

# Public health implications of metals concentrations from prescribed burns: A study adjacent to the Perth metropolitan area.

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**Abstract**— Ash is not a homogenous product. It is the solid residue of combustion and contains a complex mixture of chemical products. The ash residue resulting from fires varies and is dependent on its source, and burn characteristics such as the temperature of the fire. Ash comprises particles of carbon, soot and trace elements. Ash presents public health risk to people and communities, through direct and indirect ingestion and inhalation. The health effects of ash exposure are not limited to symptoms affecting the eyes, throat and lungs. They can contribute to chronic disease and increase the risk of cancer.

The purpose of this study was to evaluate the public health implications of controlled burns in the Darling Escarpment, adjacent to Perth's metropolitan area in Western Australia. Concentrations of metals in unburnt vegetative litter and ash (post burn), stratified by size fraction, were determined to assess the potential mobilisation of metals caused by prescribed burns and the potential public health implications associated with burns. These data can also be used in predictive modelling to ascertain the amount of metals likely to be released per hectare when authorities plan future burns in the area.

Ash samples were collected immediately following the fire to capture fine material before it was blown away. The ash samples were separated into size fractions to investigate whether there are differences within each sub sample. Australia's National Environmental Protection Measures were used to establish whether the metal concentrations were above designated thresholds for health and environmental investigation, these being the recognised levels above which metals are deemed to pose a risk to public (or environmental) health.

Vegetation and ash samples were collected from three sites immediately after the prescribed burn. Samples were analysed for thirteen (13) metals with nine (9) showing statistically significant increases in concentrations in vegetation as compared to ash. The percentages of metals are higher in ash than in vegetative ground litter. The metals identified are Manganese - Vegetation ( $158.3 \pm 89.3$  mg/kg), Ash ( $442.2 \pm 462.6$  mg/kg); Barium - Vegetation ( $19.4 \pm 25.3$  mg/kg); Ash ( $41.8 \pm 62.7$  mg/kg); Zinc - Vegetation ( $15.3 \pm 9.7$  mg/kg), Ash ( $25.6 \pm 29.7$  mg/kg); Vanadium - Vegetation ( $31.0$  mg/kg  $\pm 76.3$  mg/kg), Ash ( $32.2$  mg/kg  $\pm 51.0$  mg/kg); Copper - Vegetation ( $4.2 \pm 1.5$  mg/kg), Ash ( $10.9 \pm 9.8$  mg/kg); Chromium (Total) - Vegetation ( $8.3 \pm 15.6$  mg/kg), Ash ( $9.6 \pm 12.4$  mg/kg); Lead - Vegetation ( $6.1 \pm 8.3$  mg/kg), Ash ( $12.2 \pm 8.5$  mg/kg); Nickel - Vegetation ( $2.2 \pm 2.2$

mg/kg), Ash ( $4.7 \pm 4.4$ mg/kg) and Cadmium - Vegetation ( $0.6 \pm 0.9$  mg/kg), Ash ( $0.6 \pm 0.9$  mg/kg). The ash samples were sieved through three aperture's (2-4 mm, 1-2 mm, <1 mm) to stratify the samples by size fraction and concentrations in all but three of the metals increased as the ash size decreased.

It was demonstrated that the level of metal present within the ash samples did not exceed health investigation levels and, with the exception of Manganese, and did not exceed environmental investigations levels. Metals were unlikely to pose a risk if left in-situ. However, modelling estimated the volume of metal released and it was determined that metals can pose a subsequent risk if mobilised by wind or water. The likelihood of such mobilisation is high and this finding therefore has public health implications for surrounding communities that are subjected to increases in their exposure to metals, associated with bushfires.

The findings from this study contribute to the management of prescribed burns by providing a better understanding of the composition of ash and the effects of potential distribution via aerial deposition or runoff. Data from this study can be used to do predictive modelling of heavy metal mobilisation that may result from burns of similar vegetation environments. This becomes particularly significant where burns are conducted in water catchment areas.

**Keywords**-Smoke, Ash, Prescribed Burn, Heavy metal.

## I. INTRODUCTION

The focus of Bushfires centers on the immediate threat to life, property, infrastructure, and natural resources but they also present potential long term risks to public health through the release of chemicals in ash. This risk increases in peri-urban environments from reduced distances to residential areas (Gill & Williams, 2009). Bushfires generate ash through pyrolysis and the size of particles can vary from (2-4 mm) to microscopic ( $>1 \mu\text{m}$ ) in diameter. The particle size characteristic this ash determines how it can potentially be absorbed by exposed individuals through inhalation and ingestion. (Dennekamp and Abramson, 2011; Beer, 2001; Jonsson, *et. al.*, 1997). Large ash particles are trapped in the mucus which lines the body's respiratory tract and are transported to the mouth via the mucociliary escalator where

they can trigger a coughing reflex. Particles can be subsequently swallowed if not expectorated (Wegesser, *et. al.*, 2009).

Naeher, *et. al.*, (2007) and Kunii, *et. al.*, (2002) reported that ash material associated with bushfires can contain toxic materials, including carcinogens and metals. Al-Malki (2009) concluded that more effort is needed to protect populations from the hazardous materials contained in particulate ash material. There is currently a lack of knowledge about the release of metals from prescribed burns and as a consequence of the recent large-scale fires in south-eastern Australia there has been an increased focus on all aspects of Australian fire management including associated public health issues (Teague *et. al.*, 2010; Doogan, 2006; Gould *et. al.*, 2011).

## II. LITERATURE REVIEW

Over centuries vegetation in much of Australia has evolved to adapt to poor soil quality. Australian trees use bio-accumulation and bio-restriction to limit the uptake of metals and to ensure optimal growth and survival. Eucalypt species can store high levels of metals and are known as hyperaccumulators (Guala, *et. al.*, 2011). This study aimed to determine if metal levels increased in the environment after vegetation litter has been burned.

