduces the possibility and hence the extreme intensity of a wildfire by reducing the fuel loads in the forest ecosystems (Fernandez and Botelho, 2003; Pereira et al., 2011). As a consequence, prescribed fire is widely deemed to be an ecologically responsible and economically viable tool in forest protection and wildfire mitigation (Castellinou et al., 2010; Certini, 2005; Fernandez and Botelho, 2003). It is commonly practised in the fire-prone forest landscapes of many European and American countries including, Spain, Portugal, USA and Brazil and also in Australia.

Notwithstanding that prescribed fire occurs at low to moderate intensity, it can, however create a number of physical and biogeochemical alterations to the soil properties, and is able to remobilize potentially toxic metals including mercury (Hg) from the soil organic matter (SOM) and vegetation (Certini, 2005; Melendez-Perez et al., 2014; Pereira et al., 2011). Thus, when prescribed fire events occur in legacy gold mining landscapes, it portrays growing concern due to the presence of elevated concentrations of toxic Hg in the soil, from the gold processing activities.

Central Victoria, in Australia, has long history of gold mining dating from the 1850s with the region producing more than 2500 t of gold during this period (EER, 2015; McDonald and Powell, 2008). Mining and metal processing was an important economic driver at the time and has contributed significantly to extensive regional development. However, the closure of legacy mines, often due to economic downturns left tonnes of mine waste materials rich in fine grained potentially toxic metals and metalloids (Cd, Cr, Cu, Pb, Zn etc., and As) including substantial amount of Hg (Martin et al., 2014; Pearce et al., 2012; Sultan, 2007). These mine waste materials can cause significant contamination of soil, sediment, water, air and plants and thus require careful management to minimise ecological and social damage (Doronila et al., 2014; Martin et al., 2014; Pearce et al., 2012; Sultan, 2007).

It is known that Hg in one form or another, enters the atmospheric, terrestrial and aquatic environments through (i) natural geologic process (volcanic eruption, rock weathering and soil formation and geothermal activity), (ii) anthropogenic activities (metal mining and processing, burning of coal for energy generation, industrial activities, cement production, petroleum refining, metal recycling, artisanal and small-scale gold mining) and (iii) through re-emissions from the soil (UNEP, 2013). It has been estimated that natural sources account for 10% of the estimated 5500–8900 t of Hg currently being emitted and re-emitted into the atmosphere, whereas anthropogenic sources account for 30% of the total and re-emissions account for the remaining 60% (Agamuthu, 2013; UNEP, 2013). Half of the natural contribution is claimed to come from the marine environment and the balance arises from terrestrial sources (Abraham et al., 2017; Pirrone et al., 2010). Once it has entered the environment, Hg cycles between the air, land and water, until it is eventually sequestered from the system through the processes such as burial in deep ocean sediments or in lake sediments (Rumayor et al., 2017; UNEP, 2013).

Of particular interest to this investigation is that Hg emissions from biomass burning have recently been considered to be influential on a global scale (Pirrone et al., 2010). Average annual biomass burning estimate for a 10 year period (from 1997 to 2006), revealed that approximately 675 t of Hg was liberated into the atmosphere, which accounts for around 12% of contributions from natural sources (Friedli et al., 2009; Pirrone et al., 2010). In addition, it has been reported that as much as 260 t of Hg might have been released into the aquatic ecosystems worldwide in 2010 due to forest fire (UNEP, 2013).

The behaviour of Hg in the soil environment is very complex, and is mainly controlled by adsorption and desorption processes involving several physicochemical and biogeochemical mechanisms (Reis et al., 2015). When enters the soil environment, specifically in forest floor, soil readily absorbs Hg, resulting in the sequestration of up to 90% of the Hg in the SOM (Driscoll et al., 2013; Grigal, 2003; Hernandez et al., 2003) and the rest is absorbed by local vegetation (Skyllberg et al., 2006). Estimates indicate that in the last century, the sequestration of Hg led to a 15–20% increase in its concentrations in forest soils around the globe (Driscoll et al., 2013; Grigal, 2003). Thus, the forest ecosystem acts as a Hg sink and effectively limits its normal mobility (Melendez-Perez et al., 2014; Obrist et al., 2011). However, during forest fires (including wild and prescribed fires), Hg stored in SOM and vegetation can be released into the atmosphere, largely (80–90%) in the insoluble and unreactive gaseous elemental mercury (GEM or Hg^0) form and the remaining 10–20% manifest as particulate mercury (PHg) (Biswas et al., 2007; Burke et al., 2010; Campos et al., 2015; Friedli et al., 2009; Woodruff and Cannon, 2010). Of relevance here is that the dominance and permanence of GEM allows it to be transported long distances (Obrist et al., 2007; Talbot et al., 2008) resulting in both regional and global impacts, whereas PHg fraction may contribute significant local impacts due to its rapid deposition (Sigler et al., 2003; Wiedinmyer and Friedli, 2007).

During fire, Hg volatilization from the soil begins at 180 ^{O}C and the amount of Hg release primarily depends on the configurations of temperature and duration of fire (Webster et al., 2016). Experiments have shown that combustion of vegetation and the heating of surface soil at moderate temperatures (180 ^{O}C) for either 1 h or 4 h releases 56% and 91% of Hg respectively from soil, which highlights the significance of the duration of the fire (Biswas et al., 2007). Further investigations have shown that the amount of Hg released into the environment in such a fire event is controlled by the factors such as (i) type and density of vegetation (ii) level of Hg accumulation in the ecosystem prior to burning, (iii) fire severity and duration of heating, (iv) maximum temperature reached (v) amount of fuel available (vi) moisture content in the fuel, (vii) weather pattern and (viii) topography of the area (Biswas et al., 2007, 2008; Webster et al., 2016).

Forest fire, thus mobilizes (re-mobilizes) Hg into the terrestrial environment and plays a significant role in Hg cycling and the formation of methyl mercury (MeHg). Post-fire rainfall and resulting runoff and strong wind activity transports the mobilized Hg from soils, ash and from air into the soil or aquatic environment resulting in elevated Hg concentrations, where physical conditions such as low pH and low oxygen levels may favour the formation of MeHg (Amirbahman et al., 2004; Dittman et al., 2010). MeHg is a potent neurotoxin and has the tendency to bio-accumulate and biomagnify in the food chain (Amirbahman et al., 2004; Mergler et al., 2007). This is particularly significant in the Central Victoria region of Australia and many other fire-prone regions in the world when the region have elevated concentration of Hg in the soil, due to legacy gold processing activities. The projected rise in forest fire intensity, frequency, and areal extent catalysed by climate change, coupled with ongoing prescribed fires have broad implications owing to the liberation and remobilization of Hg (Abraham et al., 2017; Burke et al., 2010; Campos et al., 2015). The remobilised Hg may consequently contaminate all compartments of environment with subsequent effects on human and ecosystems health and biodiversity (Kelly et al., 2006; Mergler et al., 2007; Taylor et al., 2010; Zhuang et al., 2014). This is of significant concern as the forest ecosystem acts as a catchment area for surface water resources and groundwater recharging zones, which often supply potable water to the major cities and local communities.

Whilst a number of studies have reported Hg mobilization after a wild fire (for example Biswas et al., 2007, 2008; Campos et al., 2015; Friedli et al., 2009; Garcia and Carignan, 2005; Kelly et al., 2006; Obrist et al., 2008; Sigler et al., 2003; Witt et al., 2009), studies of subsequent effects of prescribed fire on Hg mobilization (Harden et al., 2004; Melendez-Perez et al., 2014) are rare, and have not been reported in the Australian context. We assert that there is a requirement to distinctly investigate and report the mobilization of Hg during and after the prescribed fires and this study may be a first attempt to provide this perspective for a gold mining affected landscape in Australia. Hence, this work aims to: (i). investigate the mobilization of Hg in a mining affected landscape immediately after a prescribed fire (ii). understand the temporal variations in soil Hg concentrations in the post-fire environment, and (iii). assess the influence of post-fire rainfall on the soil Hg concentration. Given the pervasive effect of Hg emissions on the environment, and in the expectation of increasing frequency of fire events (including wild and prescribed fires) due to climate change, the authors anticipate more release and significant mobilization of Hg into the aquatic environment leading to an increased Hg bioaccumulation in many parts of the ecosystem.

2. Materials and methods

2.1. Characteristics of the study area

Maldon, a historic mining site is located 140 km NW of the city of Melbourne and 40 km SW of the City of Greater Bendigo, and has produced more than 56 t of gold from more than 20 reefs during the mining period (Cherry and Wilkinson, 1994; Mason and Webb, 1953). Legacy mining activities included the driving of adits and shafts for deep leads, and instituting open cut mining techniques to provide access to sulphide bearing ores. The subsequent processing activities required to retrieve the gold have resulted in the accumulation of mine waste materials containing many kinds of potentially toxic metal contaminants, including Hg, which is the focus of this investigation.

From a number of legacy mine sites in the Maldon area, one in the state forest landscape, east of the Union Hill mine was selected for this study (Fig. 1). Physiographically, the northern half of the study area slightly slopes towards the south, and the southern half slopes towards north forming a small creek flowing in a west-to-east direction, which serves to funnel all the rainfall and runoff in the study area. The area is zoned a public land, where the burrows, soil heaps and scattered quartz attest to its legacy gold mining activities, and the presence of moderate-to-highly disturbed soils make the study area ideal for evaluating legacy mining impacts on the environment.

The study area falls in a temperate climate zone with winter temperature varies from 7.5 to 17.5 °C and the summer temperature varies from 16.4 to 40.3 °C. The annual average rainfall is 540 mm and is mostly occurs in winter and spring seasons (BoM, 2017). The canopy in the area is *Eucalyptus radiata* and *Acacia pycnantha,* but the shrub layer and ground cover being dominated by *Ulex europaeus* (Gorse), *Cassinia arcuta* (Chinese shrub), *Juncus acutus* (Shirp) and *Asphodelus fistulosus* (Onida). The study area is noteworthy as it is bordering with residential areas and has a creek running along the middle, which is able to transport contaminants beyond the boundaries of the study area. This situation therefore, has the potential to significantly impact on nearby state forest ecosystems as well as neighbouring communities.

2.2. Prescribed fire

In the Maldon study area, significant growth of the invasive species Gorse (*Ulex europaeus*), which is a weed of national significance, is the major ground cover vegetation (DEE, 2017). This patch of infestation required controlled burning to reduce the fuel levels, and the resultant activity burn was carried out by the State Department of Environment Land Water and Planning (DELWP) and Parks Victoria fire crews on 20th August 2015 in the late winter. Whilst a seemingly intense fire lasted only for several minutes, slow burning of plant materials was observed up to three days after ignition. The fire consumed most of the understory bush-type vegetation such as Gorse (*Ulex europaeus*), Chinese shrub (*Cassinia ar*cuta), Onida (*Asphodelus fistulosus*) and other miscellaneous vegetation, include considerable leaf litter. There were high quantities of ash observed in some locations in the burned area, where thick vegetation particularly tree branches were burned.

2.3. Soil sampling and analysis

The rainfall and temperature data in the study area were sourced from the Bureau of Meteorology stations (Station No.088161 and 08110 respectively) located close (200 m and 12 km respectively) to the study area (BoM, 2017). In between the pre-fire and immediately after fire sampling, there was no rainfall, but during spring, summer, autumn and winter seasons, the rainfall was recorded as 83,100.2, 163.8 and 213.8 mm respectively. After the winter sampling in the first week of September 2016, there was continuous and intense rainfall (120 mm in the second week of September 2016 alone) (BoM, 2017) which facilitated the investigation of the effect of short-term intense rainfall on Hg mobilization.

To address Hg mobility in the surface soils, a total of 18 (S1 to S18, Fig. 1) soil samples were collected two days before and two days after the prescribed fire, followed by sample collection at the end of the four seasons (spring, summer, autumn and winter) and after an intense rainfall in September 2016, from the same sampling stations. In most of the sampling stations, post-burn soil samples represent a mix of both soil and ash materials. Approximately 1 kg of surface soil samples (not more than 3 cm depth) were collected from an area of 1600 cm^2 (40 cm × 40 cm) from each sampling stations, after removing the vegetation debris and large rock particles. Each sampling time, STAR sampling method and established trace metal clean technique procedures were followed (Odigie and Flegal, 2011; Taylor et al., 2010). Within a period of one year (include before fire, immediately after fire, spring, summer, autumn, winter and after rainfall) a total of 126 surface soil samples (18 stations ×7 sampling times) were collected. In addition to the soil samples, four ash samples (Ash1 to 4) of 0.2 kg each were also collected immediately after the burn, from the spots where high intense burn occurred (Fig. 1). The ash sample collection was not undertaken seasonally due to the non-availability of samples as it was quickly dispersed and removed by rainfall runoff and wind activities.

From each of the sampling stations (S1 to S18), soil and ash samples were carefully transferred to clean and dry polyethylene containers and transported to the Federation University Australia laboratory. There, soil samples were transferred to aluminium containers and oven-dried for 24 h (below 60 °C). The oven-dried samples were hand crushed (after removing unnecessary rock pieces) and were sieved through a 2 mm wire mesh sieve. The pre-

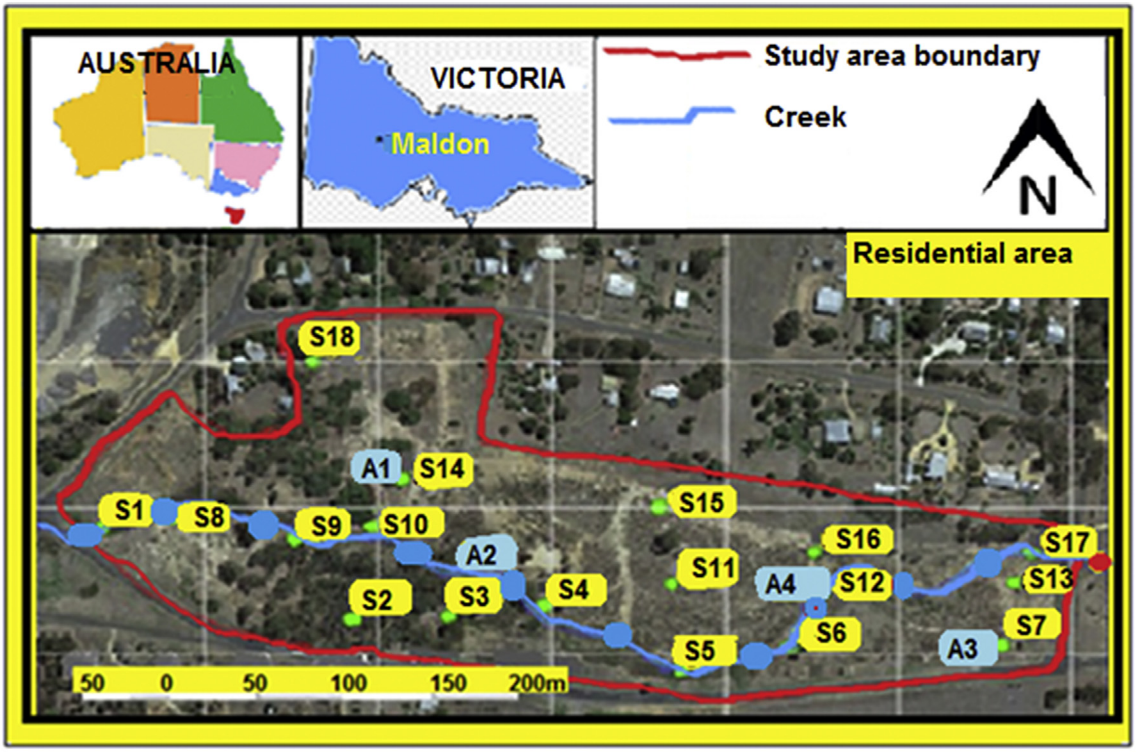


Fig. 1. Showing the Maldon study area (in Victoria, Australia) with soil sampling (S1 to S18) and ash sampling (A1 to A4) stations, with proximity to housing noted.

burn and post-burn sieved samples (<2 mm) were stored in a tightly sealed polyethylene containers until Hg analyses were completed in a NATA (National Association of Testing Authorities) accredited laboratory (Accreditation No. 825) using ICP-MS. Significant parameters of soil such as pH (US-EPA 9045D) and electrical conductivity (EC) (US-EPA 9050A) were determined with standard analytical procedure and SOM and carbonate content (both as percentage) were determined with the Loss on Ignition (LOI) method (Rayment and Lyons, 2014).

2.4. *Data analysis*

The soil and ash Hg analysis data were statistically examined using SPSS (version 23) and SIGMAPLOT (version 11) software(s). Normality of the data was checked by using the Shapiro-Wilk normality test, where data were considered as normal at $p > 0.05$, and the homogeneity of the variance was checked by using the ‘Levene median test’. Data, which did not follow the Gaussian distribution and homogeneity were treated with a logarithmic Neparian transformation and the data still did not confirm to the normal distribution were treated with a square root and Box-cox transformation (Box and Cox, 1964). Both paired sample t-tests and Wilcoxon signed rank tests were used to examine whether the before-fire and immediately after fire Hg concentration and before-rainfall and immediately after rainfall Hg concentrations were significantly different. One-way repeated measures ANOVA and Friedman's test were used to test the statistical significance of the influence of sampling periods (spring, summer, autumn, winter and after rainfall) on the Hg concentration in the soil.

2.5. *Contamination assessment*

Contamination assessment measures were carried out using number of single indices including (i) index of geo-accumulation (Igeo) (Aiman et al., 2016; Fan and Wang, 2017; Qingjie et al., 2008), (ii) contamination factor (CF) (Esshaimi et al., 2012; Olatunde et al., 2015; Qingjie et al., 2008), (iii) pollution index (PI) (Caeiro et al., 2005; Qingjie et al., 2008), (iv) integrated pollution index (IPI) (Faiz et al., 2009) and the (v) potential ecological risk index (E_{RI}) method (Hakanson, 1980; Jiang et al., 2014). The Australian and Victorian top soil average Hg concentration values of 0.03 mg kg^{-1} was used for estimating the degree of contamination (Caritat and Cooper, 2016).

The soil Hg concentrations in various sampling periods were also compared with health investigation levels set by the National Environment Protection Measures (NEPM) and the Department of Environment and Conservation (DEC) of the State of Western Australia (DEC, 2010; NEPM, 2011), and the Ecological Investigation levels of DEC (DEC, 2010) to understand the human and ecosystem health risks.

3. Results and discussions

3.1. *Mercury concentration in the pre– and post-fire environment*

SOM is a major controlling factor in Hg retention in the soil, primarily because of the affinity of Hg with sulphur containing functional groups and carboxyl groups in the soil (Biswas et al., 2007, 2008; Engle et al., 2006; Obrist et al., 2009), but all the carbon pools are not associated with Hg stock demonstrating the complexity (Obrist et al., 2012). During fire, combustion of SOM can result in the redistribution of Hg into the soil or volatilization into the atmosphere (Biswas et al., 2007, 2008; Friedli et al., 2009). Comparison between Hg concentration in soils in the pre- and post-fire environments provide quantitative perception into the consequence of forest fire on Hg mobilization and distribution. The mean Hg concentration before fire, immediately after fire, at the end of each season and after the major rainfall were depicted in Table 1,

Table 1
The mean concentration (mg kg^{-1}) of Hg in the soils of the study area (with standard error) during various sampling occasions, include Hg concentration in four ash samples.

Sampling occasion(s)	Mean concentration of Hg (mg kg^{-1})	Ash samples	Hg (mg kg^{-1})
Before fire	3.1 ± 0.6	Ash 1	0.4
Immediately after fire	2.2 ± 0.5	Ash 2	0.1
Spring	2.6 ± 0.5	Ash 3	0.03
Summer	2.2 ± 0.5	Ash 4	0.02
Autumn	3.1 ± 2.9		
Winter – (before rain)	2.2 ± 0.4		
After rain	4.9 ± 1.9		

including the Hg concentrations in ash samples, which were collected immediately after the fire.

