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# Metal accumulation in roadside soil in Melbourne, Australia: Effect of road age, traffic density and vehicular speed



Shamali De Silva <sup>a, d, \*</sup>, Andrew S. Ball <sup>b, d</sup>, Trang Huynh <sup>c</sup>, Suzie M. Reichman <sup>a, d</sup>

<sup>a</sup> School of Civil, Environmental and Chemical Engineering, RMIT University, Melbourne 3001, Australia

<sup>b</sup> School of Applied Sciences, RMIT University, Melbourne 3001, Australia

<sup>c</sup> Centre for Mined Land Rehabilitation, Sustainable Mineral Institute, The University of Queensland, Brisbane, QLD 4072, Australia

<sup>d</sup> Centre for Environmental Sustainability and Remediation, RMIT University, Melbourne 3001, Australia

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## ABSTRACT

Concentrations of vehicular emitted heavy metals in roadside soils result in long term environmental damage. This study assessed the relationships between traffic characteristics (traffic density, road age and vehicular speed) and roadside soil heavy metals. Significant levels were recorded for Cd (0.06–0.59 mg/kg), Cr (18–29 mg/kg), Cu (4–12 mg/kg), Ni (7–20 mg/kg), Mn (92–599 mg/kg), Pb (16–144 mg/kg) and Zn (10.36–88.75 mg/kg), with Mn concentrations exceeding the Ecological Investigation Level. Significant correlations were found between roadside soil metal concentration and vehicular speed ( $R = 0.90$ ), road age ( $R = 0.82$ ) and traffic density ( $R = 0.68$ ). Recently introduced metals in automotive technology (e.g. Mn and Sb) were higher in younger roads, while the metals present for many years (e.g. Cd, Cu, Pb, Zn) were higher in medium and old age roads confirming the risk of significant metal deposition and soil metal retention in roadside soils.

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## 1. Introduction

Australia has a total of 800,000 km of road network system, with about 0.06 km per capita of road network system. Melbourne is an urban metropolitan area of 9900 km<sup>2</sup> and population of 4.4 million people, one of the most densely populated areas in Australia (ABS, 2012). Many residential estates are erected beside roads and as a result highly prone to pollution such as vehicular emissions. Vehicular emissions include metals<sup>1</sup> which end up in roadside soil (Li et al., 2003). These metals come from fuel (As, Cd, Cr, Hg, Mn, Ni, Pb, Se and Zn), engine oil (Cd, Cr, Ni, Zn and W), tyre wear (Cd, Co, Cu, Cr, Pb, Ni, Se and Zn), brake wear (Ag, As, Cd, Cu, Cr, Ni, Pb, Sb and Zn) and vehicular exhaust catalysts (VEC) (Pt, Pd and Rh)

(Hjortenkrans et al., 2006, 2007; Li et al., 2001; Ravindra et al., 2004; Whiteley and Murray, 2003; Wichmann et al., 2007; Winther and Slento, 2010; Zereini and Alt, 2006). In the last 25 years, a number of new metals have been incorporated into automotive technologies which are now being introduced into the environment as a result of vehicular movement. These include Sb in brake pads as a replacement for asbestos (Hjortenkrans et al., 2007), Mn in fuel as a replacement for Pb, and Pt group metals in VEC's to reduce air pollution (Morcelli et al., 2005; Rauch et al., 2005; Wichmann et al., 2007). These metal emissions accumulate in the urban environment over time (Sternbeck et al., 2002; Wong et al., 2006; Yassoglou et al., 1987) and show low levels of leaching (Radha et al., 1997). Thus, even once vehicle emissions stop (e.g. Pb in petrol), roadside soil concentrations and potential effects are likely to persist for a long period of time. Urban areas are highly populated and as a result contaminated urban soil will have potential effects on human health and ecological systems (Li et al., 2004).

Vehicular-emitted metals can be dispersed up to 100–200 m from roadsides, although the majority are deposited within 20 m of the road edge (Dan-Badjo et al., 2008; Trombulak and Frissell, 2000). Factors which tend to result in further metal dispersion include rain, wind and gravity (Trombulak and Frissell, 2000; Wong

\* Corresponding author. School of Civil, Environmental and Chemical Engineering, RMIT University, Melbourne 3001, Australia.

E-mail address: [shamali.desilva@rmit.edu.au](mailto:shamali.desilva@rmit.edu.au) (S. De Silva).

<sup>1</sup> Throughout this study use of the term 'metal' includes metals [such as Ag (silver), Cd (cadmium), Cu (copper), Cr (chromium), Mn (manganese), Mo (molybdenum), Ni (nickel), Pb (lead), Zn (zinc) and W (tungsten)], platinum group elements (PGE) [such as Pt (platinum), Rh (rhodium) and Pd (palladium)] as well as metalloids [such as As (arsenic) Sb (antimony) and Se (selenium)].

et al., 2006). The amount of metal accumulation in soil also depends on the topography, metal solubility, soil physical and chemical properties and horizontal and ventral distance from other roads (Wong et al., 2006; Yassoglou et al., 1987).