Only a few studies have focused on the metal composition of ash derived from biomass composition in Australia (Reisen, *et. al.*, 2011; Larson and Koenig, 1993). Attempts have been made to study chemical composition of ash, but these were focused on the receptor of the pollution and, as such, confounding factors could not be excluded. Spinks, *et. al.* (2006) conducted a study of bushfire ash settling on roofs and subsequently contaminating rainwater tanks. However, this study found that there were many other confounding variables such as Iron and Zinc deposition from metal roofs that made it impossible to definitively identify ash as the source of metal contamination.

Karthikeyan, *et. al.* (2006), also conducted a study of metals in an ash haze in Singapore where the presence of metals was detected but the source of the metals could not be accurately determined. It is likely that, in addition to the burning of biomass, there were other sources of metal contamination, such as from industry and motor vehicle emissions. Researchers, such as Smith, *et. al.* (2011) and Jalaludin, *et. al.* (2004) identified the need to conduct further research to quantify the metal components of ash. The gap in the current body of knowledge of metals in ash may be due to the prominence of other contaminants within fire residue, the acute health effects of these other contaminants, and the belief that metals represented only a small component of the post fire material.

Metals are defined as elements that exhibit metallic properties and this includes a range of transitional and metalloid elements. Metals occur naturally throughout the environment, in varying concentrations, including within living organisms, such as plants and animals, at typically low or trace concentrations. Many living organisms rely on metals for normal physiological function at normal or homeostatic concentrations, however at higher concentration, many metals

and metalloids, both essential and non-essential, can be toxic to those living organisms (Garg and Singla, 2011; Kahli, 1993).

The presence of metals in ash, or as suspended airborne particulates associated with a wildfire pose a number of potential human health risks. The toxicity of metals is determined by a number of factors including the dose, exposure route, solubility, atomic weight or density and the species or oxidation state. While some metals have a relatively low level of toxicity, requiring chronic long term exposure to result in physical harm, other metals can pose a high toxicity risk even at low concentrations. These more toxic metals include a number of carcinogens and systemic toxicants that are associated with a range of biological effects including multiple organ damage (Tchounwou *et. al.*, 2014; Chaney, *et. al.*, 1984). The toxicity of individual metals varies as does the mechanism of their toxicity.

The severity and symptoms of metal toxicity, as a result of an exposure, can vary significantly depending on the duration and degree of exposure. The health effects associated with both acute and chronic exposure to toxic metals is well documented in the medical and scientific literature (Monisha, *et. al.*, 2014; Nagajyoti, *et. al.*, 2010; Naeher, *et. al.*, 2007; Nriagu and Jin Kim, 2000). The mechanism of metal toxicity typically occurs through one or a combination of the following biological processes including competitive receptor binding and protein-enzyme interference, preferential substitution of toxic metals, disruption of cellular metabolic and regulatory processes and oxidative stress through free radical accumulation and damage (Fan *et. al.*, 1996).

Competitive receptor binding and protein-enzyme interference occurs in both acute and chronic exposures to metals, resulting in an increased uptake of metals by humans. Among other biological effects, this exposure results in an increased serum and cellular concentration of metals. Many essential metal ions, such as Iron<sup>2+</sup> and Calcium<sup>2+</sup> have important biological roles in metalloenzymes and DNA binding proteins (Ellis *et. al.*, 2006). Because essential and toxic metal ions share similar chemical characteristics such as ionic radius, where an excess of non-essential or toxic metals is present, these will naturally compete within biological systems for specific protein and DNA binding sites. For example, studies have shown that Cadmium can replace Calcium in many of its binding sites owing to an almost identical ionic size (Jacobson & Turner, 1980).

This competitive binding of non-essential or toxic metals into cellular ligands alters the molecular geometry and functionality of the protein and can result in the de-activation of the protein or enzyme as well as damaging DNA and nuclear proteins resulting in conformational changes that can lead to cell cycle modulation, carcinogenesis or apoptosis (Chang, *et. al.*, 1996).

Metals such as Calcium, Copper and Zinc have important roles in normal cellular function. However, some toxic metals such as Lead may be preferentially substituted by direct competition for Calcium<sup>+</sup> and Calcium<sup>2+</sup> binding sites, particularly at hydroxyl and phosphate binding sites. This preferential substitution can result in increased absorption and tissue accumulation of toxic metals, including through

intestinal absorption, accumulation and absorption into nano-crystalline bone structure as well as other functional organs (Ellis *et. al.*, 2006).

Disruption of cellular metabolic and regulatory processes also results from competitive binding and absorption processes where non-essential or toxic metals bond to form cellular ligands and may be substituted into protein sulfhydryl, carboxyl or ammonia groups and enzymes. This substitution has also been reported to adversely affect the functionality of cellular organelles such as cellular membranes, mitochondria, endoplasmic reticulum and nuclei involved in cellular metabolism, energy and ATP production cycles as well as a number of regulatory and detoxification mechanisms (Wang and Shi, 2001). Arsenic as a specific example which is a protoplasmic poison is known to preferentially bond with sulfhydryl groups resulting in the malfunctioning of cell respiration, cell enzymes and mitosis (Gordon, *et. al.*, 1948).