In the pre-fire environment, Hg concentrations ranged from 0.1 to 9.4 mg kg^{-1} with a mean of 3.1 ± 0.6 mg kg^{-1}. Immediately after the fire, the minima and maxima were approximately similar to pre-fire levels, but the mean concentration was reduced to 2.2 ± 0.5 mg kg^{-1}, highlight that on an average 27% of Hg loss was observed immediately after the prescribed fire, which ranged from 0.4 to 6.1 mg kg^{-1} (8.3–97.3%). The highest percentage of Hg loss (97.3%) was observed at the S11 sampling station, in line with the observed high fuel load and high intensity burn. The decrease in Hg concentration in the soil immediately after the fire is consistent with other previous fire studies (Biswas et al., 2007, 2008; Burke et al., 2010; Campos et al., 2015; Melendez-Perez et al., 2014; Obrist et al., 2009). The reduction in mean Hg concentration found in the immediate post-fire soil environment indicates that some amount of Hg that had accumulated in the soil during the pre-fire environment was lost from the soil during prescribed fire into the surrounding environment (to the atmosphere) due to the low volatilization temperature of Hg (100–300 °C; Biester and Scholz, 1996) (Biswas et al., 2007, 2008; Campos et al., 2015; Friedli et al., 2009).

Campos et al. (2015) mentioned that the soil temperature of a minimum 150 °C is sufficient to destroy the Hg ligands in the SOM, and converts the Hg into a labile form and allowing subsequent emission (Campos et al., 2015). The significant increase in soil pH (maximum of 3.7 unit) immediately after the fire, is claimed to indicate the presence of an elevated temperature of maximum of 450 °C during the prescribed fire (Arocena and Opio, 2003; Granged et al., 2011). A soil temperature of 450 °C, if indeed attained during the prescribed fire, would be sufficient enough to mobilize most of the Hg stored in the vegetation and in the top soil layers, most probably in the form of gaseous elemental mercury (Biswas et al., 2007, 2008; Campos et al., 2015; Friedli et al., 2001; Melendez-Perez et al., 2014). This confirms that prescribed fire is able to volatilize Hg, even though the severity is low-to-moderate. Although, it is claimed that fire is able to mobilize Hg to a four cm soil depth, many studies indicate that a higher percentage of Hg stored in the upper two cm layers of the soil is completely volatilised during fire. From depths below two cm, the extent of loss is controlled mainly by the fire intensity, maximum temperature reached, duration of the fire, soil types and density (Campos et al., 2015; Reis, 2013). This is a significant consideration, since major portions of the entrained Hg is mostly concentrated within the top two cm surface soil layers (Biester and Scholz, 1996; Reis, 2013), a finding which is also confirmed by heating experiment studies (Biswas et al., 2007; Campos et al., 2015).

Most of the volatilised Hg (80–90%) may be in the form of GEM (Hg^0), which creates a regional and global impacts as it may transported across long distances (Biswas et al., 2007, 2008; Burke et al., 2010; Melendez-Perez et al., 2014; Obrist et al., 2009). This observation is also supported by a laboratory based investigation reported in the existing studies of Biswas et al. (2007) and Friedli et al. (2001). Compared to GEM, the mobilized PHg may settle locally within a short time span on the study area or neighbouring area without much delay, the majority of which may later mobilized to the downstream soil or water environments (Friedli et al., 2009).

The post-fire seasonal measurement showed the seasonal fluctuations in Hg concentration. During spring, the mean Hg concentration was 2.6 ± 0.5 mg kg^{-1} (ranging from 0.2 to 8.1 mg kg^{-1}), but in summer it was reduced to 2.2 ± 0.5 mg kg^{-1} (ranged from 0.1 to 7.8 mg kg^{-1}). An increase in concentration was observed in autumn (3.1 mg kg^{-1}), which ranged from 0.2 to 29.1 mg kg^{-1}. During winter, Hg concentrations were decreased (average 2.2 ± 0.4 mg kg^{-1}, range 0.17–6.1 mg kg^{-1}) compared to autumn, which is in consistent with previous concentrations in spring (2.6 mg kg^{-1}) and immediately after fire (2.2 mg kg^{-1}).

3.2. *Mercury concentration in ash*

Ash produced during fire is a heterogeneous material composed mainly of oxides and hydroxides of base cations, and its composition depends primarily on the types of fuel, combustion temperature and duration of burning. It may contain many trace elements and may include minor or major quantities of Hg (Bodí et al., 2014; Campos et al., 2015; Pereira et al., 2011). Among the four ash samples, only one ash sample (ash 1) returned notable concentration of Hg (0.4 mg kg^{-1}), while other ash samples returned results below 0.05 mg kg^{-1} (unlike Campos et al., 2015), which is close to the Australian background concentrations of 0.03 mg kg^{-1}. Ash 1 sample is located adjacent to S14 soil sampling station, a station with previously identified elevated Hg levels immediately after the fire, autumn and after major rainfall, where combustion of barks and large branches occurred. The low concentrations of Hg in ash samples are considered to be due to the volatilization of Hg, in the form of GEM, during the intense period of fire.

3.3. *Effects of rainfall on post-fire mercury concentration*

The soil Hg concentration immediately before and after the rainfall event provide insight into the effects of rainfall on the levels of Hg concentration in the soil. In the post-fire environment, the first intense rainfall (particularly) and the successive runoff plays a significant role in soil and ash erosion and transportation of sediments. This is naturally coupled with the transport of toxic elements, including Hg and other contaminants to downstream aquatic ecosystems (Malvar et al., 2011; Prats et al., 2014), contaminating the surface water systems and providing further vectors for distribution (Burke et al., 2010, 2013; Kelly et al., 2006; Prats et al., 2014). The mobilization of ash with associated surface soil in significant quantities in the post-fire environment, results in the decrease of soil pH and EC together with the concentrations of metals in them (Campos et al., 2016). However, in the case of Hg, it is possible to have a local increase in concentration immediately after the major rainfall event(s) due to the leaching of Hg from thick ash concentrate. This can also be due to the accumulation and deposition of ash along the runoff channels, washing out of Hg containing ash particles adhered to tree leaves, atmosphere fall out, include local deposition of PHg.

The short-term rainfall event of interest, which occurred during the second week of Sept 2016 was intense (compared to the previous rainfalls) and resulted in flooding in many of the Central Victorian regions. This high intensity rainfall event occurred just three days after the winter soil sampling. The immediate post-rainfall sample analysis revealed an increased mean Hg concentration in the soil samples (4.9 ± 1.9 mg kg^{-1}), which is approximately 2.1 times higher than the pre-rainfall concentration (winter) (2.2 ± 0.4 mg kg^{-1}) (Fig. 2). This was a similar finding to parallel studies (Burke et al., 2010; Caldwell et al., 2000; Engle et al., 2006). Among the 18 sampling stations, 55% stations displayed an increase in Hg concentration (varying from 10.8 to 353.5%) after the major rainfall event. Similarly, an increase in mean Hg concentration (3.1 ± 2.9 mg kg^{-1}) was also observed in the 55% soil samples collected in the autumn (varying from 11 to 297%), when compared to the previous summer samples (2.2 mg kg-1 ± 0.5).

The increase in mean Hg levels in the ‘after rainfall’ and ‘autumn’ soil samples are most probably due to the intervention of the rainfall event and the subsequent runoff as mentioned earlier (Moody et al., 2013; Prats et al., 2014; Witt et al., 2009). Moreover, Hg stored two cm below the soil surface may have been exposed as intense rainfall can cause transport of surface soil and ash with runoff. Some caution is needed here through, because while these hypothesis for Hg mobilization are valid, the results highlight a significant question regarding the mechanism behind the increase in soil Hg concentration immediately after the major rainfall event in the post-fire environment.

Although an increase in mean Hg levels was noted in the autumn and after rainfall, it is seen that a very high increase was observed only at S14 (34 mg kg^{-1}) and S17 (17 mg kg^{-1}) sampling stations, which are mainly responsible for this major increase in mean concentration in the study area. The change in Hg concentrations in the remaining sampling stations during autumn and after the major rainfall event was considerably lower (<10 mg kg^{-1}) (Fig. 2). The sampling station S14 and S17 were the locations of a higher intensity burn and thick ash deposition due to the burning of thick tree branches and small tree trunks. The observed increase in Hg concentration at S14 (29 mg kg^{-1} in autumn and 34 mg kg^{-1} after rainfall) may also be due to the leaching of Hg from the thick ash deposition close to S14. Though, high intensity rainfall results in an increase in mean Hg concentration, which is not statistically significant ($p = 0.18$), we believe that additional investigation is required to realize the increase in soil Hg accumulation immediately after the intense rainfall, in the post-fire environment.

3.4. Contamination assessment of mercury

Contamination assessment of Hg is noteworthy because Hg in various forms has the potential to create serious health impacts to humans including neurological disorders, structural and central nerve system damage and other conditions (Mahaffey et al., 2009; Sunderland et al., 2010; Sundseth et al., 2017). Moreover, Hg in the aquatic ecosystem can be methylated by microbes resulting in the formation of more toxic MeHg, which is both neuro-toxic and immuno-toxic in humans and in other animals (Mergler et al., 2007). For example, birds in the Minamata area in Japan experienced severe flying difficulty, reproductive problems and other abnormal behaviours, which are considered to be due to the increase in Hg concentrations in their tissues (UNEP, 2002).

The mean I-geo, contamination factor, pollution index, integrated pollution index and ecological risk index values of Hg concentrations in various sampling periods (before fire, immediately after fire, spring, summer, autumn, winter and after rainfall) and the corresponding soil contamination levels are depicted in Table 2. The I-geo values revealed that around 90% of the study area is heavily to extremely contaminated with Hg, irrespective of the sampling periods (seasons) (Fig. 3). The CF also displays very high contamination level with Hg in all the sampling stations during all the sampling periods. Similar to this, PI and IPI values were also highlighted the high level pollution with Hg in the study area. Like other indices, the mean E_{RI} values in each sampling periods demonstrated that the study area is creating an ecological risk with Hg irrespective of the sampling periods, and the spatial variation of E_{Ri} is depicted as supplementary figure. The mean E_{RI} values of Hg in each sampling occasions and the corresponding risk types revealed that ‘immediately after” the rainfall samples evidenced the highest mean E_{RI} followed by ‘before fire’, while the lowest mean E_{RI} value was in the autumn samples.

3.5. Comparison with background and guideline values

The average concentration of Hg in Victorian and Australian top soils together with the various health investigation levels (HILs) set by National Environmental Protection Measures (NEPM), and the Department of environment and conservation (DEC) of the state of Western Australia, include ecological investigation level (EIL) of Hg is mentioned in Table 3.

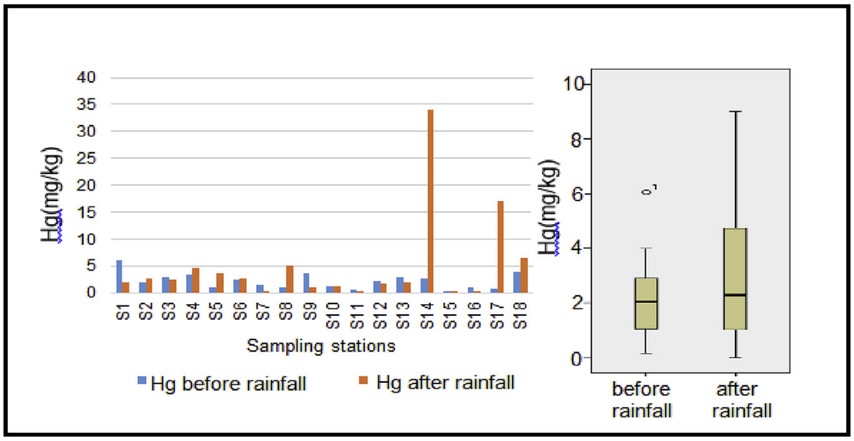


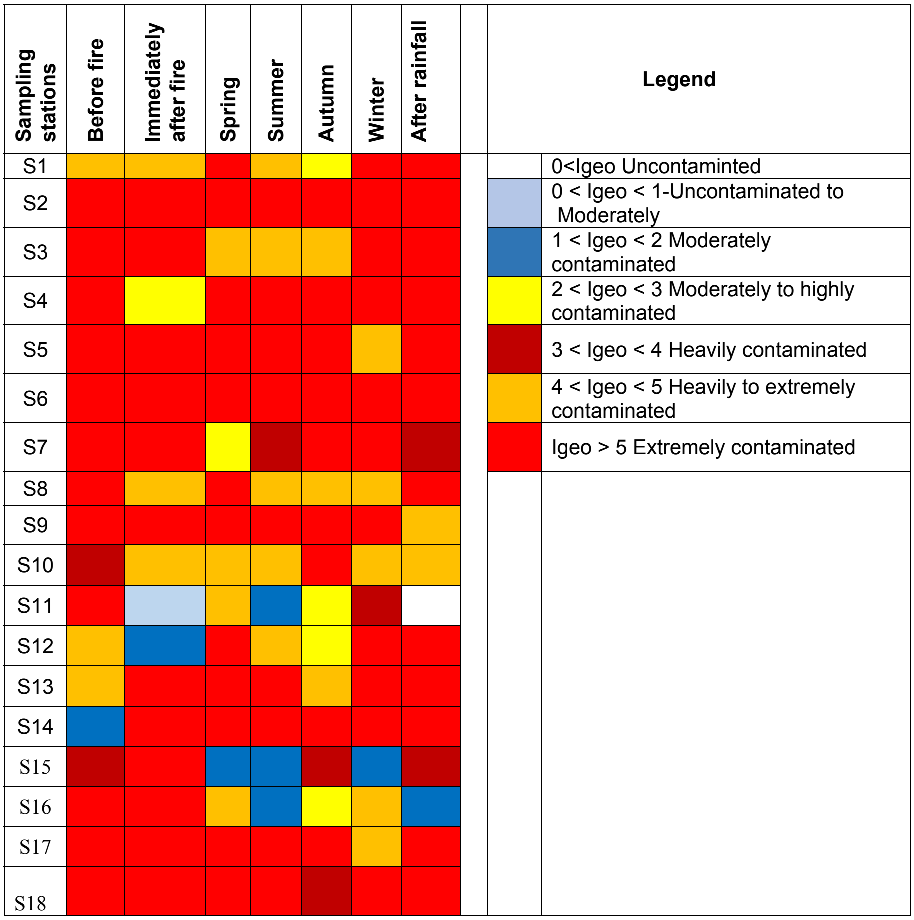
Fig. 2. Hg concentrations (mg kg $^{-1}$) observed in the soils of the Maldon study area, immediately before and after the major rainfall in September 2016.

Table 2
Mean value(s) and the corresponding soil contamination level(s) of Hg during various sampling periods, based on geo-accumulation index (I-geo), contamination factor (CF), pollution index (PI), and integrated pollution index (IPI), include mean values of the ecological risk index (Eri) and the corresponding risk type(s).

Sampling periods	Igeo (mean)	Soil contamination level	CF (mean)	Soil contamination level	PI (mean)/IPI	Contamination level (PI)/IPI	Eri value of Hg (mean)	Risk type
Before fire	5.3	Extremely contaminated	108	Very high	94	High level pollution	4128	Serious ecological risk
Immediately after fire	4.8	Heavily to extremely contaminated	84	Very high	63	High level pollution	3019.5	Serious ecological risk
Spring	5.3	Extremely contaminated	92	Very high	93	High level pollution	3531.8	Serious ecological risk
Summer	4.8	Heavily to extremely contaminated	77	Very high	66	High level pollution	2908.5	Serious ecological risk
Autumn	4.9	Heavily to extremely contaminated	143	Very high	122	High level pollution	2269.5	Serious ecological risk
Winter	5.2	Extremely contaminated	76	Very high	67	High level pollution	2991.8	Serious ecological risk
After major rainfall	9.6	Extremely contaminated	203	Very high	167	High level pollution	6615	Serious ecological risk

The mean Hg concentrations during all the sampling periods were compared with world average, Victorian and Australian top soil averages, and EIL and the results are depicted in Fig. 4. In the Maldon study area, Hg concentrations in all the sampling stations during all the sampling periods are above the world average of 0.01 mg kg^{-1}, and above the Victorian and Australian top soil average of 0.03 mg kg^{-1}. When comparing with various types of health investigation levels (HILs) set by the NEPM and DEC for Hg, the observed concentrations are well below the limits during all sampling periods, except S14 and S17 stations during autumn and after the major rainfall event (NEPM, 2011). During autumn, S14 station showed a Hg concentration of 29 mg kg^{-1}, which exceeded the residential A level set by the DEC and approaching to the recreational level of DEC. In addition, after the major rainfall, the concentration of Hg (17.2 mg kg^{-1}) at S17 station exceeded the DEC-residential A (DEC), whereas, S14 Hg level (34 mg kg^{-1}) exceeded both DEC-residential A and DEC-recreational levels.

When compared with EILs, most of the sampling stations (61%) exceeded the EIL value of 1 during all the sampling periods, creating a significant health concern (DEC, 2010). In the pre-burn environment, 14 stations (78%) showed Hg concentrations above the EIL value, which increased to 18 stations (84%) in the immediate post-fire environment, considered to be the effect of fire, even though Hg volatilization happens during fire. The areal extension of the Hg



Sampling stations	Before fire	Immediately after fire	Spring	Summer	Autumn	Winter	After rainfall
S1	🟧	🟧	🟥	🟧	🟨	🟥	🟥
S2	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S3	🟥	🟥	🟧	🟧	🟧	🟥	🟥
S4	🟥	🟨	🟥	🟥	🟥	🟥	🟥
S5	🟥	🟥	🟥	🟥	🟥	🟧	🟥
S6	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S7	🟥	🟥	🟨	🟫	🟥	🟥	🟫
S8	🟥	🟧	🟥	🟧	🟧	🟧	🟥
S9	🟥	🟥	🟥	🟥	🟥	🟥	🟧
S10	🟫	🟧	🟧	🟧	🟥	🟧	🟧
S11	🟥	▧	🟧	🟦	🟨	🟫	⬜
S12	🟧	🟦	🟥	🟧	🟨	🟥	🟥
S13	🟧	🟥	🟥	🟥	🟧	🟥	🟥
S14	🟦	🟥	🟥	🟥	🟥	🟥	🟥
S15	🟫	🟥	🟦	🟦	🟫	🟦	🟫
S16	🟥	🟥	🟧	🟦	🟨	🟧	🟦
S17	🟥	🟥	🟥	🟥	🟥	🟧	🟥
S18	🟥	🟥	🟥	🟥	🟫	🟥	🟥

Legend

⬜	0<Igeo Uncontaminted
▧	0 < Igeo < 1-Uncontaminated to Moderately
🟦	1 < Igeo < 2 Moderately contaminated
🟨	2 < Igeo < 3 Moderately to highly contaminated
🟫	3 < Igeo < 4 Heavily contaminated
🟧	4 < Igeo < 5 Heavily to extremely contaminated
🟥	Igeo > 5 Extremely contaminated

Fig. 3. Spatial variation of mercury in the study area in various sampling periods, based on Geo-accumulation index (I-geo).

Table 3
Victorian and Australian top soil average Hg concentration (Caritat and Cooper, 2016) and the various health investigations levels of Hg (mg kg^{-1}) set by NEPM and DEC (DEC, 2010; NEPM, 2011).

	Victorian/Australian top soil average (mg kg -1)	Ecological investigation level (EIL)	NEPM-Residential-A (mg kg -1)	NEPM-Residential-B (mg kg -1)	NEPM-C, Recreational (mg kg -1)	NEPM-D- Industrial (mg kg -1)	DEC-Residential-A	DEC-Residential-D (mg kg -1)	DEC-E-Recreational (mg kg -1)	DEC-F-Industrial (mg kg -1)
Hg	0.03	1	40	120	80	730	15	60	30	75

(NB: Res-A: Residential A – standard residential with garden accessible soil.
Res-B: Residential B – Residential with minimum opportunities for soil access.
Recreational: Recreational – open places such as parks, play grounds, public lands, schools and foot paths; Industrial: Industrial and commercial places include shops, offices, factories etc.).

