



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



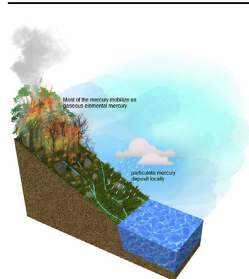
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HIGHLIGHTS

- 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 Hg⁰ 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 heightened significance. Therefore, it is recommended that prescribed fire should be cautiously considered as a forest management strategy in any mercury affected landscapes.

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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 (Skylberg 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 Hg⁰) 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 °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 °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

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