Oxidative stress occurs in cells as a result of an imbalance between the production of free radicals and the generation of antioxidants to detoxify cells through the removal of reactive oxygen species (ROS) (Monisha, *et. al.*, 2014). Essential metals such as Iron, Copper and Chromium are considered redox-active metals and readily undergo redox cycling, whereas many other transition or heavy metals, such as Lead, Cadmium and Mercury, are redox-inactive. Where acute or chronic exposures result in an increased cellular uptake of these redox-inactive metals, the result is an increased production of ROS including hydroxyl radicals (OH.), superoxide radicals (O<sub>2</sub>.-) or hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (Ercal, *et. al.*, 2001). This increase in ROS can overwhelm the normal antioxidant buffering capacity of a cell resulting in ROS or free radical damage to cell organelles including lipids, proteins, DNA and mitochondria and induce general cell dysfunction and even cell death.

The presence of metals within ash and suspended particulates as a result of the combustion of plant material poses a public health risk that must be considered, when planning a prescribed burn. During the combustion process, naturally occurring metals within plant material will predominantly be reduced through combustion to form metal oxides, which will be present in ash and as airborne suspended particulates. Given the established toxicity of metals and the potential for human exposure through various potential pathways, prescribed burning is deemed to be a high-risk environment for the formation of toxic metals that provides a vector for human exposure through thermally facilitated distribution within the environment.

The analysis of ash samples, undertaken as part of this study, included testing for the National Environmental Protection Measure (NEPM) 13 metal suite which included Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), Vanadium (V) and Zinc (Zn). This analytical suite was selected based on the broad inclusion of metals recognised as priority human health risks (USEPA, *Priority Pollutants List*, 2014), and metals typically assessed as indicators of direct toxicity or indirect toxicity to human health.

In a study of the size fraction of ash, by Pereira, *et. al.*, (2013) the metal concentration in source materials (ash) and its relationship to size, fire severity and mobilisation potential was quantified. Information derived from this study can assist land managers in estimating the quantity of metals at the receptor and assist in implementing mitigation strategies to reduce the impact of ash entering the surrounding environment.

### III. METHODOLOGY

The study area was chosen to represent a cross section of peri-urban metropolitan environments located within the Darling escarpment on the outskirts of Perth, Western Australia. The sites chosen were open jarrah forests (*Eucalyptus marginata*) managed by the Western Australia Department of Parks and Wildlife. Prescribed burns were conducted in these areas in autumn and spring to reduce the risk of uncontrolled bushfires fires during the summer months.

This research was undertaken in conjunction with the Western Australia Department of Environment and Conservation (DEC) as a trained employee, so access to the fire ground was possible during a managed fire event. For most researchers gaining access to gather samples at the source, particularly from an active fire ground, is difficult due to authorisation issues and safety concerns. However, the collection of ash samples immediately after the fire was critical to reduce the risk of losing a portion of the ash through wind movement and to reduce the potential for sample contamination by external sources.

The aim of this study was to assess the public health impacts of controlled burns through the determination of the levels of metals in ground vegetative litter and the subsequent residual ash generated during prescribed burns in the Darling escarpment adjacent to Perth's metropolitan area. Different ash size fractions were analysed to establish a link between metal concentrations, particles size, colour and fire severity. To meet this aim the project had the following objectives:

- Assess metal concentrations at three different ash size fractions (2-4 millimetres, 1-2 millimetres and less than 1 millimetre) that occur as a result of the ash generated during prescribed burns.
- Establish the relationship between ground vegetation litter and ash metal concentrations.
- Determine the potential linkage between metal concentrations in ash and public health implications.

The methods used to collect samples in the study involved the researcher obtaining specific training to be able to enter a controlled fire ground, conducting the pilot study and sampling and analysis of the main study.

#### Authorisation and Training

The Department of Parks and Wildlife required specific fire training to be completed before access was granted to enter a fire ground. This training focused on identifying the risks associated with fire and the use of team protocols to enable a shared understanding of the dangers associated with this activity. The researcher had received specific, specialised

training as part of his employment as a Senior Environmental Officer within the Environmental Hazards Branch of the Department of Environment Regulation, specifically the Pollution Response Unit. This training, in conjunction with fire operations training, was required to allow access to an active fire ground.

### **Main study operation protocol**

The parameters for conducting a prescribed burn depend on a range of factors, in particular, the suitability of local weather conditions. Once it was confirmed that a prescribed burn would be undertaken details were provided on the location of the control point. A meeting time was set to discuss the most suitable location to conduct the sampling based on prevailing winds and staff operations. A procedural protocol for the prescribed burn was established at the briefing meeting prior to commencing the sampling. On arrival at the sampling area the Incident Controller was contacted and directions were given relating to areas to be ignited or that has just been lit, the direction of the fire front, and specific risks of the area including:

- likelihood of falling branches and underground burning roots
- heavy machinery movements
- fire ground conditions
- upcoming changes in weather
- the staging of the burn activity.

Patrolling officers were directed to check on the researcher's welfare during the sampling period and to provide up-to-date information on the fire's characteristics. When the sampling was completed contact was made with the Incident Controller to advise them that the researcher would be leaving the fire ground.

At the end of the day a debrief meeting was conducted with all staff to advise on the progress of the burn, specific risks that were identified, and any observations about the characteristics of the burn. Ongoing post-burn monitoring was discussed during these meetings.

### **Main study sampling methodology**

Once the sampling location was determined a sampling grid of approximately 50 metres by 50 metres (2500 m<sup>2</sup>) was selected and a random sampling pattern commenced. Each sample was taken from a point within a 10 metre by 10 metre area. The sample location and direction to the next sample was determined by safety factors such as flame activity within the grid area, risk of underground root burn activity, and the overhead branch drop activity in the area. Figures 5.6, 5.7 and 5.8 provide a graphical representation of the sequence and where the samples were taken within the 50 metre by 50 metre grid for each of the sampling sites.

Due to the low intensity of the burn it was possible to collect both ash and vegetation litter samples within the same 10 metre by 10 metre area (100 m<sup>2</sup>) as the fire activity was sporadic and only partially burnt the area. A total of 15 ash and

15 ground vegetation litter samples were collected from each prescribed burn area.