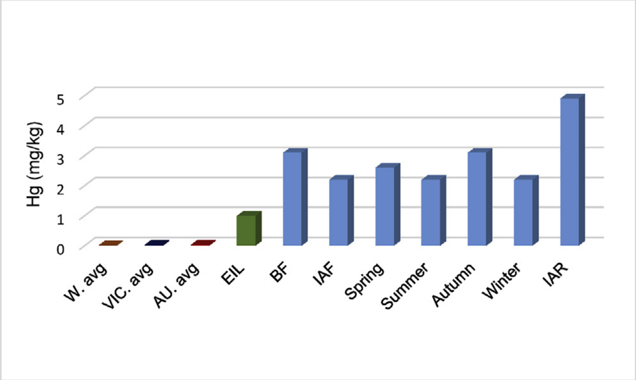


Fig. 4. The mean Hg concentration during each sampling period (BF-before fire, IAF-immediately after fire, and IAR-immediately after rainfall) were compared with World soil average (W.avg), Victorian (Vic.avg) and Australian (Au.avg) top soil averages.

concentration in the immediate post-fire environment may be due to the deposition of PHg immediately after the fire. During spring, the number of sampling stations exceeded EIL, reduced to 14 (78%), with a further reduction observed in summer (11 stations, 61%). However, It is again increased in winter (15 stations, 84%) and after the major rainfall (14 stations, 78%).

4. Conclusion

The objective of this study was to identify the level of Hg contamination in the surface soil of the Maldon legacy mine site in Central Victoria, Australia during various sampling occasions in order to realize the outcomes of prescribed fire, intense rainfall event and seasons (in the post-fire environment). Results obtained from this study revealed that the surface soil of the study area is heavily contaminated with Hg and the data clearly highlighted measurable variations in Hg concentration during all the sampling time periods. However, significant variations were observed only before and after the prescribed fire. After the prescribed fire, an 8.3–97% reduction in Hg concentration was observed in the surface soil indicating the level of volatilization of Hg during fire. After the major rainfall event, a 10–354% increase in Hg concentrations were observed, indicating that ash from the fire, plus existing mine waste leach out and atmospheric fallout are involved in the increase in concentrations. These mobility observations emphasize the requirement for additional Hg and MeHg monitoring in the downstream surface water areas.

The Hg concentration in the surface soils of the study area is evaluated with geo-accumulation index, contamination factor, pollution index and integrated pollution index, and the outcomes disclosed that the study area is highly contaminated with Hg during all sampling periods, irrespective of fire, rainfall and seasons. It was immediately after the rainfall event, however highlighted the maximum contamination level. Moreover, the ecological risk index (E_{RI}) assessment also demonstrated the possibility of serious ecological risk throughout the study area in all sampling periods, specifically immediately after the intense rainfall event.

The data were compared with the world soil average, and the Victorian and Australian top soil averages and it was found that the concentration of Hg in each sampling stations, during all of the sampling occasions were well above the world soil average of 0.01 mg kg^{-1}, and well above the Australian and Victorian soil background Hg value of 0.03 mg kg^{-1} (except in S11after rainfall). The data were also compared with residential health investigation levels set by the NEPM and DEC and the ecological investigation level set by the DEC. The results revealed that all Hg levels are well below the residential health investigation levels of NEPM and DEC except S14 and S17 in autumn and S17 after the rainfall. In addition, the EIL assessment revealed that 78% of the sampling stations values exceeded the EIL in the pre-fire environment, and this increased to 84% immediately after the fire. Only slight variations were observed during the subsequent sampling periods.

Since Hg is a mobile metal, which can cause serious impacts on human and ecosystems health, its potential mobility in the Maldon study area indicates that it is a concern that should be addressed. In particular, the study area is adjacent to residential areas and a forest catchment, which provide potable water resources to local communities. Climate related studied highlighted that climate change may increase the frequency and areal extend of the wildfires and we may in need of more number of prescribed fires in additional fire-prone areas to decrease the possibility and intensity of wild fires. If prescribed fire happens in additional mining affected landscapes, fires may release and remobilize more amount of Hg in to the atmosphere and soil compartment, which may reach to the water resources by precipitation and subsequent runoff and by wind activity. If conditions favour, Hg may convert to more toxic methyl mercury in the aquatic environment. Aquatic plants and animals including fish may thus absorb Hg through direct exposure such as dermal contact, inhalation and ingestion of soil particles or through food chain mechanism, which may reach the human consumer. This exacerbate the concern due to the negative impacts of Hg on human and ecosystems health.

The study area is a small legacy mine site in Australia, but these effects are highly significant as more than a million legacy mine sites occur around the world and many of them are located in the fire-prone forest catchments. The risk to adjacent populations, water catchments and ecosystems are significant. Therefore, we recommend that all levels of prescribed fires should be carefully considered before using them as a forest and land management strategy, specifically on Hg contaminated landscapes. The mobility of Hg may be further elevated by increased flooding or intense storm events, both of which are predicted to increase in frequency with Global warming. Our results clearly indicates that un-rehabilitated mine sites, which inevitably house a concentrated source of Hg contamination pose, a long-term risk to the local and extended environments that require investigation before changes to land use management, weed control measures and fire mitigation strategies are applied.

Conflict of interest

Authors declared that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2017.09.117.

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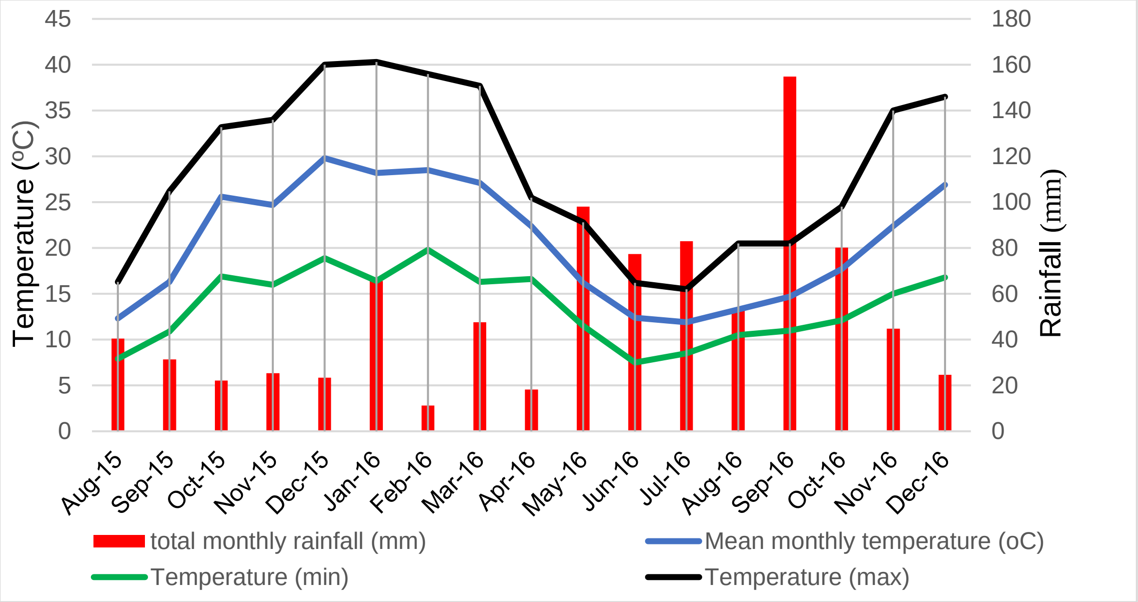


Fig. S1. Total monthly rainfall (mm) and monthly temperature (minimum, mean and maximum) (ºC) at the study area (Maldon) during the first 16 months after the prescribed fire in August 2015. (Source: BOM, 2017).

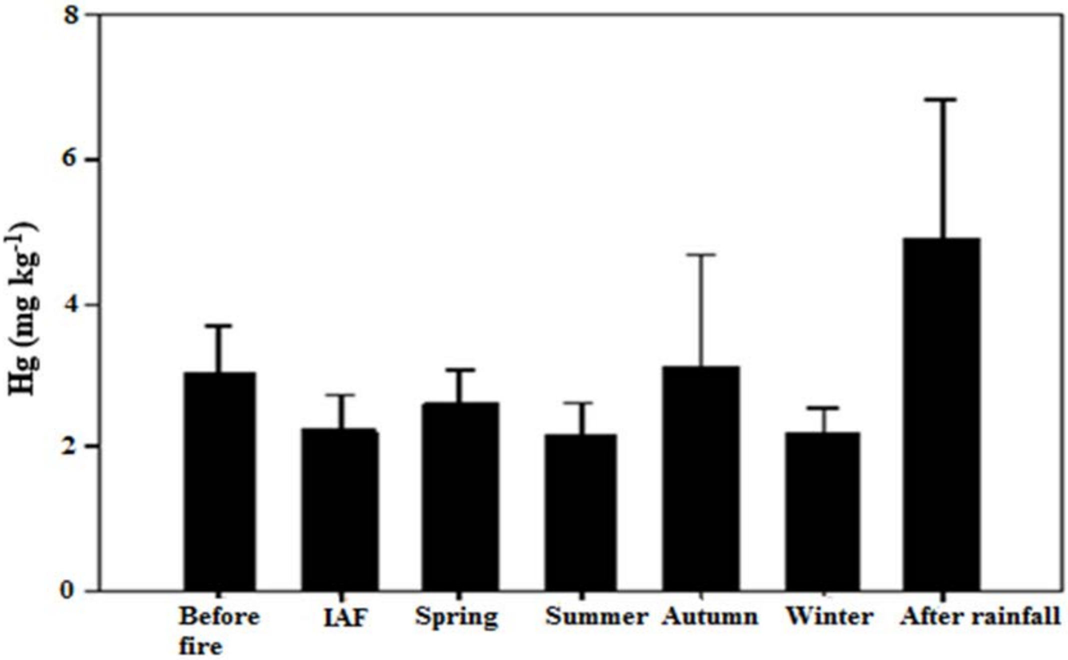


Fig. S2. The average Hg concentration (mg kg^{-1}) in the soils of the study area in seven different sampling occasions (IAF – Immediately after fire).

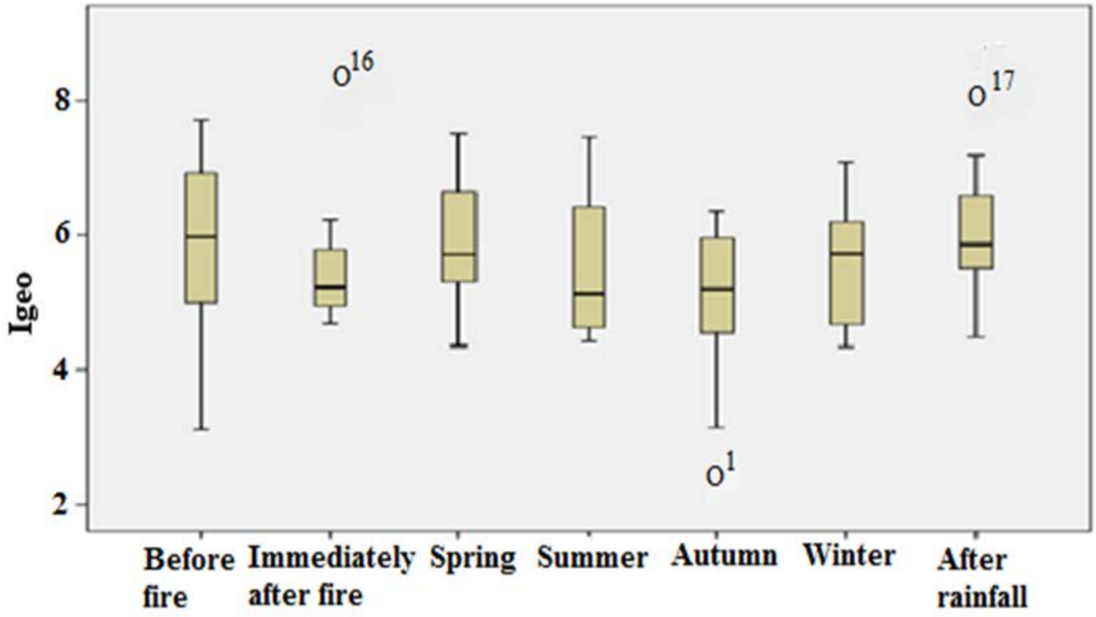


Fig. S3. The Igeo values of Hg in various sampling occasions (NB: the number at the outlier denote sampling station ID).

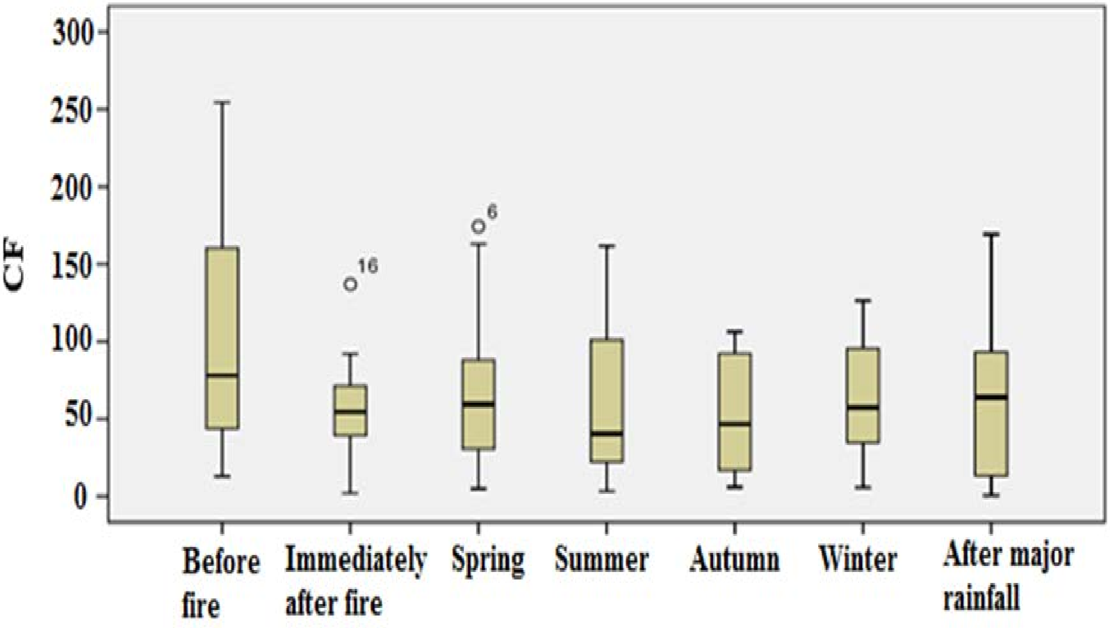


Fig. S4. Box plot showing the contamination factor of Hg in the study area (Maldon) in various sampling occasions (NB: the number at the outlier denote sampling station ID).

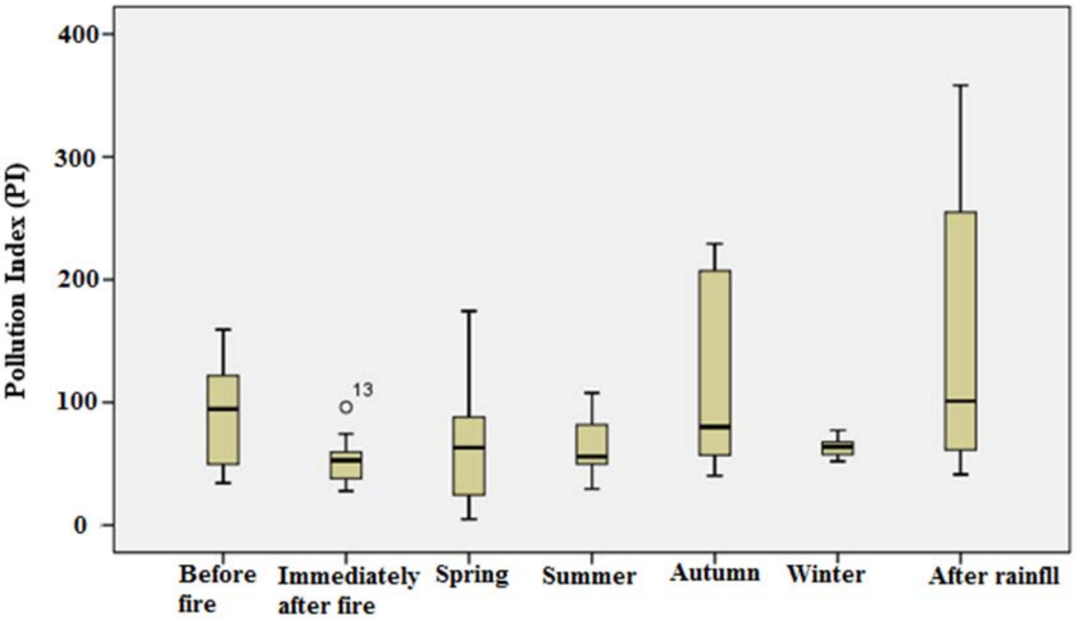
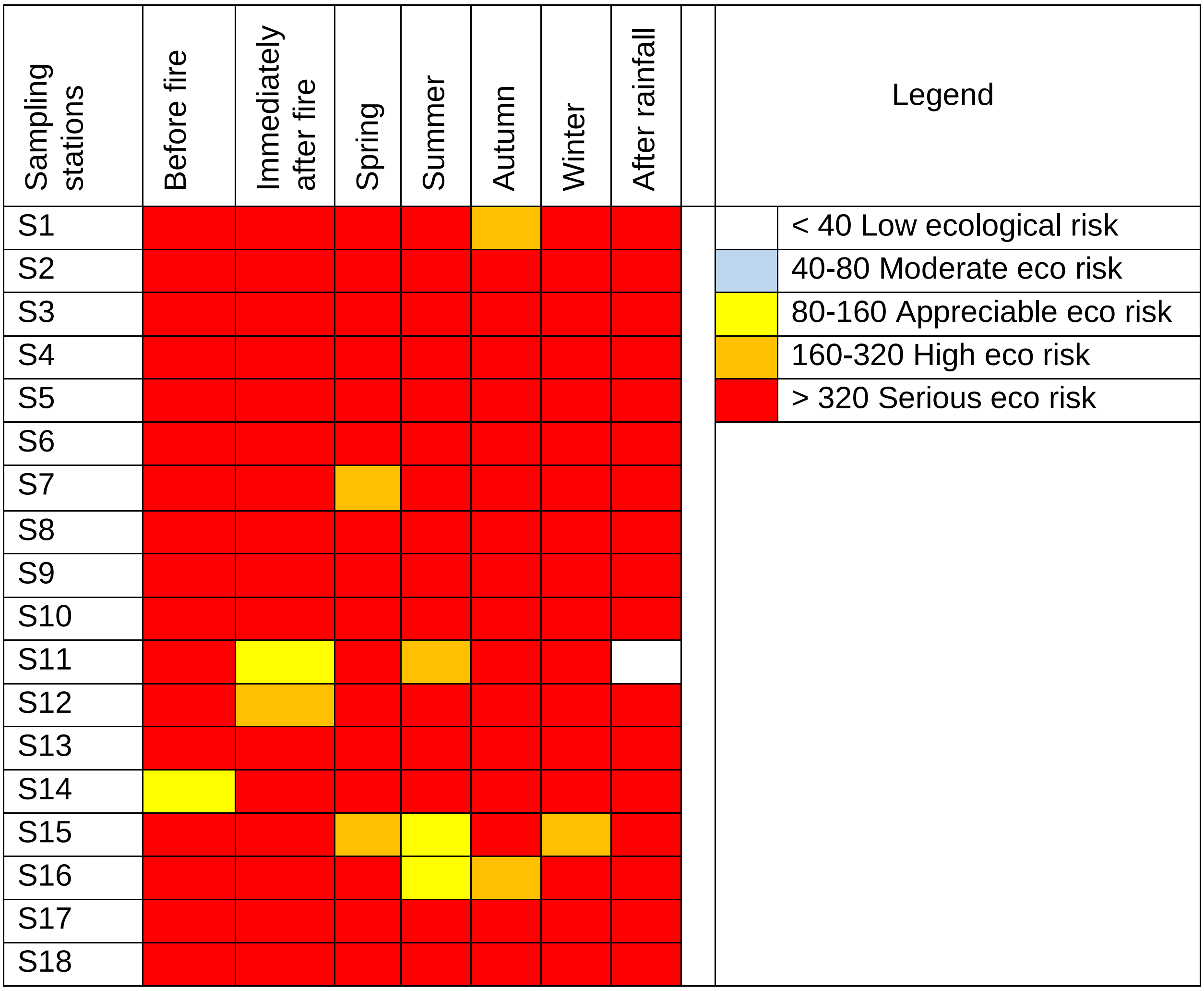


Fig. S5. Boxplot showing the pollution index (PI) of Hg in the study area in various sampling periods (NB: the number at the outlier denote sampling station ID).



Sampling stations	Before fire	Immediately after fire	Spring	Summer	Autumn	Winter	After rainfall
S1	🟥	🟥	🟥	🟥	🟧	🟥	🟥
S2	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S3	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S4	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S5	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S6	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S7	🟥	🟥	🟧	🟥	🟥	🟥	🟥
S8	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S9	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S10	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S11	🟥	🟨	🟥	🟧	🟥	🟥	⬜
S12	🟥	🟧	🟥	🟥	🟥	🟥	🟥
S13	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S14	🟨	🟥	🟥	🟥	🟥	🟥	🟥
S15	🟥	🟥	🟧	🟨	🟥	🟧	🟥
S16	🟥	🟥	🟥	🟨	🟧	🟥	🟥
S17	🟥	🟥	🟥	🟥	🟥	🟥	🟥
S18	🟥	🟥	🟥	🟥	🟥	🟥	🟥

Legend	
⬜	< 40 Low ecological risk
🟦	40-80 Moderate eco risk
🟨	80-160 Appreciable eco risk
🟧	160-320 High eco risk
🟥	> 320 Serious eco risk

Fig. S6. Spatial variation of ecological risk index (E_{RI}) (based on Hg concentrations in the soil) in the study area, during various sampling periods.

Chapter- 8

Influence of controlled burning on the mobility and temporal variations of potentially toxic metals (PTMs) in the soils of a legacy gold mine site in Central Victoria, Australia

Influence of controlled burning on the mobility and temporal variations of potentially toxic metals (PTMs) in the soils of a legacy gold mine site in Central Victoria, Australia

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Abstract

Controlled burns also known as managed burns or prescribed fires conducted in fire-prone areas are an efficient and economic option to reduce the frequency and intensity of wildfires. The objective of this study is to investigate the remobilization of potentially toxic metals (PTMs) in the soils of a legacy gold mine site in Central Victoria, Australia after a controlled burn and to describe their temporal variations in concentrations. Soil samples were collected two days before, two days after and five times later (3, 6, 9, 12 months and after major rainfall) in the post-burn environment after a controlled burn, from the Maldon legacy mine site and analysed for PTM concentrations. The results revealed PTM mobilization after the burn and most of the PTMs (As, Cd, Cu, Mn, Ni, and Zn) evidenced an increase immediately after the burn but a reduction in the subsequent post-burn environment. The increase is postulated to be associated with addition of PTM enriched ash to the soil, while the decrease is due to the removal of ash and surface soil by wind activity as well as rainfall runoff and leaching. The PTM mobility is of specific concern due to the negative impacts on human and ecosystems health. Climate change and the resulting projection of increased forest fire frequency highlight the environmental significance, given the expected concomitant increase in PTM mobilization through wildfires and controlled burns. Hence, the practice of controlled burning should be carefully considered as a forest management option in any legacy mining areas and indeed in other areas where PTM contamination is reported.

Key words: ash, forest fire, forest management, metal mobility, prescribed fire, soil and water contamination

1. Introduction

Potentially toxic metal (PTM) (As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) contamination associated with mining and mineral processing, places a significant financial and environmental burden on communities around the world (Pearce at al., 2010, Esshaimi et al., 2012; Cobbina et al., 2013; Martin et al., 2013; Schaider et al., 2014; Martin et al., 2016, 2017). This is predominantly because of the negative impacts of PTMs on human and environmental health, particularly their toxicity, bioaccumulation and biomagnification tendency in the food chain and the environmental persistency (Adriano, 2001; Ignatavicius et al., 2006). PTM contamination is a significant problem at legacy or historical mining areas as well, due to the lack of environmental regulations during mining and following closure resulting in the accumulation of millions of tonnes of mine waste materials rich in PTMs. The volume of the land affected by PTMs makes this a significant global issue as more than a million legacy mine sites estimated to exist across the globe (UNEP, 2001; Lottermoser, 2007; Ericson et al., 2008; Zhou et al., 2010; Esshaimi et al., 2012; Zornoza et al., 2012; Garcia-Lorenzo et al., 2014; Armeinta et al., 2016).

Soil PTM contamination from both existing and legacy mine sites has been reported from around the world. Harrison et al. (2003) investigated the PTM contamination around the Yerranderie legacy Ag-Pb-Zn mine site in New South Wales, Australia and reported higher PTM (Ag, As, Cd, Cu, Hg, Pb, and Zn) concentrations in soil surrounding the mine site, which are up to 400 times the guideline values. Soil core sample analysis showed that an overall increase occurred in and around 1950, which is coincident with high rainfall and preceded drought periods (Harrison et al., 2003). Similarly, Schaider et al. (2007) studied the levels of Zn, Pb and Cd in a legacy mine site (Tar Creek Superfund site) in Oklahoma, USA and found elevated concentrations of Zn (9100 ± 2500 mg kg^{-1}), Pb (650 ± 360 mg kg^{-1}) and Cd (42 ± 10 mg kg^{-1}) in soil samples, which are relatively labile and are present in bio-accessible mineral phases. In a similar manner, Esshaimi et al. (2012) investigated soil and water contamination in the vicinity of the Kettara abandoned mine, south Morocco and reported high concentrations of Cu, Pb and Zn in the tailings (76, 80, 79 mg kg^{-1} respectively) and in soil (68, 52 and 26 mg kg^{-1} respectively) samples. Moreover, PTM dispersion to downstream and downslope areas was also observed, and this was considered to be due to the surface runoff and strong wind actions (Esshaimi et al., 2012). Other studies such as Clark et al. (2001) from Australia, Zornoza et al. (2012) from Spain, Lee et al. (2001, 2005) from South Korea, Zou et al. (2010) from China and Cobbina et al. (2013) from Ghana are all significant in this context, as each of these study sites documents the extent of contamination of soil, sediments, water bodies and general vegetation with PTMs from legacy mine sites.

Central Victoria in Australia, is not exempt from PTM contamination as it has seen extensive mining since 1850, and has produced more than 2500 t of gold with resulting accumulation of tonnes of mine waste materials rich in PTMs (Sultan, 2006, 2007; Pearce et al., 2010, 2012; Martin et al., 2013, 2014, 2017). Any disturbance of this contaminant pool is of concern, since it will act as a catalyst for enhanced mobility and dispersion of PTMs. One such major agent of disturbance is forest fire, which includes controlled burns (Certini, 2005; Neary et al., 2006; Pereira et al., 2011; Abraham et al., 2017a, b; Alcaniz et al., 2018).

Fires are natural process in many terrestrial ecosystems and some are severely destructive in nature to the vegetation and surface soil (Neary et al., 2006; Beganyi and Batzer, 2011). The human-fire relationship goes back to the pre-historic period, where humans used fire in preparing food, hunting and agricultural land preparation (Pyne, 2015). Recent studies show the adverse and diverse impacts of fire to the environment, economic sustainability and social structures. (Smith et al., 2011; Liu et al., 2014). For example, fire may disturb the forest ecosystem structure and functions by affecting the nutrient cycling, vegetation distribution and composition and herbivore distribution (Augustine et al., 2014; Alcaniz et al., 2018), however, some ecosystems are fire dependent (Alcaniz et al., 2018). Fire may alter a range of substantial physical and biogeochemical soil properties and affect the catchment behaviour by affecting key hydrological factors such as infiltration and runoff (Certini, 2005; Shakesby and Doerr, 2006; Knoepp et al., 2008; Verma and Jayakumar, 2012; Abraham et al., 2017b). The contaminant mobilization associated with forest fire is of global significance but region specific (Jovanovic et al., 2011; Costa et al., 2014; Campos et al., 2015, 2016; Abraham et al., 2017a, b). The fire potentiality depends on the increased fuel load, dry weather patterns with increased atmospheric temperature and wind speed, all of which enhance ignition potential (Certini, 2005; Hennessy et al., 2005; Westerling et al., 2006; Alcaniz et al., 2018). Recent climate change studies highlight the increase in frequency and areal extend of fire in many parts of the world in association with rural depopulation, land abandonment and afforestation with fire-prone species (Hennessy et al., 2005; Westerling et al., 2006; Moreira et al., 2009; IPCC, 2013; Campos et al., 2015, 2016). This resulting fuel-rich environment consequently requires added controlled burning events as a fire risk mitigation strategy.

Controlled' or 'prescribed burning' is a type of managed forest fire, where deliberate application of fire, acts primarily to reduce the available fuel load and to reduce the frequency and intensity of wildfires (Hatten et al., 2005; Pereira et al., 2011; Fernandez et al., 2013; Bennet et al., 2014; Alcaniz et al., 2018). This low-to-moderate intensity fire event reduces the fuel load by consuming the understory vegetation and part of the forest floor layers, and has long been considered as an efficient and economic option for fire control (Fernandez and Botelho, 2003; Pereira et al., 2011; Alcaniz et al., 2018). Controlled burning is also used for agricultural land preparation, weed and insect control, biodiversity management amongst other land management applications (Pereira et al., 2011; Fernandez et al., 2013) and is widely practised in fire-prone areas in the American, European and Australian continents (Wade et al., 1989; Fernandez and Botelho, 2003; Certini, 2005; Castellinou et al., 2010; Pereira et al., 2011). Although it has a number of benefits, controlled burn constitutes a disturbance on the forest environment, alters the ecological processes and affects the properties of the surface soil (Santin and Doerr, 2016; Alcaniz et al., 2018). Moreover, precipitation and subsequent runoff events in the post-burn environment may result in the transport of surface soil and ash, which contains elevated levels of various contaminants, including PTMs to downslope and downstream surface water resources (Ignatavicius et al., 2006; Burk et al., 2010; Stein et al., 2012; Burk et al., 2013; Costa et al. 2014; Abraham et al., 2017b). This has heightened concern that this series of events may act as a contaminant source for potable water resources serving local communities and may negatively impact the health of ecosystems (Ignatavicius et al., 2006; Burk et al., 2010; Smith et al., 2011; Stein et al., 2012; Burton et al., 2016; Abraham et al., 2017a,b).

Information regarding PTM mobility in the environment is vital for ecosystem management and sustainability due to the potential environmental persistence, toxicity and health impacts on human and ecosystems, together with their potential bioaccumulation characteristics (Adriano, 2001; Ignatavicius et al., 2006; Abraham et al., 2017a,b). Wildfires have been found to mobilize PTMs in the atmospheric, terrestrial and aquatic compartments mostly by the combustion of vegetation and the subsequent release of ash and the burning of soil organic matter (Costa et al., 2014; Kristensen et al., 2014; Campos et al., 2015, 2016; Abraham et al., 2017a, b, 2018). While some studies report the influence of wildfire on PTM mobilization (Odigie and Flegal, 2011, 2014; Kristensen et al., 2014; Burton et al., 2016; Campos et al., 2015, 2016; Odigie et al., 2016; Nunes et al., 2017; Wu and Taylor, 2017), no studies have been reported from a legacy gold mine site, associated either with wildfire or controlled burn. Since, wildfire has the potent to release and remobilize PTMs, we hypothesis that a controlled burn is also able to release and remobilise PTMs, specifically from a legacy mining landscape, even though the burning temperature is comparably low. Hence, the current study is designed (i) to identify the mobility and distribution of PTMs in soil, immediately after controlled burn event and (ii) to identify the temporal variations of PTMs concentrations in the post-burn soil environment. This study provides geochemical information to land and water managers to inform their decision-making to achieve better environmental and health outcomes, including water quality in fire-prone areas (specifically mining affected and PTM affected landscapes) in Australia and in number of countries across the globe.

2. Materials and Methods

2.1 Study area

Central Victoria in Australia has hundreds of legacy gold mine sites and most of them are located in forest areas. The study area Maldon is a legacy gold mining township, located 145 km NW of the City of Melbourne and 40 km SW of Greater Bendigo in Victoria, Australia. In the Maldon area, gold mining started in 1853 and the phase of deep mining ceased in 1926, mainly because of difficulties in the mining process, but later (in 1990s) mining restarted in the area with modern technology (Parkweb, 2018). Cradle and gold pan to separate gold from alluvium was the early gold extraction techniques, but later moved to puddling, quartz reef mining, deep lead mining and various forms of sluicing, among them quarts reef mining was the widespread technique (Egold, 2017). Open cut trenches, shafts and adits, which used to access sulphide bearing ores can be seen in the area as mining remnants (Cherry and Wilkinson, 1994; Maldon, 2017). During this early mining period, the area produced 56 t of gold from various mining sites (Cherry and Wilkinson, 1994). Mining and the lack of environmental regulations during historical mining period, resulted in the accumulation of tonnes of mine waste materials in the area, which are rich in PTMs (Sultan 2006, 2007; Martin et al., 2013, 2014). From an area with a number of legacy mine sites, one, which was located on public land, east of the Union Hill mine was selected for controlled burn related PTM mobility study (Fig.1). Whilst the study area is a public forest land (State forest) under the jurisdiction, it is located near the Maldon town centre, and is thus close to a residential area.

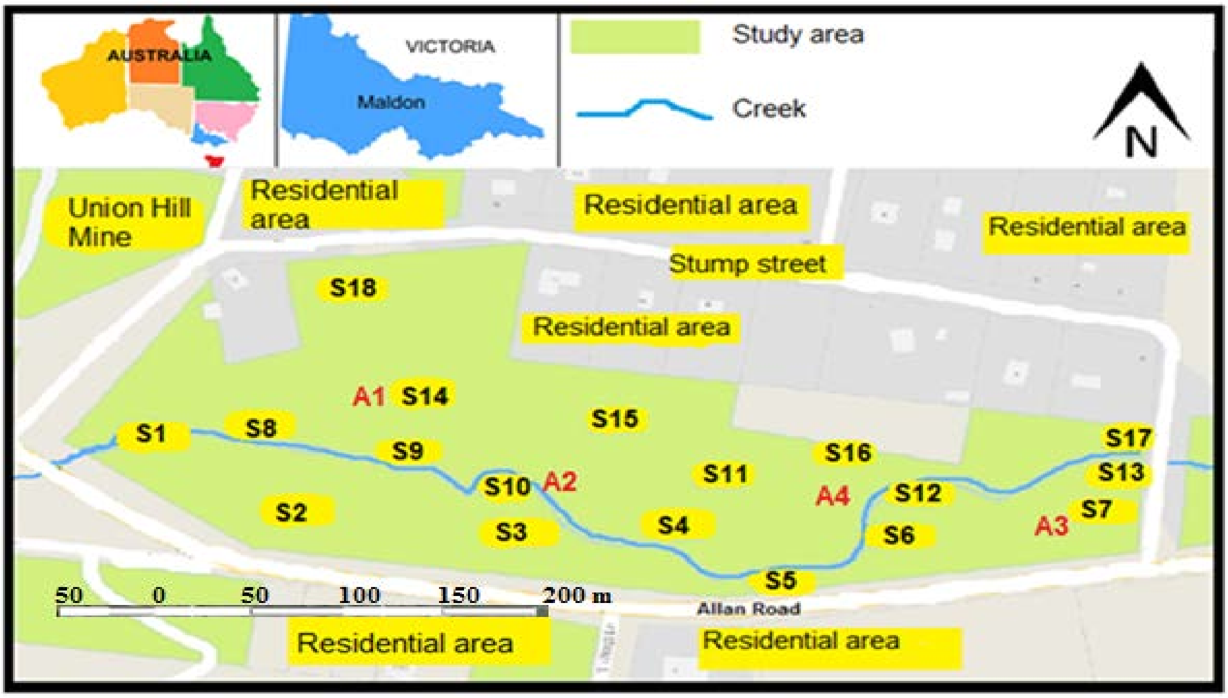

Fig. 1. Location of the study area with soil sampling (S1 to S18) and ash sampling (A1 to A4) stations identified.

The area receives an average annual rainfall of 540 mm, with cold wet winters (7.5–20.5 °C) and warm dry summers (16.4–40.3 °C) (Taylor et al., 2000; BoM, 2017). A creek running from west to east channels much of the rainfall falling in the study area, which is significant as it may carry all contaminants including PTMs to the downstream water resources. The canopy in the area is native acacia (*Acacia pycnantha) (60%)*, and eucalyptus (*Eucalyptus radiata) (40%),* whereas, the understory species are the introduced gorse (*Ulex europaeus)* (70%), Chinese shrub *(Cassina arcuta)* (10%), golden shrimp *(Pachystachys lutea)* (10%) and Onion weed (*Asphodelus fistulosus*) (10%).

A controlled burn was conducted in the area in late August 2015 (end of winter) for fire risk mitigation and land management (weed control) purposes by the Department of Environment, Land, Water and Planning (DELWP) of the State of Victoria and Parks Victoria fire crews, and we capitalised this opportunity to study PTM mobility. The Parks Victoria fire crews ignited the fire around 10:00 am at the western part of the study area and moved to the east. Immediately after the ignition, fire grew quickly because of the presence of high dry fuel load and the smoke moved to the SW in conjunction with wind direction. The fire observed as 'seemingly intense' for several minutes due to the observed rise in flame, around 2 m in height (Fig. 2). It took around one and half hours to burn the major fuel loads in the area, followed by slow burning of plant materials which continued for two days. The fire burned most of the ground cover litter and shrub type vegetation (< 2 m in height). Around 80% of the study area was affected by the burn and the government agency responsible for the burn had no history of previous fire use in this area (DELWP pers comm). There were large amounts of ash observed close to some of the experimental sampling stations (S13, S14 and S10) where high fuel load and tree trunks (down wood) were burned. In some spots, it was grey or light grey in colour, while other spots mostly black in colour. The fire consumed the shrubs completely, but had limited impact on the canopy.

There was no rainfall in between before burn (2DBB- two days before burn) (first) and immediately after burn (2DAB – two days after burn) (second) sampling occasions, however the cumulative rainfall in between the second and third (3MAB- three months after burn) sampling period was 79 mm and between third and fourth (6MAB- six months after burn) sampling period was 100.2 mm respectively. Between the fourth and fifth (9MAB- nine months after burn) sampling period, the cumulative rainfall was 164 mm and between fifth and sixth (12MAB- twelve months after burn) sampling period received the highest rainfall of 243 mm. However, the rainfall after the sixth sampling period is defined as the major event with 155 mm rainfall within a fortnight. The total monthly rainfall and mean monthly temperature are given in Fig.3 (BoM, 2018).

Fig. 2. Showing the fire intensity during the controlled burn.