Ash samples were collected from each grid using a plastic trowel and placed into a plastic bag for subsequent size separation. The samples were then divided based on size fractions using three Endecott's 200 mm diameter test sieves and a receiver. The apertures of the sieves were 4 mm, 2 mm and 1 mm that could be interconnected. The material was carefully deposited on the top largest sieve and gently agitated so that the finer particles would not blow away. The partially burnt material remaining in the top sieve consisted of twigs and stones etc. and was discarded. As the smaller particles passed through each sieve the larger ash samples were captured by each aperture until the very fine particles were collected in the receiver. This provided sample material that was between 2 and 4 mm, 1 and 2 mm and less than 1 mm. All material collected was placed in sealed plastic bags and labelled for laboratory analysis.

The vegetation samples were collected from the same grid as close as possible to the area where the ash samples were collected and placed in plastic bags for analysis. These samples consisted of leaf material and small twigs.

### **Laboratory Analysis**

The analysis of samples was undertaken at Analytical Reference Laboratory (WA), which is accredited by National Association of Testing Authorities (NATA), which analysed the vegetative litter and ash in accordance with the American Society for Testing and Materials (ASTM) standards. The analysis included testing for the National Environmental Protection Measures (NEPM) suite of 13 metals (Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Mercury, Nickel, Vanadium and Zinc). The vegetative litter was prepared by acid digestion of Nitric and Hydrochloric acid (Ratio 3:1) at 95°C for two hours and analysed in accordance with biological samples for metals methodology. The ash was prepared using the same methodology to ensure consistency in sample preparation and was analysed using Metals in soil ICP-OES methodology. Mercury was analysed by Cold Vapour AA methodology (ARL, 2013).

### **Statistical analysis of results**

All data tests with numerical output were reported as mean  $\pm$  standard error. A skew and kurtosis test was performed to test for parametric data, it was considered that the sample size (>15 samples) satisfied the requirement to use the ANOVA parametric test (Frost, 2015). An Analysis of Variance (ANOVA) to test for statistically significant differences in measurement means was conducted on samples. Pairwise comparisons between sample sizes and vegetation were completed using a Levine's test and a Games-Howell post-hoc test at  $p < 0.05$  significance level. All statistical analysis was conducted using SPSS V.23 software. Where a Limit of Detection (LoD) recording was not obtained, a reference value of 70% of the LoD was used as a conservative figure for statistical analysis. Ogden *et. al.*, (2011) states that the use of a value for the LoD is debatable and no single method can be recommended as being the preferred methodology. As such,

the LoD value of 70% was chosen as this option was previously used in other studies, thus making comparison of results valid (CJCU, 2015). Local fire front weather data (temperature, wind speed and direction, and relative humidity) were collected during the sampling phase with the aid of a Davis Vantage Pro two mobile weather station (Davis Instruments Corp., Hayward, CA, USA). Regional weather data were also sourced from the Bureau of Meteorology and compared to the local fire front data.

#### IV. RESULTS

##### Field observations

On the day of sampling an initial briefing was conducted with the Incident Controller to discuss the anticipated direction of the fire and the most suitable place to sample. The objective of the briefing was to become familiar with the day's activities and the resources that would be operating in the area. These resources included earth moving equipment, fire appliances and 4WDs patrolling for potential break outs. A safety component was included so authorised people on the fire ground knew the area where the study was being conducted. They could include that area in their patrols in the event any unforeseen safety issues might occur.

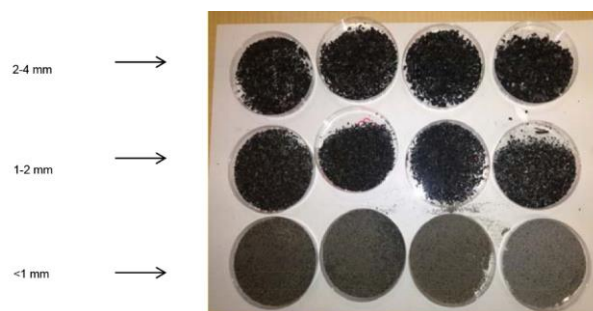
Safety was a major consideration in the selection of sample sites. The sites were selected based on the predicted path of the fire in relation to topography and wind speed as these factors can influence the fire's rate of spread. The area chosen provided extended egress options in case the fire conditions changed. Table 4.1 provides information about the characteristics of each site that was provided during the initial operational briefing.

**Table 4.1: Site characteristics provided during the initial operational briefing on the day of sampling**

	Site 1: PHS 807 Welshpool Road, Lesmurdie	Site 2: PHS 204 Zamia Forest, Mundaring	Site 3: PHS Moondyne Nature Reserve Bullsbrook
Sample date	1 July 2013	9 Sept 2013	7 October 2013
Temperature (°C)	16	20	20
Wind Direction	North West	Variable	North West
Wind Speed (km/h)	15	5	20
Wind Gust (km/h)	25	10	35
Fuel Load (t/ha)	19.3	12.5	9
Litter Depth (mm)	39	19	11
Flame Height (m)	10	6	8
Rate of flame spread (m/hr)	34 - 44	28 - 34	65 - 72

##### Study sample observations

The ash was separated into the various size fractions and was distinctive in their appearance with the larger diameter samples displaying a characteristic similar to charcoal. Within the matrix of the 2-4 mm size fraction ash there was partially burnt carbonaceous material from small stems and twigs. There was no evidence of unburnt leaf litter in the ash samples. The 1-2 mm size fraction samples displayed similar characteristics to the 2-4 mm size fraction, however there were distinctive white ash particles that were wafer-like in appearance and could easily be broken up if disturbed. The <1 mm size fraction samples presented a completely different appearance to that of the larger sized samples. The <1 mm samples appeared to be like a fine grey particle, uniform in size. The charcoal aspect was generally not visible except for small dark specks within the sample. Figure 6.6 provides a visual representation of the characteristics of the different sized samples.