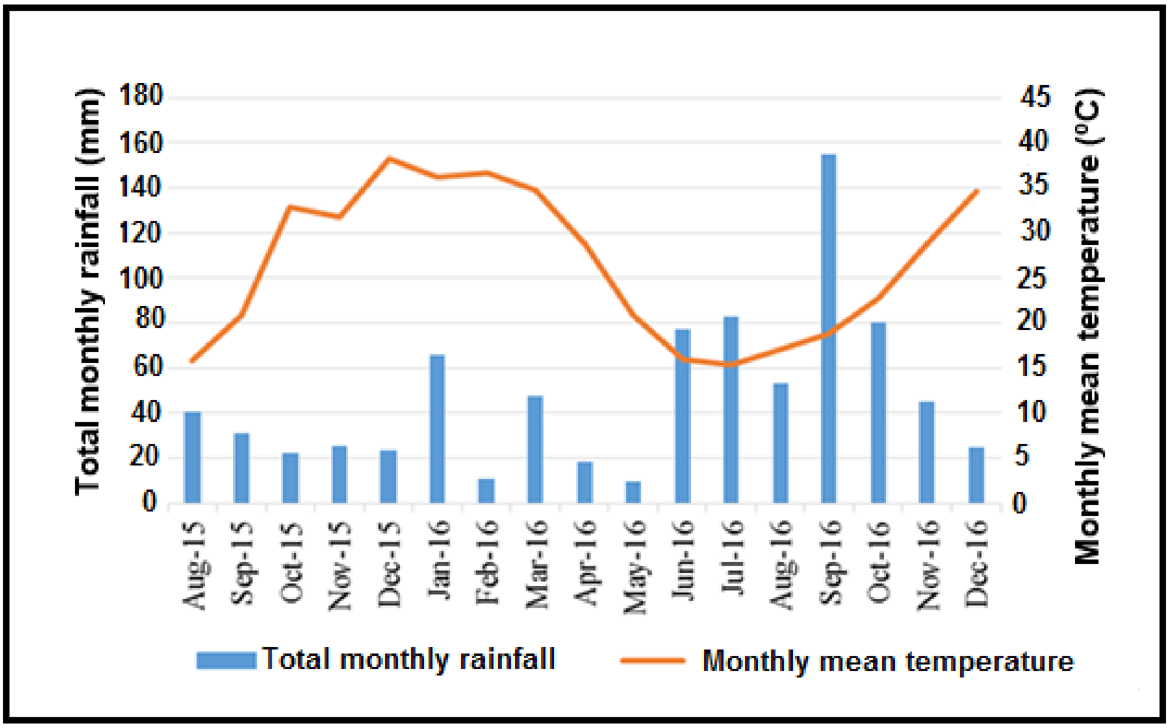

Fig. 3. Total monthly rainfall (mm) and mean monthly temperature (ºC) at the Maldon study area during the first 16 months after the controlled burn in late August 2015 (BoM, 2018).

2.2 Soil sampling

The nature and composition of surface soil is reported to be considerably affected by the intensity and duration of fire. In addition, during the post-fire environment, the soil is susceptible to human intrusion, wind-borne transport of fine materials and to rainfall and surface runoff (Hernandez et al., 2003; Mandal and Sengupta, 2006; Schaider et al., 2007, Shcherbov, 2012). With these exogenous influences in mind, in order to assess the extent of PTM mobility in the surface soils after a controlled burn and to examine their dispersal in the post-burn environment, 18 surface soil samples (variable depth up to 3 cm) were collected at one time. These samples were gathered (i). two days before burn (2DBB), (ii). two days after burn (2DAB), (iii). 03 / 06 / 09 / 12 months after burn (3MAB / 6MAB / 9MAB / 12MAB) and (iv). immediately after a major rainfall event (IAMR) (155 mm within a fortnight) in September 2016 (two weeks after the 12MAB sampling). All the seven sets of samples were collected from the same sampling stations (S1 to S18, noted in Fig. 1), using the STAR sampling method with an established trace metal clean technique procedures (Ritson et al., 1999; Soto-Jimenez et al., 2006; Taylor et al., 2010; Odigie and Flegal, 2011). STAR sampling is a soil sampling method in which surface soil samples were collect at the centre and five corners of a STAR (in shape) in a location and mixed together before transfer to the sampling container. Approximately 1 kg of bulk surface soil samples (up to 3 cm of depth) were collected within an area of 1600 cm^2 (40 cm x 40 cm) from each sampling station (S1 to S18) with STAR method and were transferred to clean and dry polyethylene containers at the sampling site and brought to the Federation University Australia laboratory for analysis. A total of 126 soil samples (18 stations x 7 sampling times) were collected over a period of one year from the study area.

2.3 Ash sampling

Ash is defined as the organic and inorganic residue formed by the burning action of fire and the colour of the ash can provide some indication of the fire intensity (Bento-Goncalves et al., 2012). White coloured ash denotes complete combustion of the fuel load in a high intense fire environment, whereas, grey ash represents a moderate to high fire intensity (Ubeda et al., 2009). In the study area, after fire, patches of grey and light grey ash were observed, but most of the ash was black in colour consistent with a low to moderate intensity fire (Ubeda et al., 2009; Bento-Goncalves et al., 2012).

The thickness and colour of ash covering the soil surface after the fire varied in space and time. This heterogeneous distribution of ash is mainly due to the types of fuel load, amount of fuel, burning temperature, duration of burning, wind pattern and different degree of combustion completeness (Bodi et al., 2014). During the controlled burn, thick ash layers were formed where thick fuel loads were available. A total of four ash samples (each of approximately 200 g) were opportunistically collected immediately after the burn, from locations (Fig.1) were thick ash (>1 cm) were available, using the trace metal clean technique procedures. Since ash samples were collected only from the thick ash locations so as to limit any soil or other contamination. The ash samples were stored in glass containers and transported to the Federation University Australia soil laboratory for analysis.

2.4 Sample Analysis

In the soil laboratory, soil and ash samples were transferred to aluminium trays and placed in the oven for 24 hours (below 60 ^{O}C). The oven dried samples were sieved through the 2 mm wire mesh sieve, and < 2mm fractions were used for analyses. Soil and ash pH and electrical conductivity (EC) were determined with US-EPA 9045D and 9050A analytical procedures respectively, and organic matter (SOM/ AOM) and carbonate content (both expressed as percentage) were determined with the Loss on Ignition (LOI) method as detailed mentioned in Rayment and Lyons (2014).

All PTMs analysis in the soil samples were conducted in a NATA (National Association of Testing Authorities) accredited laboratory (Accreditation No. 825) by Ultra-Trace Level Methods using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) with Aqua Regia Digestion (GEO-AR01). Oven dried and sieved (using stainless steel wire mesh) soil samples were milled using stainless steel bowls, and 0.5 g of the milled sample was used for PTM analysis. Aqua regia was used to digest the sample on a graphite heating block and allowed to cool. The cooled solution was mixed with deionised water and analysed by ICP-AES. Results that returned a higher than scoped concentration of Hg were diluted accordingly. These diluted samples were then analysed by ICP-MS for the remaining set of metals and the results were corrected for inter-elemental spectral interference (Santoro et al., 2017).

2.5 Data Analysis

The data were statistically analysed using IBM SPSS (version 23) and R (version 3.4.1) software(s). Descriptive statistics including minimum, maximum, median, percentiles and interquartile range (IQR) were obtained for the following soil properties: pH, EC, SOM, carbonate content and PTM concentrations in the soil in the pre- and post-burn environments. Wilcoxon signed rank sum tests were conducted to determine if statistically significant differences existed between (i) the median concentrations of each PTM and (ii) the physicochemical characteristics of the soil immediately before and after the controlled burn, and immediately before and after the rainfall event. Friedman's test has applied to test the statistical significance of the influence of the time (03 / 06/ 09 / 12 months) on the soil pH, EC, SOM, carbonate content and PTM concentrations in the soil. The Spearman rank correlation coefficient was used to relate the concentration of physicochemical properties of the soil to the PTMs in the soil, both from the corresponding sampling periods and the metals themselves.

3. Results and Discussion

Pre- and immediate post-burn soil data from the Maldon legacy mine site (study area) were collated and compared in terms of pH, EC, SOM, carbonate content and PTM concentrations, in order to understand the effect of controlled burn on the physicochemical characteristics of the soil and the PTM concentrations in the soil. All data from the post-burn environment were also analysed to determine the influence of time, specifically the effect of major rainfall (in September 2016 after a year of controlled burn) on the soil physicochemical characteristics and the PTM concentrations in the soil.

3.1 Immediate effects of controlled burn on soil characteristics

A summary of the physicochemical characteristics (pH, EC, SOM and carbonate content) of soil, two days before and two days after the controlled burn, followed by five times (four times of sampling at three months intervals and the last sampling was two weeks after the previous and immediately after a major rainfall event). A combined data set spanning more than a year is measured and the relevant details are presented in Fig. 4 and in a supplementary table (Table.S1). The immediate post-burn soil samples demonstrated significantly higher median values of pH ($p < 0.05$) and EC ($p < 0.01$), and higher SOM ($p < 0.08$) compared with pre-burn soil samples with differences in these values amounting to a factor(s) of 1.1, 2.3, and 1.7 respectively.

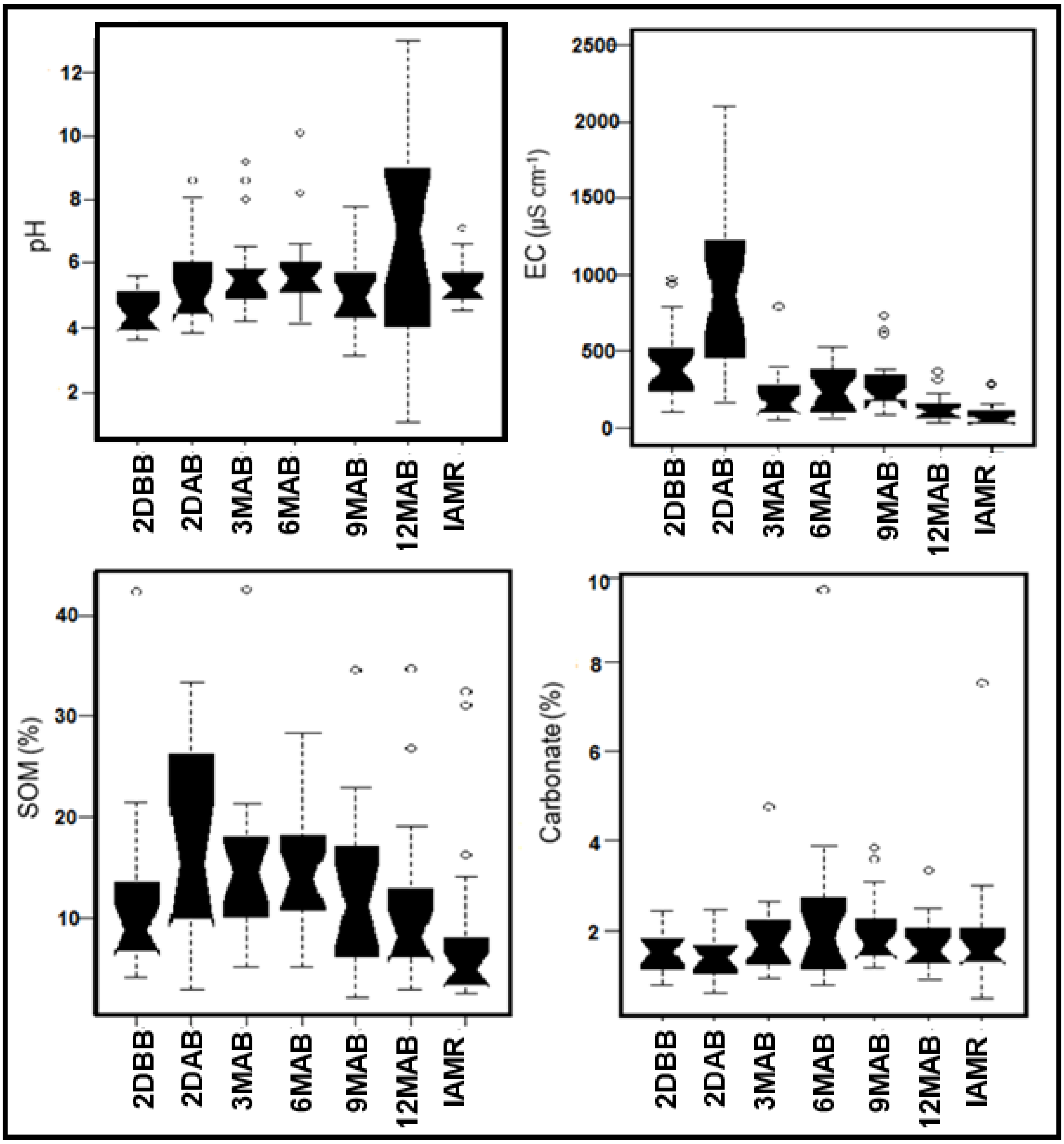

Fig.4. Notched boxplot showing the concentrations of pH, EC ($\mu S\ cm^{-1}$), SOM (%) and carbonate content (%) in soils during various sampling occasions (2DBB- two days before burn, 2DAB- two days after burn, 3MAB -three months after burn, 6MAB-six months after burn, 9MAB-nine months after burn, 12MAB-twelve months after burn, and IAMR- immediately after major rainfall in September 2016) (n=18). Note the increase in pH, EC and SOM immediately after the fire.

Immediately after the controlled burn, the median pH of the soil (4.8) was significantly higher ($p < 0.05$) than that of the pre-burn soils (4.3) with values differing up to 1.9 times were observed. The minimum observed pH in the pre-burn environment was 3.6 and the maximum was 5.6, whereas in the post-burn environment, the observed minimum was 3.8 and the maximum increased to 8.6. Among the 18 sample stations in the study area, 12 stations (66%) showed an increase in pH value immediately after the burn.

Similarly, immediately after the burn, median EC of the soil (863 µS cm^{-1}) was significantly higher ($p < 0.01$) than that of the pre-burn soil (375 µS cm^{-1}), with values differing up to 5.6 times greater were observed. The minimum EC observed in the pre-burn environment was 95 µS cm^{-1} and the maximum was 970 µS cm^{-1}, but in the immediate post-burn environment, the minimum observed increased to 174 µS cm^{-1} and the maximum increased to 2800 µS cm^{-1}. Among the 18 sampling stations, 13 stations (72%) showed increases in EC values, and five stations (28%) showed decrease in values immediately after the burn. The highest EC variation observed was 2011 µS cm^{-1}, followed by 2005 µS cm^{-1}, and the lowest being 28 µS cm^{-1}.

The SOM (median) almost doubled (15.2%) immediately after burn, compared to the pre-burn median value (8.7%). Similar to pH, 12 sampling stations (66%) demonstrated increase in SOM content and the remaining (34%) stations shown decrease in concentration. The minimum SOM value in the pre-burn environment was 4% and the maximum was 42.3%. Even though, median SOM highlighted increase, the minimum value reduced to 2.7%, and the maximum reduced to 33.3% in the immediate post-burn environment. The highest increase observed was at S3 and the lowest was S17, whereas, the highest decrease observed was at S4 and the lowest decrease was at S18.

The median carbonate value in the immediate post-burn environment did not show any significant variation in concentration compared with the pre-burn median value. However, if we take individual sample stations, S4 station records the highest increase in concentration and S13 shown lowest increase. Among the 18 stations, 10 stations shown reduction on carbonate value and the highest reduction observed was at S11 and lowest deduction observed was at S18.

The fire-induced increases in soil pH and EC, noted immediately after the burn are consistent with existing studies (Ulery et al., 1993; Hernandez et al., 1997; Ubeda et al., 2005; Quintana et al., 2007; Granged et al., 2011; Campos et al., 2015, 2016). The increase is considered to be due to the combustion of vegetation with subsequent deposition of ash, which adds large amounts of alkaline oxides and hydroxides to the surface soil (Arocena and Opio, 2003; Certini, 2005, Verma and Jayakumar, 2012, Alkaniz et al., 2018). The decrease in pH also relates to the reduction in the concentration of organic acids (Ulery et al., 1993,1995; Verma and Jayakumar, 2012; Campos et al., 2016). The high pH and EC of ash samples compared to the surrounding soil samples were consistent with this postulate and similar results were reported earlier (Naidu and Srivasuki, 1994; Kim et al., 2003; Goforth et al., 2005; Campos et al., 2016). In the study area, the major fuel load was understory vegetation gorse, Chinese shrub, golden shrimp, onion weed and the leaf litters of canopies such as eucalyptus and acacia and were burned almost completely, resulting in the deposition of thick ash layer in specific places where fuels were available in high quantity. Other sampling locations, ash dispersed by burning and wind activities. The sampling stations, which shown high pH variations were close to the thick ash production sites.

Several laboratory studies address the behaviour of soil pH during fire (Sever et al., 2001; Badia and Marti, 2003; Certini, 2005; Marcos et al., 2007; Moreno et al., 2015; Thomaz, 2017). However, the laboratory studies largely ignore the production of ash and the interaction of ash with soil as most of the laboratory studies are conducted by heating the soil in controlled environment. Moreover, the laboratory studies use residence time much longer than those experienced by soil during the forest fire. Fluctuation in temperature which is highly likely in a real fire environment is also difficult to model in laboratory studies. Even though, laboratory studies can’t model the real time fire environment, most of the studies highlighted the increase in soil pH according to the rise in temperature (Badia and Marti, 2003; Certini, 2005; Marcos et al., 2007; Moreno et al., 2015; Thomaz, 2017).

Low severity controlled burns result in only a slight change in SOM concentration, whilst high severity wildfires results in a more significant alterations (Johnson, 1992; Bogacz et al., 2011; Verma and Jayakumar, 2012). The effect of fire on SOM is highly variable, and depends on (i) the type and intensity of the fire, (ii) the nature of fuels, (iii) prevailing soil moisture levels, and (iv) other physical attributes, so that generalizations are challenging (Gonzalez-Perez et al., 2004; Verma and Jayakumar, 2012). In this study, immediately after the controlled burn, median SOM (15.2%) were higher than that of the pre-burn soils (8.7%), where it was observed that values differed up to 3.8 times across the samples taken. This increase in SOM is in agreement with existing studies (Pardini et al., 2004; Jovanovic et al., 2011; Faria et al., 2015; Campos et al., 2016) and is considered to be due to the accumulation of pyrogenic carbon (partially charred leaves, litter, forest necromass and the deposition of ash) formed by the incomplete combustion of biomass (Gonzalez-Perez et al., 2004; Goforth et al., 2005; Jovanovic et al., 2011; Bodi et al., 2014; Faria et al., 2015).

After the burn, 8 stations showed a slight increase (1.3%) and 10 stations showed a small decrease (1.5%) in carbonate content. The limited variation is probably due to the capability of carbonate to resist temperatures of up to 1000 ^{O}C (Rabenhorst, 1988). When the burning temperature exceed 580 ^{o}C, the carbonate may be converted into oxides with distinct morphological changes from massive to sponge-like being reported (Klopporge et al., 2004). New carbonate can be formed by the interaction of ash with atmospheric CO_2 and moisture resulting in the increase in particle size due to agglomeration (Steenary et al. 1999) or swelling of ash particles (Stoof et al., 2010; Bodi et al., 2014). However, in this study, the lack of substantive change in carbonate concentration is attributed to the low burning temperature (below 580 ^{o}C).

3.2 Soil physicochemical characteristics – Temporal variations

It is reported that both soil pH and EC increase after a forest fire, but they return to the pre-burn level after several months as observed in many previous studies (Ulery et al., 1995; Hernandez et al., 1997; Kim et al., 2003; Granged et al., 2011). In this study, three months after burn (3M) samples displayed a minor increase (compared to the immediately after burn samples (IAB)) in median pH from 4.8 to 5.5 with a maximum of 3.7 units. The pH is similar in six months after burn (6M) samples (5.5) with a maximum observed increase of 1 unit only. However, in nine months after burn samples (9M), it showed a reduction from 5.5 to 4.9 (with the observed maximum of 2.3 units), followed by an increase in twelve months after samples (12M) (5.7). The increase in 12M after burn is considered to be due to the increase in rainfall in winter and the subsequent interaction of ash with the surface soil. Compared to 12M samples, the samples collected immediately after the major rainfall (IAMR) highlighted a slight reduction in pH (5.2). All variations noted here in pH levels were statistically significant ($p< 0.01$).

The controlled burn doubled the median EC value of the surface soil (from 375 to 863 µS cm^{-1}), which displayed a reduction after 3M sapling (155 µS cm^{-1}) (with a maximum observed decrease of 2047 µS cm^{-1}). After the 6M samples, the median EC increased from 155 to 228 µS cm^{-1} (with a maximum observed increase of 1160 µS cm^{-1}), but in 9M, the mean EC reduced to 196 (with a maximum observed decrease of 3530 µS cm^{-1}). A further median EC reduction was observed in 12M samples (102 µS cm^{-1}) and after the major rainfall event (50 µS cm^{-1}). The mean EC value dropped below the pre-burn value in 3M sampling onwards until after the rainfall sampling, displaying the ephemeral characteristic of EC. All EC reductions are considered to be caused by the rainfall events and all variations are noted as statistically significant ($p < 0.001$).