The results from the data on levels of metals are presented in order of average concentration of metals, from highest to lowest (Manganese, Barium, Vanadium, Zinc, Lead, Copper, Chromium, Nickel, Cadmium).

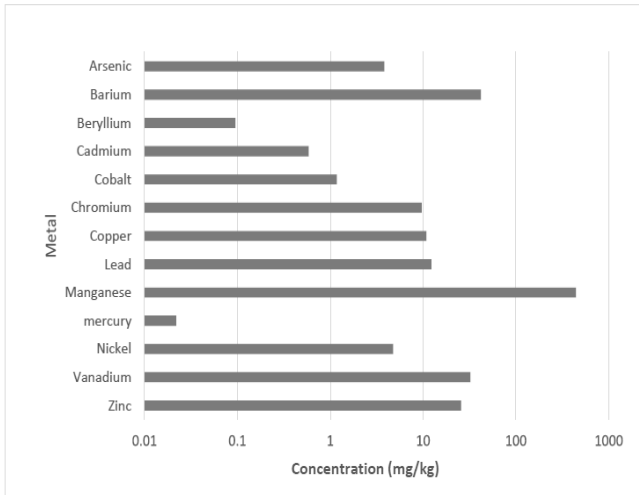
**Table 4.2: Sampling Results including size fractions and vegetation material**

	Overall	<1mm Mean	1-2mm Mean	2-4mm Mean	Vegetation
Manganese	442.1	808.0	426.7	375.6	158.4
Barium	41.8	68.0	64.87	51.96	19.4
Vanadium	32.2	20.1	37.1	40.5	31.0
Zinc	25.6	47.0	20.1	19.9	15.3
Lead	12.2	15.2	14.1	13.5	6.1
Copper	10.8	20.9	9.6	8.7	4.2
Chromium	9.6	7.7	10.7	11.8	8.3
Nickel	4.7	7.7	4.9	4.2	2.2
Cadmium	0.6	0.4	0.7	0.8	0.5

#### V. DISCUSSION

This study demonstrates the relationship between metals in vegetative matter prior to, and in ash after a prescribed burn.

The average concentrations of metals in ash and unburnt vegetation litter are presented in Figure 7.1.



**Figure 5.1: Average metal concentrations found in ash at the sample sites on the Darling Escarpment in WA**

The average concentrations of the metals varied and ranged from 0.02 mg/kg for Mercury to 442 mg/kg for Manganese. A total of 180 ash and vegetation samples were collected and analysed for speciation of 13 metals thus giving a total of 2 340 results, of which 71% were above the LoD. This increased to 93% when the four metals (Arsenic, Beryllium, Cobalt, and Mercury) were removed from the analysis due to the low level (below LoD) of results from these samples. The results above LoD from all the vegetation samples was 58% but once the lowest four metals were removed from the analysis this increased the vegetation sampling rate to 78% of samples above LoD.

The metals found in the ash and vegetation of this study were compared with the results of other studies conducted in Australia, Europe, USA, Jordan and other multiple jurisdictions. Only the two United States studies (Etiegni and Campbell, 1991; Plumlee, 2007). Generally, the findings from this study were that metal concentrations in Western Australian ash were lower than those reported from the USA (Etiegni and Campbell, 1991; Plumlee, 2007). This can be attributed to the higher soil metal levels in California and that the majority of studies were from hotter uncontrolled bushfires. These other studies did not consider the public health risks associated with the metal concentrations.

Only nine metals of the thirteen provided a statistically representative sample. Cobalt, Mercury, Arsenic and Beryllium provided insufficient results and will not be discussed further. Of the nine samples that provided sufficient results the average metal concentrations ranged from 0.56 mg/kg for Cadmium to 442.2 mg/kg for Manganese and the order based on quantity of material was Manganese > Barium > Zinc > Vanadium > Copper > Chromium > Lead > Nickel > Cadmium.

Comparisons are made between the concentrations identified in this study, the HIL levels and the potential risk to public health in situ. The discussion does not measure the effects of mobilisation of the ash offsite either through wind or

water runoff, even though this is a distinct possibility. Also comparisons with EILs are mentioned as this not only presents a risk to the environment but could also provide low level impacts for humans. The public health implications of each metal from this study will be discussed below.

### Manganese

Manganese was the most prevalent metal analysed in this study with concentrations ranging from 21 mg/kg to 3300 mg/kg, however 98% of samples exhibited concentrations below 200 mg/kg. The average results of this study were below the HIL threshold of 1500 mg/kg for Manganese in residential (A) areas but seven individual sample results exceeded the HIL threshold, with a maximum value of 3300 mg/kg recorded. Even though these individual samples exceeded threshold limits, the average level of Manganese found in the ash was not considered an acute risk to human health or the environment, based on consideration of overall average concentrations. This view was taken in light of the inherently heterogeneous nature of ash deposition, and areas of ash exhibiting above average concentrations of Manganese being isolated and not representative of the majority of samples collected or locations tested.

It should be noted that the 2010 DEC guidelines set the Environmental Impact level threshold level for Manganese at 500 mg/kg. The average Manganese levels in this study were approaching this threshold level with the overall average being  $442.2 \pm 462.6$  mg/kg and 27% of individual samples were in excess of 500 mg/kg.