In the post-burn environment SOM demonstrated statistically significant ($p<0.01$) reduction (IAB-15.2, 3M-14.4, 6M-13.8, 9M-11.1, 12M-8.1 and IAR-4.8%) in all the sampling periods and in 9M samples it fell below the pre-burn level of 8.7%. Compared to pH, EC and SOM, variation of carbonate is negligible in the post-burn environment (variations are from 1.4, to 1.7, 1.8, 1.7, 1.6 and 1.5% only).

The post-burn temporal reductions in pH, EC and SOM are in agreement with other studies (Hernandez et al., 1997; Kim et al., 2003; Granged et al., 2011; Campos et al., 2016), and were attributed to the influence of wind erosion as well as rainfall and subsequent runoff, which may have transported ash and surface soil downslope, downstream and down wind direction (Ulery et al., 1993; Zabala et al., 2014; Campos et al., 2016). The increase in soil pH during 3M and 6M after burn is probably due to the continued mixing of ions from the existing ash with surface soil, and the reduction in 9M after burn is probably associated with the leaching effect of the increase in rainfall (163 mm) similar to that reported by Costa et al. (2014). The decreases in EC during 3M and 9M are also explained by the effects of rainfall, while the increase in levels in 6M compared to 3M and 9M may be due to the lack of rainfall in summer.

3.3 Physicochemical characteristics of ash

Bodi et al. (2014) defined "Forest fire ash is the particular residue, remaining on the ground from the burning of forest fuels consisting of mineral materials and charred organic components". It is a complex mixture of organic and inorganic residues, include soil materials present in the litter and vegetation before fire. Ash may also contain burned soils, which has lost its structure, oxides and hydroxides of base cations, silica, phosphorous, nutrients, major and trace metals and potential contaminants produced by fire. (Goforth et al., 2005; Plumlee et al., 2007; Gabet and Bookter, 2011; Bento-Golcalves et al., 2012; Bodi et al., 2014; Campos et al., 2016; Abraham et al., 2017a, b). These materials may be subsequently deposited on the soil surface in burned areas. Ash can provide valuable information about the fire severity and consumption completeness of fuels (Keeley 2009; Pereira et al., 2014). The low to moderate severity burns result in black ash, whereas, high fire severity results in white or grey ash (Pereira et al., 2014). The presence of various ions in ash generally correlates with alkaline nature and elevated EC (Ulery et al., 1993; Gabet and Bookter, 2011). The pH, EC, OM, carbonate content and the colour of four ash samples collected just after the controlled burn, are summarised in Table 1.

Table 1. pH, EC, OM and carbonate content observed in ash samples, including colour.

Sample	pH	EC (µS cm^{-1})	OM (%)	Carbonate (%)	Colour
Ash1	11.6	1173	1.11	37.77	grey
Ash2	9.1	28500	39.83	10.37	light grey
Ash3	9.7	2600	18.89	19.28	black
Ash4	9.6	18900	17.77	17.13	black

The ash samples demonstrated relatively high pH (ranges from 9.1 to 11.6) and EC (ranges from 1173 to 28500 µS cm^{-1}) similar to previous studies (Kim et al., 2003; Goforth et al., 2005; Ubeda et al., 2009; Pereira et al., 2011, 2013; Campos et al., 2015, 2016). The high pH and EC values of ash (compared with soils) immediately after the burn is explained by the presence of various ions in the ash (Pino et al., 2008;

Ubeda et al., 2009; Pereira et al., 2011; Campos et al., 2016). The high pH value of ash 1 sample, which includes a high carbonate content, and the grey colour suggests that this ash was produced at high temperature with high fire severity (Etiegni and Campbell 1991; Ulery and Graham 1993; Hening Sever et al., 2001; Goforth et al., 2005; Pereira et al., 2008). The organic matter levels vary from 1.1% to 39.8% and the carbonate values range from 10.4% to 37.8%. The extremely high OM content (39.8%) in ash 2 together with the high values in ash 3 (18.9%) and ash 4 (17.8%) coupled with their dark colours suggests the incomplete combustion of vegetation (Goforth et al., 2005; Bodi et al., 2014).

3.4 Potentially Toxic Metals (PTMs) in ash

A study of ash is significant in understanding the PTM mobility in fire-affected landscapes, as ash often contains elevated concentration of PTMs (Plumlee et al., 2007; Pereira and Ubeda, 2010; Odigie and Flegal, 2011, 2014). Though light grey, and grey coloured ash were present in the study area, most of the area was covered with black ash, consistent with incomplete combustion of vegetation. Due to the increase in areal coverage, black ash may have significantly influenced the soil characteristics and the PTM concentrations in the soil. The PTM concentrations in ash and the descriptive statistics are given in Table 2.

Table 2. PTM concentrations in ash samples include descriptive statistics.

Sample ID	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Colour
Ash 1	260.0	0.22	9.1	9.0	56.1	330.0	9.5	14.9	221.0	grey
Ash 2	24.0	0.08	5.7	8.0	147.0	980.0	19.1	6.0	555.0	light grey
Ash 3	21.7	0.02	12.6	5.0	142.5	2790.0	37.6	3.6	527.0	black
Ash 4	20.8	0.03	9.0	9.0	207.0	1560.0	35.9	1.8	422.0	black
Median	22.9	0.06	9.1	8.5	144.8	1270	27.5	4.8	474.5	
Range	239.2	0.2	6.9	4	150.9	2460	28.1	13.1	334	
IQR	180	0.16	5.2	3.3	114.3	1990	25.3	10.4	276.8	

The ash residue after the controlled burn revealed variation in PTM concentrations compared to PTM concentrations in the immediate post-burn soil environment. Ash sample 1 is sourced from the burning of a fallen tree trunks whereas, other samples are mostly attributed to being formed from bush and canopy leaf litter. Based on the PTM analysis data, it was found that grey coloured ash displayed the lowest Mn and Ni values, and the light grey ash displayed the second lowest. The Mn and Ni values were highest in the black ash attributes to the increase in concentrations of Mn and Ni, in incomplete combustion ash (black ash), most probably related to burn intensity. Conversely Pb and As shown higher concentration in the grey ash when compared to the black ash. Among the nine PTMs, Mn (1270 mg kg^{-1}) and Zn (474 mg kg^{-1}) achieved the highest and second highest median concentrations in ash respectively, whereas, Cd (0.06 mg kg^{-1}) represented the lowest concentration. All these values correspond with PTM concentrations in the immediate post-burn soil environment.

The median concentration of Mn, Zn, Cu, Ni and Co in ash is found to be higher than the concentration in the surrounding immediate post-burn soil environment, whereas the concentration of As, Cd, Cr and Pb are found to be higher in soil than in ash. Relative increases in concentration of Cu (56.1 to 207 mg kg^{-1}) and Mn (329 to 1270 mg kg^{-1}) found in ash from this study is of concern as ash represents a significant vector for PTM redistribution in the environment. The varying concentrations of PTMs in ash depends on a number of factors such as pre-burn metal concentration in the soil due to legacy mining activities, percentage SOM, age of the litter level, types of vegetation and vegetation density in the forest, the nature of materials burned (such as barks, leaves and litter), duration of the fire, maximum temperature reached, soil types, moisture content in the soil, post-burn meteorological conditions and many other local factors (Someshwar 1996; Pereira et al., 2009; Pereira and Ubeda, 2010; Machado et al., 2015). Plants in the study area usually absorb PTMs from soil and the PTM concentration in the vegetation particularly depends on the PTM levels in the soil and the age of the vegetation. During controlled burn, the PTM in the vegetation comes back to the soil through ash, which may result in a significant increase in PTM concentration in soil and it can be considered as a cyclic concentration process (Fig. 5).

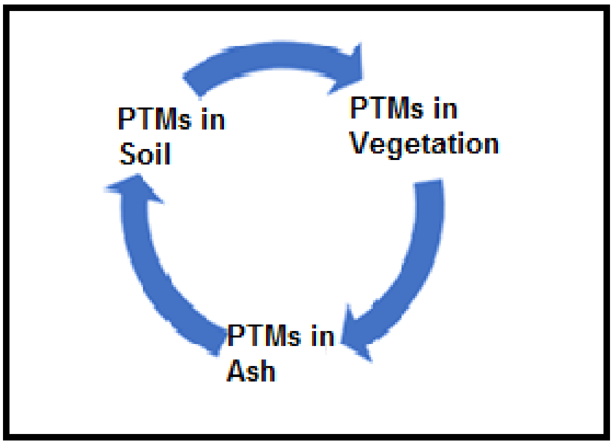

Fig. 5. Showing the mobilisation of PTMs in the forest ecosystem during fire.

Previous studies revealed the presence of PTMs (Mn, Zn, Cu, Pb, Hg, Cd and As) in ash samples found in forests across the globe (Ferreira et al., 2005; Plumlee et al., 2007; Pereira and Ubeda, 2010; Bogacz et al., 2011; Odigie and Flegal, 2011, 2014; Campos et al., 2016). To illustrate this, Plumlee et al. (2007) reported significantly elevated concentration of PTMs (As (up to 140 mg kg^{-1}), Pb (up to 344 mg kg^{-1}), Cu (1370 mg kg^{-1}) and Zn (up to 2800 mg kg^{-1})) in ash samples after the southern California forest fire in USA, and these results persisted for a year following the fire. Similarly, distribution of Co (3-11 mg kg^{-1}), Cu (15-69 mg kg^{-1}), Ni (6-15 mg kg^{-1}), Pb (7-42 mg kg^{-1}) and Zn (65-500 mg kg^{-1}) were observed in ash after the 2012 Williams fire in Los Angeles, USA (Odigie and Flegal, 2014) and Kristensen et al. (2014) reported mobilisation of natural and industrial Pb in ash samples after three large uncontrolled intense wildfire events in 2011 in Australia. Many of the PTM mobilised studies highlight Mn as being present in the highest concentration (Parra et al., 1996; Costa et al., 2014; Campos et al., 2016). The broad ranges of PTM concentrations found in Maldon Study area reflect the heterogeneous nature of ash formed in a historical mining site, probably due to the variation in plant species and parts burned, a mixture of the flammable materials and their original chemistry, burn intensity, and combustion completeness (Someshwar, 1996; Bodi et al., 2014). Thus, in general forest fires, including controlled burns can be considered as a vector for environmental alterations that may influence human and ecosystems health due to mobilization on PTM.

3.5 Effects of controlled burn on PTMs in soil and post-burn temporal Variations

The concentration of PTMs (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) in the soils of the study area (Maldon legacy mine site) two days before the controlled burn (2DBB), two days after burn (2DAB), at the end of 03 / 06 / 09 / 12 months (3MAB / 6 MAB / 9MAB / 12MAB) and immediately after the major rainfall (IAMR) event(s) in the post-burn environment are depicted in Fig 6. The median concentrations of PTMs before burn was in the order: Mn > Zn > As > Cr > Cr > Pb > Ni > Co > Cd. When comparing the BB (before burn) PTM concentrations with Australian and Victorian top soil averages (Caritat and Cooper, 2016), As, Pb, Cu and Zn exceeded the averages, mostly attributable legacy mining activities. When comparing with ecological investigation levels (EILs) set by the Department of Environment and Conservation (DEC) of the State of Western Australia, As exceeded the EIL and are considered a risk to the human and ecosystems health due to their increase in concentration and toxicity (DEC, 2010)

The median concentrations of Zn, Mn, Cd, As, Co, and Ni in the soil immediately after the burn were 1.9, 1.7, 1.5, 1.1, 1.1 and 1.1 times higher (respectively) than their levels in the pre-burn soil, with statistical significance ($p<0.05$) observed only in Mn and Zn concentrations. By contrast, Cr and Cu concentrations varied by a factor of 0.9 and Pb concentrations varied by a factor of 0.8. The maximum increases observed in the study area were As (28.9), Zn (9.7), Mn (9.3), Cd (5.9), Cu (3.7) and Ni (2.7) times the pre-burn concentrations.

Of the PTMs considered, Zn (87%) and Mn (72%) record the highest and second highest increase in median values in the study area in the immediate post-burn soil environment, followed by Cd (45%), and As (11%). Other PTM variations are <10% and are thus considered not to be significant. All the PTMs, except Cr, Cu and Pb showed an increase in concentration immediately after the controlled burn. The PTMs mobilization observed in this study is consistent with other studies, which report toxic metal mobilization after wild fires (Ignatavicious et al., 2006; Plumlee et al., 2007; Bogacz et al., 2011; Odigie and Flegal, 2011; Norouzi and Ramesanpour, 2013; Costa et al., 2014, Kristensen et al., 2014; Odigie and Flegal, 2014; Campos et al., 2016).

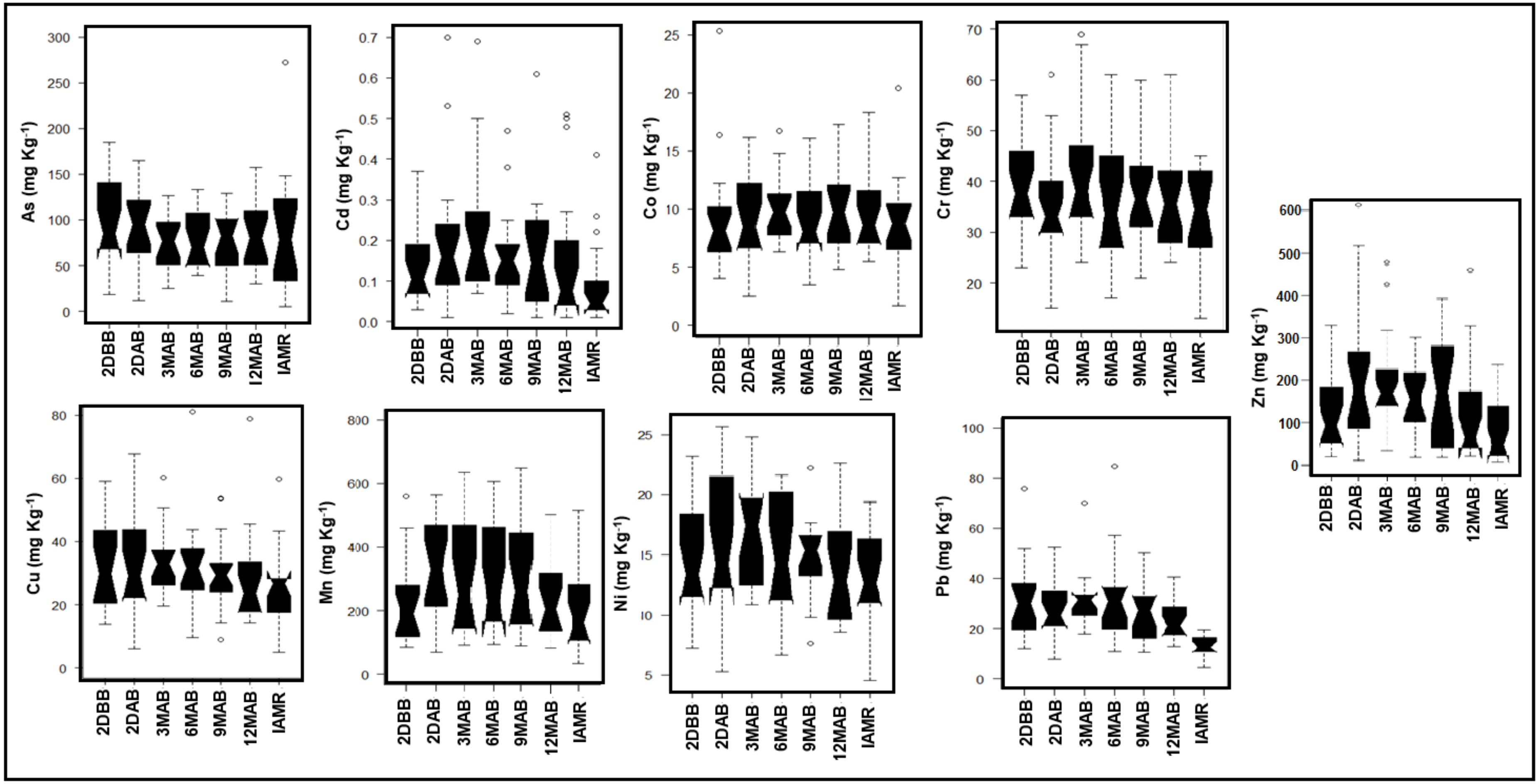

Fig. 6. Concentrations of PTMs in soils during various sampling period (2DBB- two days before burn, 2DAB- two days after burn, 3MAB- three months after burn, 6MAB- six months after burn, 9MAB- nine months after burn, 12MAB- twelve months after burn and IAMR- immediately after major rainfall) (n=18).

For example, Parra et al., (1996) noted a 100% increase in Mn concentrations and Costa et al. (2014) noted a five times Mn enrichment in ash relative to the surrounding soil after forest fires, whereas Chambers and Attiwill (1994) observed 279% increase in water soluble Mn concentrations after a laboratory heating experiment. The increase in Mn is attributed to a significant contribution to the soil from ash (in the form of oxides) from burned vegetation, as Mn is known to be concentrated in tree leaves compared to bark (Kabata-Pendias, 2011). Some results of this study support the above postulate. To illustrate this, ash sample 1, formed by the burning of a tree trunk showed only 330 mg kg^{-1} of Mn, whereas ash sample 4, formed by the burning of tree leaves and bush (mostly) showed a high Mn concentration of 2790 mg kg^{-1}.

Although the concentration of Cd is less (compared to other metals) in the soil, it showed a 45% increase immediately after the controlled burn. Existing studies revealed that increase in Cd concentration in soil in the immediate post-burn environment is due to sorption by organic matter, coupled with the association of Mn oxides, Fe and Al hydroxides and clay mineral fixation (Sipos et al., 2005; Kabata-Pendias, 2011). Cu showed no change in concentration in the immediate post-burn environment (from 30 to 29 mg kg^{-1} only), but showed higher concentrations (145 mg kg-1) in ash, consistent with other studies (Costa et al., 2014; Campos et al., 2016). The results clearly illustrate that PTM mobility in the soil environment during and after the controlled burn. The increase in concentration is considered to be due to the accumulation and dispersion of ash which contains elevated PTM concentrations (Plumlee et al., 2007; Costa et al., 2014; Campos et al., 2016), while the decrease may be due to the volatilization of metals during burning (Biswas et al., 2007; Campos et al., 2015; Abraham et al., 2018). The PTM mobility or change characteristics depends on a number of factors including accumulation and deposition of PTMs in the soil, type and density of the vegetation in the area, duration of the fire, maximum temperature reached and many other local factors (Pereira et al., 2011). Thus, further studies are needed to establish the relative influence of these factors in mining affected landscapes.

A knowledge of the detailed PTM dynamics in the environment is essential for ecosystem management and sustainability (Campos et al., 2016). The concentrations of PTMs in the post-burn environment during all the sampling periods are given in Fig 6 and the descriptive statistics are depicted in Table S2 (supplementary table). Among the nine PTMs considered in the study, As, Cd, Co, Mn, Ni and Zn showed increase in median concentration (only Mn and Zn are statistically significant) two days after burn (2DAB), however, Cr and Pb showed a reduction in concentration, with no variation in the case of Cu.

Among the first group of PTMs, Mn and Zn evidenced approximately similar distribution patterns in the post-burn environment. Two days after burn, both have increased their concentrations compared to pre-burn concentrations and showed a reduction in the succeeding sampling periods, except 9MAB sampling, were both showed a small increase. The reduction was in such a way that 12MAB, Zn falls below pre-burn levels, whereas Mn falls below its pre-burn level only after the major rainfall event. Two other PTMs, Cd and Ni, demonstrated similar kinds of post-burn temporal distribution patterns. Two days after burn, both displayed increase in concentrations, and the increase continued till 3MAB. Then the levels started decreasing (except in 9MAB samples, where Cd level is same as previous level and Ni showed negligible increase), and after the major rainfall event, both levels reached or reduced below pre-burn levels. Cobalt also showed a similar pattern to Cd and Ni, except no change was observed after the major rainfall. The increase in concentration of Cd, Ni and Co 3MAB samples is attributed to the continued mixing of ash with the soil. In the case of As, it showed an increase in median concentration immediately after the burn, which was reduced in 3MAB and 6MAB, but further increases were observed in 9MAB followed by a slight reduction in 12MAB and IAMR samples.