Also, the average <1 mm size fraction ( $808.0 \pm 716.8$ ) exceeded the EIL threshold

Manganese levels found in this study were the closest to the relevant HIL or EIL screening criteria of all of the metals analysed. This is due to the prevalence of Manganese specifically within green leaf material as a result of its structural and activation role within chlorophyll protein complexes. Given that the majority of plant matter subject to combustion during a prescribed burn is leaf material, this would account for high concentrations of Manganese identified in this study. It would be presumed that future studies will also record high levels of Manganese when assessing ash from combustion of leaf and other plant matter.

The release of Manganese in ash still poses a cumulative public health risk through the mobilisation of ash into water catchment areas and the potential concentration of metals in a plume that can cause a periodic exceedance of water quality parameters.

### Barium

Barium was detected in 100% of samples analysed, with concentrations ranging from 3 mg/kg up to 400 mg/kg, with 96% of samples having concentrations below 200 mg/kg. The results of this study were well below the HIL of 15 000 mg/kg for residential (A) areas as well as being predominantly below the EIL of 300 mg/kg.

Based on the consistently low levels of Barium detected within samples, in comparison to the HIL, it was concluded that Barium is unlikely to pose a serious risk to public health.

## **Zinc**

Zinc was detected in 97% of samples in concentrations ranging from 0.7 mg/kg to 190 mg/kg with 87% of samples reporting concentrations between 1 mg/kg and 50 mg/kg. The average results of this study were significantly below the HIL threshold of 7000 mg/kg for Zinc in residential (A) areas. The 2010 guidelines set the EIL threshold level for Zinc at 200 mg/kg. The average Zinc concentrations determined for ash samples analysed in this study were significantly below this threshold with the overall average being  $25.6 \pm 29.7$  mg/kg, while no individual samples were recorded in excess of the EIL, four samples recorded concentrations above 150 mg/kg.

The overall Zinc levels were significantly below both the HIL and EIL criteria indicating that despite the presence of Zinc within 97% of samples, it is unlikely to pose a serious risk to human health or the environment.

## **Vanadium**

Vanadium was detected in 88% of ash samples analysed with concentration ranges from 1.4 to 140 mg/kg, and 87% of samples recording concentrations between only 2 mg/kg and 5 mg/kg. The average results Vanadium in this study were significantly below the HIL threshold of 550 mg/kg for Vanadium in residential (A) areas and only one sample recorded a maximum concentration of 410mg/kg.

Overall the level of Vanadium found in this study was not considered to be of consequence to human health or the environment, based on relatively low reported concentrations and considering the level and oxidised form of Vanadium being unlikely to represent either a public health exposure or toxicity risk.

Even though the current NEPM guidelines do not have a level set for Vanadium the 2010 guidelines set the EIL threshold level for Vanadium at 50 mg/kg. The average Vanadium levels in this study were below this threshold level with the overall average being  $32.2 \pm 51.0$  mg/kg and only 16% of individual samples were in excess of 50 mg/kg.

## **Copper**

Copper was detected within 100% of samples analysed, recording average concentrations between 3 mg/kg and 57 mg/kg, with 87% of samples reporting concentrations below 20 mg/kg. These results were all significantly below the HIL criteria of 1 000 mg/kg for residential (A) areas and the level of Copper found in the ash was not considered to be of consequence to human health or the environment considering both the concentrations detected and the relatively high concentrations of Copper required to represent a risk of harm or to result in Copperiedus.

The 2010 guidelines set the EIL threshold for Copper at 100 mg/kg. The average Copper levels in ash samples analysed within this study were on average 50% below the EIL criteria, with the maximum concentration recorded being 57mg/kg and the overall average only 10.8 mg/kg.

## **Chromium**

Chromium was detected in 88% of samples analysed in this study with average concentrations ranging from 0.7 mg/kg to 72 mg/kg, and 75% of samples yielding concentrations between 1.0 mg/kg and 20 mg/kg. Despite analysis being conducted for total Chromium, with speciation for Chromium III and VI, it is considered reasonable to compare the results obtained for total Chromium to HIL and EIL values for Chromium III, due to the fact that given the sample matrix was composed of ash material, Chromium VI is unlikely to be present based on the oxidative conditions which occur during combustion.

The highest total Chromium level recorded was 72 mg/kg (mean 9.64) and this was lower than the HIL of 120,000 mg/kg for Chromium III Residential (A) or 100 mg/hg for Chromium VI Residential (A) (DEC, 2010). The 2010 guidelines set the EIL threshold level for Chromium (III) at 400 mg/kg.

Overall the level of Chromium detected within samples in this study was not considered likely to represent either a health or environmental risk. This assertion is supported by the fact that the with combustion conditions favouring the formation of Chromium II and Chromium III species, these species are generally considered benign based on their weak membrane permeability, and are unlikely to pose risk, regardless of the concentrations reported.

## **Lead**

The analysis for Lead undertaken in this study identified Lead in 86% of samples analysed. However, the average concentrations only ranged between 1 mg/kg and 38 mg/kg, with 83% of samples returning results between 1 mg/kg and 20 mg/kg.

The results of this study were significantly below the HIL of 1000 mg/kg for residential (A) areas and the level of Lead found in the ash was considered to be unlikely to pose a risk to human health, with overall Lead levels in this study below the HIL threshold. Notwithstanding the relative toxicity of Lead generally, considering likely exposure routes of ingestion, toxic effects would still require consumption of gram quantities of Lead for acute exposure, which are considered unlikely.

The 2010 guideline set the EIL threshold for Lead at 600 mg/kg. The average Lead concentration identified in this study were significantly below these threshold criteria with the maximum concentration recorded being only 38 mg/kg and the overall average being 12.2 mg/kg.