Unlike other six PTMs, the concentrations of Cr and Pb decreased two days after the controlled burn, but both showed an increase 3MAB. In the following sampling period, there was reduction or ‘no change’ in both the cases, except an increase in Cr concentration 9MAB samples, compared to previous (6MAB) samples.

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Even though, a number of minor rainfall events occurred before September 2016 in the post-burn environment, they were not substantial enough to remobilise ash and surface soils.. These less intense rainfall events, specifically rainfall occurred 6MAB sampling may have mobilised ash and ash enriched surface soils, including the associated contaminants within the study area itself resulting in the increase in median concentrations of some of the PTMs in 9MAB samples (Shakesby, 2011; Moody et al., 2013; Devi et al., 2018). The rainfall during the second week of Sep 2016 was so intense that more than 155 mm rainfall occurred within a fortnight. The subsequent erosion was so severe that it deepened and widened the existing creek in many places and flooded number of locations in Central Victoria. This intense rainfall may have transported much of the ash-soil mixture away from the study area, resulting in the observed significant decreases in PTM concentrations immediately after the rainfall event, consistent with other studies (Gallahar and Koch, 2004; Businelli et al., 2009; Burke et al., 2010; Violante et al., 2010; Stein et al., 2012; Prats et al., 2014; Machado et al., 2015). In support of this postulation, Costa et al., (2014) noted the decrease in concentration of Mn in soil and the subsequent increase in the downstream water environment eight and 12 months after a fire. Conversely, the slight increase in concentration of Cu in the study area after the rainfall is consistent with the reduced solubility and reduced mobility of Cu compounds than other PTM compounds (Wuana and Okieimen, 2011; Zheng et al., 2012; Devi et al., 2018). In addition to this lateral mobilization, some of the PTMs may be leached into subsurface soil layers, thus influencing groundwater, especially when the groundwater levels are close to the surface (Verma et al., 2016; Tahiri et al., 2017; Vink et al., 2017). This potential impact required further investigation, specifically where frequent controlled burns practicing and the groundwater is supply as potable water resources.

3.6 Relationship between soil physicochemical characteristics and PTMs concentrations

PTMs in the soils of legacy mine sites generally have complex chemical and physical relationships with soil characteristics (pH, EC and SOM), and it is known that numerous factors control their relative abundance (Krishna et al., 2013). This includes, but is not limited to, PTM concentration in the parent rock or material, extent of weathering and soil formation, anthropogenic activities include intensity and types of mining, duration of the mining, types of metal processing and distance to the processing site, mode of transport to the processing site, topography of the area, and climate (Wei and Yang, 2010; Krishna et al., 2013). This inhomogeneity is visible in the study area.

Table 3. Spearman rank correlation coefficient between the physicochemical properties of soil and PTMs in the pre-burn (above diagonal elements) and the post-burn (below the diagonal elements) environment (number of samples = 18)

	pH	EC	SOM	Carb	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
pH		-.48	.43	.04	.32	.37	***.61*****	**.54***	.38	.35	***.62*****	-.04	*.46*
EC	-.48		.28	.37	-.23	-.10	-.03	-.02	0.14	0.04	-.08	-.03	-.21
SOM	.43	.28		.37	.10	**.53***	.38	.44	**.51***	.36	**.50***	.28	.49
Carb	.04	.38	.37		.32	.43	.46	**.57***	.48	.45	**.50***	.48	.40
As	.32	-.23	.10	.32		***.75*****	***.65*****	.48	***.60*****	***.80*****	**.53***	***.77*****	***.76*****
Cd	.37	-.10	**.53***	.43	***.74*****		***.70*****	***.66*****	***.72*****	***.73*****	***.75*****	***.75*****	***.98*****
Co	***.61*****	-.03	.38	.46	***.65*****	***.70*****		***.86*****	***.76*****	***.73*****	***.94*****	.30	***.76*****
Cr	**.54***	-.02	.44	**.57***	.48	***.66*****	***.86*****		***.77*****	*.47*	***.95*****	.32	***.72*****
Cu	.38	*.14*	**.51***	*.48*	***.60*****	***.72*****	***.76*****	***.77*****		**.58***	***.79*****	.46	***.74*****
Mn	.35	.04	.36	.45	***.80*****	***.73*****	***.73*****	.47	**.57***		***.61*****	***.62*****	***.71*****
Ni	***.62*****	-.08	**.50***	**.50***	**.53***	***.75*****	***.94*****	***.95*****	***.79*****	***.61*****		.32	***.82*****
Pb	-.04	-.03	.28	.48	***.77*****	***.75*****	*.30*	.32	.46	***.62*****	.32		***.67*****
Zn	.46	-.21	.49	.40	***.76*****	***.98*****	***.76*****	***.72*****	***.74*****	***.71*****	***.81*****	***.67*****	

NB: **Significant positive correlations ($p < 0.01$, ***bold italics***; *$p < 0.05$, **bold**) are highlighted

Table 4. Spearman rank correlation coefficient between the physicochemical properties of soil and PTMs in the pre-rainfall (12MAB) (above diagonal elements) and the post-rainfall (IAMR) (below the diagonal elements) environment(s). (number of samples = 18)

	pH	EC	SOM	Carb	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
pH		-.04	-.11	***.55****	***.53****	.49	***.54****	.48	***.63*****	***.71*****	***.54****	***.51****	***.67*****
EC	.42		.31	***.56****	.19	***.58****	.32	.06	.48	.45	.40	.44	.46
SOM	.34	***.89*****		.18	.18	.33	-.21	.30	.13	.09	.40	.28	.22
Carb	.38	***.53****	***.68*****		.28	***.68*****	***.77*****	***.55****	***.82*****	***.62*****	***.87*****	***.76*****	***.81*****
As	.48	.43	.19	.18		.52	.28	.04	***.61*****	***.56****	.28	.47	***.52****
Cd	***.54****	***.91*****	***.75*****	.49	***.62*****		***.53****	.35	***.78*****	***.84*****	***.70*****	***.85*****	***.90*****
Co	.48	***.54****	.43	***.64*****	***.72*****	***.66*****		***.54****	***.80*****	***.61****	***.85*****	***.64*****	***.67*****
Cr	.24	.37	.42	***.58****	.45	***.53****	***.66*****		***.52****	.30	***.69****	.47	.43
Cu	***.69*****	***.75*****	***.57****	.49	***.79*****	***.88*****	***.81*****	***.54****		***.77*****	***.83*****	***.88*****	***.83*****
Mn	***.59****	***.89*****	***.74*****	.45	***.65*****	***.90*****	***.67*****	.44	***.88*****		***.60*****	***.84*****	***.84*****
Ni	***.60*****	***.60*****	***.52****	***.58****	***.66*****	***.79*****	***.85*****	***.74*****	***.86*****	***.71*****		***.67*****	***.83*****
Pb	.31	***.67*****	***.54****	.43	***.71*****	***.83*****	***.69*****	***.63*****	***.76*****	***.75*****	***.78*****		***.88*****
Zn	***.67*****	***.83*****	***.71*****	***.58****	***.64*****	***.93*****	***.72*****	***.63*****	***.92*****	***.89*****	***.88*****	***.83*****	

NB: **Significant positive correlations ($p < 0.01$, ***bold italics***; *$p < 0.05$, **bold**) are highlighted

Many studies have revealed that the physicochemical characteristics of soil, specifically pH and SOM played a significant role in the retention and mobilization of PTMs in the soil (Chlopecka et al., 1996; Certini, 2005; Zheng et al., 2012; Mehes-Smith et al., 2013). We applied the Spearman Rank correlation in R (version 3.4.1) to investigate the relationship between physicochemical characteristics (pH, EC, SOM and carbonate) of the soil and the PTM in the soil in four sampling periods. The correlation coefficient of before burn (2DBB) and immediately after burn (2DAB) samples and before major rainfall (12MAB) and immediately after major rainfall (IAMR) samples are depicted in Table 3 and 4 respectively. In both the pre-burn and immediate post-burn environment, statistically strong (0.6–0.79) correlation are observed between the physicochemical properties and PTMs for pH with Ni ($r = 0.62$, $p<0.01$) and Co ($r = 0.60$, $p<0.01$) (both environment), and the PTMs themselves (Table. 3). Similar correlation between pH with Ni and Co has been reported by Wilde et al. (2014). Apart from this, other observed moderate positive linear correlations are reported for Cr ($r = 0.54$, $p<0.05$), SOM with Cd ($r = 0.53$, $p<0.05$), Cu ($r = 0.51$, $p<0.05$) and Ni ($r = 0.50$, $p<0.05$) and carbonate with Cr ($r = 0.57$, $p<0.05$) and Ni ($r = 0.50$, $p<0.05$) in both the pre-burn and immediate post-burn environment. For the other PTMs, these correlations are not statistically significant with physicochemical characteristics. The very strong and strong correlations observed between the PTMs themselves (Cd with Zn, Cu with Pb and Zn; etc.) highlight their common origin and behaviour patterns. The strong correlation between Pb with As ($r =0.77$, $p< 0.01$) and Zn with As ($r = 0.76$, $p < 0.01$) suggest a common origin that being the mineralized Ordovician sedimentary rock with galena (PbS) and sphalerite (ZnS) as potential primary sulphides. The very strong correlation between As and Mn ($r = 0.80$, $p<0.01$) determined that Mn is a significant metal in the soil, and may control arsenate (major form of As) mobility, also reported by Sultan (2007).

The correlation coefficient of data collected from 12MAB samples are significant as the samples collected few days before the occurrence of major rainfall. Here, pH has a strong correlation with Mn ($r = 0.71$, $p<0.01$), Zn ($r = 0.67$, $p<0.01$), and Cu ($r = 0.63$, $p<0.01$) and carbonate shown very strong correlation with Ni ($r = 0.87$, $p<0.01$), Cu ($r = 0.82$, $p<0.01$), and Zn ($r = 0.81$, $p<0.01$), and strong correlation with Co ($r = 0.77$, $p<0.01$), Pb ($r = 0.76$, $p<0.01$), Cd ($r = 0.68$, $p<0.01$) and Mn ($r = 0.62$, $p<0.01$). EC displayed correlation only with Cd ($r = 0.58$, $p<0.05$) and is a moderate one. The correlation between the physicochemical characteristics and PTMs has altered immediately after the major rainfall due to the influence of the rainfall on surface soil. For example, pH has a strong correlation with Cu(r = 0.69, p<0.01), Zn (r = 0.67, p<0.01) and Ni (r = 0.60, p<0.01) only, not with Mn as in the pre-rainfall environment. The relationship of EC and SOM with PTMs has increased after the major rainfall. To illustrate this: (i) EC highlighted very strong correlation with number of PTMs such as Cd (r = 0.91, p<0.01), Mn (r = 0.89, p<0.01), and Zn (r = 0.83, p<0.01), and strong correlation with Cu (r = 0.75, p<0.01), Pb (r = 0.67, p<0.01) and Ni (r = 0.60, p<0.01). (ii) SOM shown significant strong correlation with Cd (r = 0.75, p<0.01), Mn (r = 0.74, p<0.01) and Zn (r = 0.71, p<0.01). However, the relationship of carbonate with PTMs decreased in the immediate post-rainfall environment. For example, carbonate shown strong correlation only with Co (r = 0.64, p<0.01), unlike the previous environment.

Previous studies noted the relationship between soil physicochemical properties and PTM concentrations, including their retention and mobility in the soil (Chlopecka et al., 1996; Mehes-Smith et al. 2013). However, in this study there is limited strong linear positive correlation observed between the physicochemical characteristics and PTMs in the pre-burn and immediate post-burn environment, and this warrants more investigation. However, the relationship changed after one year, in the pre-rainfall and immediate post-rainfall environment. Moreover, although the correlation between the physicochemical characteristics of the soil and PTMs in the soil are similar in the pre-burn and immediate post-burn environment, it is considerably inhomogeneous when we compare pre-rainfall and immediate post-rainfall environment. This suggest that controlled burn has not influenced the relationship, whereas, strong a rainfall event significantly influenced the soil physicochemical and PTM concentration relationship.

4. Conclusion

This study investigates the remobilisation of potentially toxic metals (PTMs) in the surface soils of a legacy mine site in the Maldon area of Central Victoria, Australia after a controlled burn to assess their temporal concentration variations. Surface soil samples were collected two days before, two days after the controlled burn and five more times in the succeeding post-fire environment with three months interval, and analysed for PTM concentrations and physicochemical characteristics.

The results revealed the presence of PTM mobilization after the controlled burn and most of the PTMs (As, Cd, Cu, Mn, Ni, and Zn) evidenced an increase immediately after the burn but a reduction in the subsequent post-burn environment. The increase is postulated to be associated with addition of PTM enriched ash to the soil, while the decrease is due to the removal of ash and surface soil by rainfall runoff. The study also highlighted the increase in pH, EC and SOM (%) immediately after the fire, which subsequently reduced in the post-burn environment. The increase in soil pH and EC immediately after fire is attributed to the presence of various alkaline oxides and hydroxides derived from ash. The increase in SOM is due to the presence of pyrogenic carbon compounds in the ash resulting from incomplete combustion. Unlike other physicochemical characteristics, carbonate showed little variation in concentration, potentially due to insufficient temperature during fire. In general, controlled burn has been found to alter the PTMs concentrations in the soil by combustion, heating and ash deposition.

The controlled burn or prescribed fire land management strategy may result in the remobilization of considerable amounts of PTMs, which may create significant offsite environmental impacts. Notwithstanding the relatively small study area related to this investigation the results have global ramifications as more than a million legacy mine sites exist across the globe, many of which are in fire-prone forest areas. Moreover, climate change and the resulting projected increased in forest fire frequency highlights the environmental significance of increased PTM mobilization. Hence, the practice of controlled burning should be carefully considered as a wildfire mitigation and land management strategy, and consideration must be given to avoid mobilization of metals in legacy mining areas and indeed other areas where PTM contamination is reported

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Conflict of Interest

Authors declared that there is no conflict of interest

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Chapter- 9

Synthesis of key findings, management implications and recommendations

9.1 Overview

This thesis investigates the remobilization of Potentially Toxic Element (PTE) (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn) concentrations in the soils of the Maldon legacy gold mining affected landscape in the Central Victorian region of Australia after a controlled fire and monitors the temporal variations in PTE concentration for a period of one year. The study also monitors the change in physicochemical characteristics of soil properties such as pH, electrical conductivity (EC), soil organic matter (SOM) and carbonate content and considers the relationship with PTE concentration in the soil. This is achieved through a series of soil sample collection (two days before and two days after the controlled fire, and end of each seasons and after an intense rainfall in September 2016) and laboratory analysis followed by statistical data analysis.

A detailed literature review revealed studies, which highlighted the mobilization of PTEs after wild fire (Biswas et al., 2007, 2008; Jovanovic et al., 2011; Odigie and Flegal, 2011, 2014; Costa et al., 2014; Burton et al., 2016; Campos et al., 2016; Nunes et al., 2017; Wu and Taylor, 2017), however, details regarding the PTE mobilization after a controlled fire is limited and not reported from a mining affected landscape. In order to address this knowledge gap, the objective of the research was focussed on the investigation of PTE mobilization after a controlled fire and their temporal variations in concentrations on a legacy gold mining landscape in the Maldon area of Central Victoria, Australia, including the implications for land management and environmental health.

The present work provides a significant contribution to evaluate the role of controlled fire in the release and mobilization of PTEs. The study adopts a integrative (two steps) approach. Firstly the influence of controlled fire on PTE concentration in the soil and ash is assessed, and secondly the influence of time in the post-fire environment (immediately after fire, end of spring, summer, autumn, and winter seasons, and after an intense rainfall in September 2016) on the mobilization of PTEs is considered.

The role of controlled fire on the PTE mobility is significant. The increase in concentrations of Mn, Zn, Cd, and Ni in the immediate post-fire environment compared with pre-fire environment suggest an input of these PTEs in the burned soils, and ash is considered to be the significant contributor. The 27% decrease in average concentration of Hg is attributed to the release of Hg, which has a low volatilisation temperature, and this mobilized Hg has the potential to have local, regional and global impacts.

9.2 Synthesis of key findings

The key findings reported in each chapter (2-8) are summarised here as a synthesis, with a view to developing suitable environmental and land management based recommendations in controlled burn sites, specifically in mining affected landscapes or any landscapes with elevated level of PTE concentrations.

Key findings 1 and 2 support a common theme observed in the published literature, specifically that wild fire influences metal (PTE) mobility in the soil and surface water environment respectively. The literature review identified the research problems and the knowledge gaps. However, other key findings (3-7) were developed from the original research component of this work. Though the study is based on a relatively small area, the key findings are relevant to other regions across the globe as more than a million legacy mine sites are identified across the world and many of them are in the fire-prone forest areas (UNEP, 2001; Park et al., 2014).

Key finding 1: Fire has the potential to affect the soil profile. PTEs in the forest soil are liberated after fire, with extensive re-distribution in the soil environment, sometimes hundreds of kilo meters away from the original source.

The literature review (Chapter 2) highlighted the influence of forest fire on PTEs in the soil environment including mobility and the associated risks to human and ecosystems health. The negative impacts of PTEs on human health are also highlighted in this review. This finding provided a justification for the original research in this thesis, and also reinforces the need to address the land and water management, and environmental health in case of any kinds of forest fires include controlled fire.

Key finding 2: The remobilised PTEs after the forest fire move down slope and downstream facilitated by rainfall runoff and wind activity, and extend the contamination into the downstream water bodies. This types of contaminant mobility occurs around the world, and requires quantification and health assessment as forest catchments supply potable water resources to major cities and local communities globally.

Chapter 2 describes the PTE mobility in the post-fire soil environment and Chapter 3 describes the PTE mobility towards the downstream surface water bodies through rainfall runoff and wind activity, where it may affect the aquatic ecosystems. To illustrate this, Hg may mobilised into downstream aquatic ecosystem, where, the conditions may be favourable for the formation of toxic methyl Hg (MeHg). This complex form is very neuro-toxic and immuno-toxic and may affect organisms, including humans through food chain dynamics. The mobility of PTEs into adjacent landscapes, and over long distances is not ruled out. The review concluded that the frequency and areal extent of forest fire may increase due to climate change and the associated increase in atmospheric temperature and extended summer seasons. This is concomitant with an increase in the quantity of the PTE mobilization and heightens the concern of the effects of these PTEs on the environment, ecosystems and to the human health. This is highly significant as approximately 4 billion ha of forest catchments provide high quality water to many major cities and communities around the world.

Both literature reviews highlighted a gap in the literature regarding the mobilization of PTEs from controlled burn sites, specifically in legacy mining environments, which have elevated concentrations of PTEs in the surface soils due to the mining activities. The study is particularly significant in Central Victorian forest soils due to the presence of a large number of legacy mine sites in the region and the annual practice of controlled burns as a standard fire risk reduction strategy.

Key finding 3: The Maldon study area has elevated concentration of a number of PTEs, especially Hg and As, when compared to Victorian and Australian top soil averages and international standards.

In order to investigate the PTE mobility after the controlled fire, determination of soil PTE concentrations before and after the controlled fire is essential. Soil samples were collected two days before the controlled fire and analysed for PTE concentrations and soil physicochemical characteristics such as pH, EC, SOM and carbonate with the results given in Chapter 4. The order of concentration of PTEs from highest to lowest levels observed in the study area are: Mn > Zn > As > Cr > Pb > Cu > Ni > Co > Hg > Cd. In order to understand the status of the current soil PTE concentration, the median PTE values were compared with Australian and Victorian soil metal averages, health investigation levels and the ecological investigation levels set by the National Environmental Protection Measures (NEPM) and the Department of Environment and Conservation (DEC) in the State of Western Australia respectively. The comparisons revealed that the study area is heavily contaminated with Hg and As.

Key finding 4: Soil contamination assessment in the pre-burn environment were carried out using appropriate pollution indices such as geo-accumulation index (I*geo*), contamination factor (CF), pollution index (PI), pollution load index (PLI), integrated pollution index (IPI) and Nemerow integrated pollution index (NIPI), and all indices revealed that the study area is heavily contaminated with Hg and As. Moreover, the enrichment factor revealed severe enrichment with As, moderate enrichment with Cu, Pb and Zn and no enrichment with Hg.

Chapter 5, reported the soil contamination status of the study area for the pre-burn conditions with the help of a number of appropriate indices. Assessment with the geo-accumulation index (I-*geo*) revealed that the study area is extremely contaminated with Hg and heavily contaminated with As. This is supported by the assessment of contamination factor (CF), which confirms very high contamination observed with Hg and As, and together with Pb, Zn are considered as high level contaminants. However, the pollution load index (PLI) revealed that the entire study area is contaminated with PTEs. Assessment with the integrated pollution index (IPI) noted that Hg had the highest IPI, followed by As and both are considered as high level contaminants, besides Pb and Zn. According to IPI, Cd and Cu are considered as middle level contaminants, whereas other PTEs are low level contaminants. Based on the Nemerow integrated pollution index (NIPI), the study area is highly polluted with Hg, As, Zn and Pb, moderately polluted with Cu and showing low level pollution by Cd, Co, Cr and Ni, but Mn showing no contamination. Assessment with enrichment factor highlighted that As has shown very severe enrichment, and Cu, Pb and Zn shown moderate enrichment, and Hg shown no enrichment at all.

Evaluation of the potential ecological risk factor (ERI) and the potential ecological risk index (RI) where assessed based on the PTE concentrations in the soil. The order of potential ecological risk coefficients of (ERI) toxic elements in the soils of the Maldon study area is Hg > As > Cd > Pb > Cu > Ni > Zn > Cr. Based on the potential ecological risk coefficients, Hg falls in the ‘serious ecological risk’ and As falls in the ‘high ecological risk’ category, whereas, Cd belongs to ‘moderate risk’ and other metals falls in the ‘low risk’ category. This clearly demonstrates that the overall site contamination issue is linked to the presence of Hg and As. The Risk Index (RI) values demonstrated that all the sampling stations (except S14) are at ‘significantly high ecological risk’ category and hence the entire study area.

Key finding 5: The immediate post-fire PTE concentrations in the soil and their comparison with pre-fire concentrations revealed that As, Cd, Cu, Mn and Zn concentrations increased by a factor(s) of 1.2, 1.5, 1.1, 2.9 and 1.7 respectively, whereas, the concentrations of Hg, Cr and Pb levels decreased by factor(s) of 0.7, 0.9 and 0.9 times respectively. Such findings are consistent with PTE mobility after the controlled fire.

Investigation of the PTE (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn) dynamics in the environment is vital for ecosystems management and sustainability. The overall increase in concentrations of PTEs (As, Cd, Cu, Mn, Ni, Zn) and the physicochemical characteristics of the soil as defined by the pH, EC and SOM in the post-fire soil environment emphasized (Chapter 6) that the controlled fire acts as a mobility vector for PTE contamination. Ash formation and subsequent deposition during and immediately after the fire and its propensity for mobility influence the PTE concentrations in soil, water and air environment. The increase in soil pH, EC, SOM and increase in water pH and EC also attributed to the presence of ash mobility, which has elevated quantities of oxides, hydroxides, carbonates and many other minerals and nutrients as reported in previous studies (Khanna et al., 1994; Certini, 2005; Verma and Jayakumar, 2012; Bodi et al., 2014). The decrease in levels of Hg and Pb in the post-burn soil environment suggests that volatilization of these toxic elements during fire. This PTE mobility has substantial implications for the environment due to its influence on all aspects of biota from soil microbes to terrestrial and aquatic vertebrates including humans and ecosystem resilience in general.

PTE concentrations in the post-burn environment directly linked to their original concentrations in the pre-burn environment. If the pre-burn soil has elevated amount of PTEs such as in legacy mine sites or any kinds of mining or industry contaminated landscapes, the mobilization of the PTEs will also be elevated during or after the controlled fire. The controlled fire and the resulting PTE mobility and their health impacts on human and ecosystems must be further examined to ensure that PTE mobility in various landscapes is fully understand and the possible influence of controlled fire when use as a forest management tool in the mining affected landscapes must be addressed.

Key finding 6: Surface soil of Maldon is heavily contaminated with Hg and the data clearly highlighted variations in Hg concentration during all the sampling time periods. However, significant variations were observed only before and after the prescribed fire and before and after a major rainfall event.

Surface soil of the study area is heavily contaminated with Hg and the data clearly highlighted variations in Hg concentration across all the sampling time periods. After the prescribed fire, 8.3 to 97% reduction in Hg concentration is observed in the surface soil indicating the volatilization of Hg during fire. After the major rainfall event, a 10 to 354% increase in Hg concentration is observed and is consistent with ash leach out and the mobilization of Hg from atmosphere, plants, and also from the newly formed soil organic matter.

In order to understand the degree of contamination, the Hg concentrations in various sampling periods were compared with Victorian and Australian top soil averages, world soil average, integrated soil quality guidelines (ISQG) (low and high), ecological investigation levels (EIL), residential health investigation levels (RHIL) and with appropriate indices. The concentration of Hg in all sampling stations, during all the sampling occasions were well above the Australian soil back ground Hg value of 0.03 mg kg-1 (except S11 after rainfall) and well above the world soil average of 0.01 mg kg-1. Moreover, the ecological risk index (ERI) assessment also demonstrated the possibility of serious ecological risk throughout the study area in all sampling occasions.

Key finding 7: The PTE analysis immediately before and after the controlled burn, and each season in the post-burn environment revealed that PTE mobilization occurred after the controlled burn with an increase in As, Cd, Mn, Ni and Zn concentrations, whereas Hg, Cr and Pb showed decrease in concentration in the immediate post-burn environment. The PTE, which increased immediately after the fire were reduced in concentrations temporally, is attributed to the removal of ash and the associated PTEs, and the decrease immediately after the fire is attributed to the volatilization of PTEs during fire.

This study highlights the significance of controlled fire in the mobilization of PTEs. The results revealed PTE mobilization after the burn and most of the PTEs (As, Cd, Cu, Mn, Ni, and Zn) shown an increase in concentrations immediately after the fire, which reduced during the subsequent post-fire environment. The temporal increase in PTE concentration is postulated to be associated with addition of PTE enriched ash to the soil and the decrease is due to the removal of ash and surface soil by rainfall runoff and wind activity.

The overall increase in concentrations of PTEs in the immediate post-burn environment, indicates that controlled fires are able to remobilize PTEs from vegetation and soil organic matter into ash, which may subsequently increase these PTE levels in the soil. The first or second post-fire rainfall event and the subsequent erosion and runoff in the post-fire environment, mobilizes these PTEs down slope and potentially into downstream surface water resources increasing the contaminant levels in the aquatic ecosystems. This is of particular concern due to the known impacts of these PTEs on human and ecosystems health (toxicity), their environmental persistence, water solubility and biomagnification tendency (Sabin et al., 2005; Stein et al., 2012; Odigie et al., 2016; Nunes et al., 2017).

In general, the study revealed that following findings:

- The study area is highly contaminated with Hg and As due to the legacy mining activities.
- Controlled fire is able to mobilize PTEs sequestered in the soil organic matter and vegetation, which may increase the contamination level in the soil.
- The increase in PTE concentrations (As, Cd, Cu, Mn and Zn) in the immediate post-fire environment is postulated to be associated with the addition of PTE enriched ash to the soil.
- The decrease in PTE concentrations (Hg, Cr and Pb) is due to the volatilization of PTEs during fire.
- In the post-burn environment, temporal reduction in PTE concentrations observed in the soil is attributed to the removal of ash and ash enriched surface soil by rainfall runoff and wind activity.
- The temporal increase in PTE concentration in the post-fire environment is attributed to the ash leach out, atmospheric mobilization and mobilization from newly formed soil organic matter.

This study suggests vigilance with the use of controlled burning in mining affected landscapes due to the possibility of PTE mobilization and the resulting potential health impacts. Controlled burn also require close monitoring as the impacts of burning to fire-fighting personal, local residents, local and sometimes distal landscapes and the impacts on communities are to be fully quantified.

9.3 Land management implications

Central Victoria in Australia has hundreds of abandoned legacy mine sites, and many are located in forest areas. The legacy mine sites and their locations generate concern, due to the elevated concentrations of PTE in the surface soil and the likelihood of significant wild fires because of the weather pattern changes and the types of vegetation. Moreover, controlled fires are commonly used in the Central Victorian forest area by the Department of Environment, Land, Water and Planning (DELWP) as a standard fire risk reduction strategy. During and after the fire, PTE enriched ash act as a mobile toxic source to surrounding residential areas and the ecosystems through the water-born transport of dissolved and particulate matter and wind-bone dispersal of fine particles. Forest fire, either wild or controlled, and the resulting PTE mobility from the soil organic matter and vegetation is of growing concern to society, as these elements are bioavailable and the health impacts of PTEs to human and ecosystems are only poorly quantified.

The data presented in this thesis confirms that application of controlled fire at a legacy gold mine site in Central Victoria has mobilized PTEs, specifically Mn, Zn, Cd, Hg and As. In addition to this, elevated concentrations of Mn (1270 mg kg-1), Zn (475 mg kg1), Cu (145 mg kg-1) and Ni (28 mg kg-1) were observed in the ash samples. Given the abundance of similar legacy mine sites and the occurrence of controlled fire at national and international scales, it is recommended that the potential for the mobilization of toxic elements should be investigated further and their human and ecological health impacts should be studied carefully with a consistent approach. The findings have significant practical implications to all residents, specifically to long-term residents and children under five years of age due to the continuous exposure to PTEs.

Legacy mine sites are a significant source of PTE contamination, and the UN estimated the presence of more than a million such sites across the world (UNEP, 2001; Park et al., 2014). Despite improved legislation and practice, PTE contamination persists and the scope of the impact on human and ecosystem health is still not well understood (Fields, 2003; Martin, 2017). Contaminated land management is a challenging task, partly due to the absence of a globally consistent approach to investigate the contamination, the long-term persistence of PTEs in the soil, and their impacts on human and ecosystems health (Martin, 2017). Therefore, suitable global guidelines are crucial to minimize the resulting negative impacts of PTEs on human and ecosystems health.

Elevated concentrations of PTEs in the mining affected landscape is considered to be a risk to the human and ecosystems health due to their persistence, mobility, bioaccumulation and biomagnification characteristics. Hence, land managers should develop tools to assess the risk in mining affected landscapes, specifically before the controlled fire due to the mobility of PTEs. Substantial evidence supports climate change studies, with increase in atmospheric temperatures, and duration of summer seasons and droughts, resulting in the increase in frequency and areal extent of forest fire (Hennessy et al., 2005; Westerling et al., 2006; Pechony and Schindell, 2010). This may require increased use of controlled fires to mitigate the possibility of wild fires, resulting in the liberation of more amount of PTEs from the mining affected landscapes, and from forest with elevated PTE concentrations. Therefore, land managers should definitely consider PTEs and the consequences of mobility at the planning stage of controlled fires with regards to the climate change.

Land managers may not be sufficiently aware of the PTE mobilization during and after the forest fire, including controlled fire and consequently PTE mobilization has not been taken into consideration in the past land management activities. Based on the PTE mobilization evidence, after the controlled fire, it is recommended that land managers should provide due consideration to the PTE mobility after the wild and controlled fires in the mining affected landscapes or any forest area with elevated PTE concentrations and suggest the following precautionary steps to the land managers.

- In the planning stage of the controlled fire, land managers should consider if the proposed area is a legacy mine site and assess the elevated PTE concentrations in the soil from the available data from various agencies.
- If the PTE analysis data is not available, a preliminary site assessment, including collection and analysis of surface soil samples for PTE is essential.
- If elevated PTE concentrations observed in the surface soils of the proposed burn area, based on the current study, other control options should be

considered. This will help to avoid spreading of the PTEs to the surface soils and adjacent downslope surface water systems.

- If no other land management option is available:
    (i). Consideration should be given to the low intensity controlled fire to reduce the mobility of PTEs.
    (ii). Use of earth moving equipment(s) to cluster forest floor fuels, including leaf litter and bushes to limited locations (away from water resources) and make low severity burn, to reduce the areal extend of the fire and thus the PTE mobilization.
    (iii). Avoid burns close to the creeks and other surface water resources, including at riparian zones to exclude the possibility of PTE mobilization to the surface water resources.
    (iv). Avoid burn at areas, most susceptible for erosion such as steep slope areas, gullies and channels to avoid spreading of PTEs and other contaminants to downstream and downslope environment.

- Based on the result of this study, land managers across the world should develop strategies, policies and procedures to minimise the impacts of controlled fires on ecosystem, human and environmental health(s), specifically at mining affected landscapes and areas with elevated concentrations of PTEs.

- Land managers, water authorities and water distribution companies should make reasonable risk assessments based on forest catchment attributes, fire and erosion potential to identify areas and water catchments that might be highly vulnerable following the controlled fire. This may assist to the formation of pre-fire contingency plans to allow for a more rapid response in managing adverse water quality outcomes following fire.

- Land managers should develop a controlled fire risk management plan, specifically in mining affected landscape or in forest areas with elevated PTE concentrations, which will enable better coordination of management actions designed to mitigate controlled fire impact on water quality.

- Land managers should develop a rehabilitation plan, with multiple positive objectives in mind, especially about the protection of water resources and should start the remediation / rehabilitation works immediately after the fire.

- Immediately after the fire, land and water quality managers should undertake the following activities:
    - Identify the possible change in soil properties, which affect the hydrologic functions.
    - Identify risk area for post-fire flash flooding or debris flow.
    - Soil burn severity mapping.
    - Identify sediment source areas and estimate the erosion potential.
    - Identify the potential threat to human life, property and critical natural and cultural resources.

The recommended first management action is the rehabilitation of fire control measures, which reduces the supply of ash and sediment to water resources, followed by erosion mitigation works such as mulching, revegetation and bank stabilization and sediment control measures. Moreover water quality monitoring is suggested to ensure that remediation activities are effective in reducing water quality impacts. Thus necessary planning and rehabilitation works can reduce the negative impacts of controlled fire to the environment, ecosystems and ultimately to the human beings.

9.4. Implications for Environmental Health

Though intensity and areal extent is not comparable to wild fires, controlled fire is also able to alter the forest ecosystem structure and functions such as shift in the dominant invertebrate taxa, nutrient levels in the soil, soil pH, EC, levels of organic matter, and concentrations of PTEs, all of which may take months and years to recover (Certini, 2005; Garcia-Marco and Gonzalez-Prieto, 2008; Beganyi and Batzer, 2011; Jovanovic et al., 2011; Verma and Jayakumar, 2012). Soil and ash have the potential to provide insight into the environmental changes brought about by controlled fire and the PTE dynamics, which is essential for risk assessment, ecosystem management and sustainability. Overall the findings of the study provide a new insight in the role of controlled fire and subsequent rainfall in PTE mobilization, which is essential for environmental health risk assessment and management. The environmental impacts of controlled fire generally depends on fire intensity, types of fuel, degree of combustion, total area burned, nature of the surface soil, PTE and other contaminants in the soil, influence of heat on soil properties and many more (Kokaly et al., 2007).

Increase in soil pH and EC observed immediately after the fire is attributed to the incorporation of ash with the surface soil, as ash is formed by the oxides, hydroxides and carbonates of base cations (Khanna et al., 1994). Ash also contains elevated concentrations of PTE, specifically As, Cu, Mn and Zn, which may contaminate the surface soil as well as the downstream surface water systems by rainfall runoff and wind activity. Among them, As mobility generates significant concern, as it is known carcinogen. Moreover, during fire, Hg stored in the soil organic matter and vegetation will move into the atmosphere as gaseous elemental mercury (GEM) (85%) and the rest as particulate Hg (PHg). GEM has the potentiality to mobilize distal areas through atmospheric activity, but PHg fall down and deposit at the burned or adjoining area. The mobilised Hg may ultimately reach surface water bodies, where if the condition is suitable, it may be converted as methyl Hg (MeHg). The neuro-toxic and immune-toxic characteristics of MeHg increase the concern as it can affect the aquatic ecosystems. The presence of increase in concentrations of many PTEs, specifically Cd and Pb can interfere the normal functioning of the plants, resulting in cellular stress response (Jovanovic et al., 2011). The long-term retaining and mobility characteristics of Zn and Cd encourage their accumulation in plant cells.

In the post-fire environment, stream flow is typically increased due to the reduction in infiltration as a result of the formation of a water repellent layer on the soil (Shakesby et al., 2000; Martin and Moody, 2001; Rulli and Rosso, 2007), which may increase the mobility of ash with enriched contaminants towards the downstream surface water body, affect the water quality. This is highly significant when these water bodies act as potable water resources to number of major cities and neighbouring communities.

9.5 Recommendations for future studies

- PTEs in the adjacent surface water and in stream sediments should be analysed immediately before and after fire to determine the possibility and the extent of contaminant mobility through the wind activity.
- PTE mobility towards the downstream surface water and the deposition in the bottom sediments is highly probable after the major rainfall in the post-fire environment. Hence, the investigation of PTE in the downstream surface water and bottom sediment is highly recommended after the major rainfall in the post-fire environment.
- Since Hg is volatilised during fire, its presence in the smoke should be quantified and the mobility should be monitored.
- Since Hg is of specific concern in the aquatic environment, the possible formation and distribution of methyl mercury (MeHg) should be investigated immediately after the fire and after the major rainfall, and for a period of at least one year in the post-fire environment.
- To obtain a better understanding of the potential hazard, it would be necessary to determine the bioavailable fraction of significant PTEs.
- PTEs in the air environment (other than Hg) also should be investigated during and immediately after the fire and the mobility also should be monitored.

9.6 Conclusion

Legacy mining affected landscapes have elevated PTEs in the surface soils and the mine waste materials, which represent a widespread and ongoing global problems due to PTE’s persistence, mobility, biomagnification characteristics and impacts on human and ecosystems health. The mobilization of PTEs during forest fire, specifically during controlled fires are not well understood. In order to investigate the PTE mobilization during controlled fire, a legacy mine site located in Maldon area in Central Victoria, Australia has been selected. Surface soil sample collection and PTE analysis in the pre-fire environment revealed that the study area is contaminated with PTEs. The completed contamination assessment in conjunction with number of indices and in comparison with Victorian and Australian top soil averages and various health investigation levels such as NEPM and DEC is significant. The result revealed that the studied legacy mining affected landscape is contaminated with PTEs, specifically with Hg and As.

Soil sample collection two days before and two days after the controlled fire, and end of each seasons, and after the major rainfall in the post-fire environment, followed by the soil sample analysis and data interpretation demonstrated that controlled fire is able to mobilize PTEs from the soil organic matter and vegetation. Results revealed the increase in concentrations of Mn, Zn, Cd, As and Ni and decrease in the concentrations of Hg, Cr and Pb. The increase in concentration is associated with the addition of PTE enriched ash to the soil and the decrease in concentration is due to the volatilization of PTEs during fire. The temporal decrease in PTE concentration in the post-fire soil environment is attributed to the removal of ash and ash enriched surface soil by rainfall runoff, however Hg shown increase in concentration after the rainfall event attributed to the ash leach out, mobilization from atmosphere and plants, and also from the newly formed organic matter in the soil.

The PTE mobility is of specific concern due to their impacts on human and ecosystems health. Climate change and the resulting projection of increased forest fire frequency including controlled fire, highlight the environmental and human health significance given the expected concomitant increase in PTE mobilization. Hence, the practice of controlled burning should be carefully considered as a forest management strategy in any legacy mining areas and indeed in other areas where PTE contamination is reported.

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