## **Nickel**

The study identified Nickel in 94% of samples analysed, with average concentrations ranging from 0.7 mg/kg to 18 mg/kg, and 73% of samples concentrations ranging between only 1.0 mg/kg and 10 mg/kg. The results of this study were also significantly below the HIL of 600 mg/kg for residential (A) areas. Given the primary toxicity and exposure risk associated with Nickel being an increased risk of pulmonary and nasal carcinogenesis, typically associated with long-term chronic exposures, the concentrations of Nickel reported in ash samples from this study are not considered likely to pose a public health or environmental risk.

The 2010 guidelines set the EIL threshold level for Nickel at 60 mg/kg. The average Nickel levels in this study were significantly below this figure with the maximum concentration recorded being 19 mg/kg, and an overall average concentration of 4.7 mg/kg.

### Cadmium

The study identified Cadmium in 81% of samples analysed, reporting concentrations from 0.07 mg/kg to 5.7 mg/kg, and 78% of samples between 0.1 mg/kg and 3 mg/kg. All samples analysed for Cadmium were below the HIL criteria of 20 mg/kg for residential (A) areas, with the maximum concentration recorded at 5.7 mg/kg and the overall average only 0.6 mg/kg. The 2010 guidelines set the EIL threshold criteria for Cadmium at 3 mg/kg. The average Cadmium levels in the ash were below this criterion with the maximum concentration reported being 0.8 mg/kg in the 2-4 mm size fraction sample.

However, there were two individual samples collected that exceeded the EIL of 3 mg/kg. One of the samples from the Lesmurdie area recorded a result of 5.3 mg/kg and one sample from Mundaring returned a result of 5.7 mg/kg. However, considering the heterogeneous nature of ash deposition and overall average concentrations and sample distribution, these results are not considered statistically significant.

The results of this study demonstrate that Cadmium concentrations in the ash are consistent with background levels reported in the 2010 DEC technical document. Overall, it was found that Cadmium concentrations measured in this study do not pose a health or environmental exposure risk.

### Public health implications

The metal levels in this study do not present a health or environmental risk if left in-situ but they may pose problems if they become mobilised by either wind or water. There is the potential for metals to accumulate in rainwater tanks from aerial deposition of ash (Spinks *et. al.*, 2006). Studies into water quality have also shown that metal levels can increase significantly from pre-fire conditions due to wind deposition, increased runoff and potential accumulation in temporal or dry waterways (Ebel, *et. al.*, 2012; Bowman and Bloggs, 2006). The period between May and October where the majority of prescribed burns are conducted is associated with high rainfall levels thus increasing the likelihood of mobility of the ash through runoff (BOM, 2017).

It was possible to estimate the total amount of metals in the ash released during each burn and over the total of the three burns. The total area burnt during the prescribed burns was approximately 3 320 hectares having the potential to generate between 30.8 and 153.7 tonnes of ash. This ash release estimation is based on the percentage of ash generated during the prescribed burns using 0.4% lower limit and 2% upper limit as identified in the literature (Misra *et. al.*, 1993; Santin, *et. al.*, 2012; Kumar *et. al.*, 2009).

As seen in Table 7.3 there were nine metals that provided statistical results with Cadmium having the lowest release quantity with between 117 and 585 grams being released from

all burns while Manganese had the highest quantity released between approximately 19.2 and 461.9 kilograms.

**Table 7.3: Estimation of total release of metals during prescribed burns during this study**

Metal	Concentration mg/kg	Lesmurdie		Mundaring		Bullsbrook		Total	
		0.4%	2%	0.4%	2%	0.4%	2%	0.4%	2.0%
Barium	41.8	96.1 g	480.5 g	827.6 g	4.1 kg	363.7 g	1.8 kg	1.3 kg	6.5 kg
Cadmium	0.56	1.3 g	6.5 g	11.1 g	55.5 g	4.9 g	24.5 g	17.2 g	86.1 g
Chromium	9.6	22.1 g	110.5 g	190.1 g	950.5 g	83.5 g	417.5 g	295.7 g	1.5 kg
Copper	10.8	24.8 g	124.0 g	213.8 g	1.1 kg	94.0 g	470.0 g	332.6 g	1.7 kg
Lead	6.1	14.0 g	70.0 g	120.8 g	604 g	53.1 g	265.5 g	187.9 g	939.5 g
Manganese	442.2	1017.1 g	5.1 kg	8.8 kg	44.0 kg	3.8 kg	19.0 kg	13.6 kg	68.0 kg
Nickel	4.7	10.8 g	54.0 g	93.1 g	465.5 g	40.9 g	204.5 g	144.8 g	724.0 g
Vanadium	20.1	46.2 g	231.0 g	397.9 g	1.9 kg	174.9 g	874.5 g	619.1 g	3.1 kg
Zinc	25.6	58.9 g	294.5 g	506.9 g	2.5 kg	222.7 g	1.1 kg	788.5 g	3.9 kg

The WA Government aims to burn 200 000 hectares of forest each year; it is therefore possible to estimate the total potential release of metals from prescribed burns. Using the average fuel reduction from this study of 2.3 tonnes per hectare, this provides a total of 460,000 tonnes consumed to generate between 1 840 (0.4%) tonnes and 9 200 (2.0%) tonnes of ash.

The potential quantities of metals released in WA from prescribed burns become quite large (Table 7.4) with 4.1 tonnes of Manganese being mobilised in the ash. When considering the quantity release it is also important to note the TRV for ingestion of each metal. These values are outlined in Chapter 2.3 with Cadmium being the most toxic (ingestion) with a TRV of 0.0008 mg/kg/day while Zinc being the least toxic with a TRV of 0.15 mg/kg/day.

**Table 7.4: Estimation of total release of metals during the yearly goal of 200,000 hectares burnt through prescribed burns**

Metal	Concentration mg/kg	0.4 % ash content	2.0 % Ash content
Barium	41.8	76.9 kg	384.5 kg
Cadmium	0.56	1.0 kg	5.0 kg
Chromium	9.6	17.7 kg	88.5 kg
Copper	10.8	19.9 kg	99.5 kg
Lead	6.1	11.2 kg	56.0 kg
Manganese	442.2	813.7 kg	4.1 t
Nickel	4.7	8.7 kg	43.5 kg
Vanadium	20.1	37.0 kg	185.0 kg
Zinc	25.6	47.1 kg	235.5 kg

This modelling quantifies the possible public health risk posed by the release and mobilisation of metals in ash. The volumes released across WA and especially the south west of the state, with a high population density and fuel source, can potentially cause significant long term and accumulative health issues for nearby population water supplies. The factors associated with mobilisation are complex but as Canberra and other areas have experienced with the right conditions can become a distinct possibility.



Over the long term it would be difficult to identify a direct public health causal effect relationship of metal toxicity and prescribed burns due to the low level cumulative nature of the exposure. However due to an increasing population age profile and the likely increased occurrence due to population encroachment this exposure cannot be discounted.

### Management Implications

The results obtained from this study provide important information for the State Government. In the future, vegetation litter analysis can be utilised to identify background levels of metals in areas identified for fire management to determine what levels of post fire contamination might be contaminated from other sources. The findings from this study are useful for comparison of ash from the source with metals found in sediment.

In terms of management application prescribed burns are seen as a preventive method of reducing the potential of uncontrolled fires but the potential for metals in sediment flow through runoff cannot be ignored. Elevated Cadmium levels in Canberra's water supply after the 2003 fires (Smith, *et. al*, 2011a) are an example of this occurrence. Where areas are burnt adjacent to water edges, prescribed burns can contribute to sediment flow and the introduction of metals into waterways and consideration should be made to restrict the movement of ash into these water ways.

## VI. CONCLUSION

This study investigated the potential public health effects from the release of metals from a prescribed burn. The overall aim of this study was to determine the public health implications from concentration of metals in ash. The focus of the study was specifically on 13 metals (Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Mercury, Nickel, Vanadium and Zinc), which are used for screening purposes in contamination investigations, often referred to as the NEPM 13. To satisfy the aim of the study a number of objectives were established.

The first objective involved the measurement of metals in unburnt vegetation in the location of a prescribed burn. This was achieved through the collection of forest ground vegetative litter within the sample area. The results of the analysis identified metals were present in the vegetative material.

The second objective was to collect and analyse resulting ash. A measurement of metal concentrations was conducted using three ash size fractions (<1 mm, 1-2 mm, 2-4 mm) as a result of the ash generated during prescribed burns. Ash from three sites was collected to provide an overall profile of the metal characteristics found in the Darling escarpment prescribes burn sites. The final and main objective was to explore the relationship between metal concentrations of the ash pollutants studied and potential adverse health and environmental effects. The results from this study were below the HILs and the results, and with the exception of Manganese in the <1 mm size fraction, were below EILs.

The results identified the presence of metals in all ash samples. With the exception of Arsenic, metal results were recorded in the unburnt vegetation samples.

Due to the fact that the majority of Arsenic, (3.8 +/- 1.6 mg/kg), Beryllium (0.095 +/- 0.056 mg/kg), Cobalt (1.18 +/- 0.79 mg/kg) and Mercury (0.022 +/- 0.077 mg/kg) samples were below the detection level of the analytical laboratory method a detailed statistical analysis for these metals could not be conducted. Of the remaining metals analysed the order of concentration levels are as follows; Manganese > Barium > Vanadium > Zinc > Lead > Copper > Chromium > Nickel > Cadmium.

The study demonstrated a relationship between the size fractions and levels of heavy metals. A distinct pattern emerged as the combustion process became more complete; metals concentrated in the smaller ash fractions due to the carbon component being burnt off. In some of the samples this increase tapered off. A review of other studies provides a possible explanation in that the formation of Calcium Carbonate at around 400oC reduced the metal levels available for analysis. Even though this aspect was not explored in this study it does provide a possible explanation. Prescribed burns are considered low to medium in their heat generation and this corresponds with the 400oC temperature threshold.

The results of this study established a relationship between vegetation and ash. Metals in vegetation samples were lower than those found in the ash. It is expected that the removal of carbonaceous material is the main contributor to the increased metal composition found in the smaller fractions of ash.

The final aspect of the study was whether the concentrations of metals in ash are within the acceptable HIL and EIL as established by NEPM and other government standards. When compared to the 2010 guidelines, the concentrations of metals in the ash were within the acceptable HILs and EILs. Only Manganese in the <1 mm size fraction exceeded the EIL but, overall, Manganese was below the level of 500 mg/kg.

Overall the results of this study highlighted that metals were present in the post-fire ash and that the concentrations varied with the ash size fraction. The study also established a relationship between the ash generated from the prescribed burn and the unburnt vegetation in the area prior to the burn. It was also shown that the metal concentration levels identified did not exceed HILs and, with the exception of Manganese, did not exceed EILs.

An issue of concern is that the ash could potentially be mobilised into waterways through runoff or rainwater systems by the airborne deposition. Modelling has shown that between 1200 and 9200 tonnes of ash can be generated when burning an area of 200,000 Ha. Though this is dependent on the weather characteristics at each event. This mobilised ash can potentially concentrate to levels that make the water non-potable, as was the case after the Canberra bushfires in 2003. Further research is required to determine mechanisms associated with this process.

The findings of this study have a public health application. They contribute to estimating the amount and concentration of

metals that can be expected in the ash after a fire, and to approximate any metal loading if the ash is mobilised by wind or water into drinking water catchment areas. Agencies and landowners can use this information to conduct remedial erosion work to prevent the mobilisation of the ash. They can also advise on-site drinking consumers about methods for testing and preventing ash contaminating their drinking water supplies.

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