Roadside soils in cities are consistently found to contain elevated concentrations of Cd, Cu, Cr, Mn, Ni, Pb, Pd, Pt, Rh, Sb and Zn. Roadside metal deposition studies from around the world have demonstrated that significant quantities of metals are deposited from vehicle emissions e.g. Turkey-Istanbul (Sezgin et al., 2003), Germany (Alt et al., 1997), United Kingdom (Charlesworth et al., 2003), China (Chen et al., 2010; Lu and Bai, 2010), Nigeria (Li et al., 2001), Dubai UAE (Aslam et al., 2013), Korea (Duong and Lee, 2011). Some of the metal concentrations recorded were Cd (3.1 mg/kg) from Seoul (Chon et al., 1995); Cr (191 mg/kg) and Ni (209 mg/kg) from Torino (Biaoli et al., 2006); Cu (146.6 mg/kg) and Zn (516 mg/kg) from Hamburg (Lux, 1993); Mn (625.1 mg/kg) from Spain (Garcia and Millán, 1998); Pb (6292 mg/kg) from Caracas, Venezuela (Garcia-Miragaya et al., 1981); Sb (1.61 mg/kg) from Jeddah, Saudi Arabia (Kadi, 2009) and Pd (440 mg/kg) from Perth, Australia (Whiteley and Murray, 2003).

Some studies have found that the concentrations of vehicular emitted heavy metals in roadside soils can reach potentially toxic concentrations to roadside flora (Flanagan et al., 1980; Sharma et al., 2008) and fauna (Hamers et al., 2002; Muskett and Jones, 1980; Wade et al., 1980). Plant related studies have reported concentrations of Pb (863 mg/kg) and Cd (2.9 mg/kg) in plant material from the UK (Muskett and Jones, 1980); Ni (23.4 mg/kg), Cr (38.6 mg/kg), Cu (75 mg/kg), Mn (286 mg/kg), As (16.4 mg/kg), Sb (798.1 mg/kg), Sn (12.5 mg/kg) in plant material from Nigeria (Olajire and Ayodele, 1997); Zn (9169 mg/kg) from Australian plants; Se (9.96 mg/kg) from plants in Turkey (Hamurcu et al., 2010) and Rh, Pd, Pt (1.6, 10.4 and 8.94 mg/kg) respectively from roadside plants sampled in the UK (Hooda et al., 2007). Studies from the UK reported the highest concentrations of Pb (420.4 mg/kg), Cd (8.15 mg/kg) (Ash and Lee, 1980), and Cu (620 mg/kg) (Mariño et al., 1992) in earthworms. Also, concentrations of metals in mammals have been found to increase with proximity to roads (Hamers et al., 2002). Studies show that metals accumulate in the fatty tissues of animals, affecting the functions of organs, the nervous system and the endocrine system (Bocca et al., 2004). Lead, Zn and Cd levels in organ tissues confirm the accumulation of metals in metal sensitive organs (Johnson et al., 1978).

Most studies that have investigated the effects of traffic contribution to roadside metal pollution have concentrated on a few metals such as Cd, Cu, Pb and Zn. However, other metals are likely to be currently increasing in urban roadside soils e.g. Mn, Pt group metals and Sb. The possible relationships between road age (the time of exposure), the speed of vehicles and traffic density have not yet been studied. In addition, there have been few studies on roadside soil metal pollution and vehicular emissions in Australia. To the authors' best knowledge, the research presented here represents the first study to relate metal accumulation to road age effects and also the first Melbourne-based study to record vehicular emitted roadside metal pollution levels for a broad range of metals.

This study investigated transition metals (Ag, Cd, Co, Cr, Cu, Mn, Ni, Se, Sn, Pb, Zn and W), platinum group metals (Pd, Pt, Rh) and metalloids (As and Sb) loading in roadside soil with respect to traffic, age of roads (time of exposure), and the speed of vehicles.

## 2. Materials and methods

### 2.1. Selection of sites and sampling

Samples were collected in December 2012, from roadside soils on Newer Volcanic (basalt) geology (Price et al., 1997) in the west of

Melbourne, Australia. The choice of one underlying geology ensured soil derived from similar parent material to reduce variation due to intrinsic soil characteristics. All the chosen roads were constructed from the same surface material, i.e. asphalt roads (Woodall and Thakur, 2013).

Roadside sites were chosen to provide a range of road ages, traffic volumes and speed of vehicles. Road ages were selected in three categories: new (N, = 2–5 years old), medium (M, = 10–15 years old) and old (O,  $\geq 30$  years old). Traffic volumes were selected from three categories: low (L,  $\leq 5000$  vehicles/day), medium (M,  $\geq 5000$ –10,000 vehicles/day) and high (H,  $\geq 15,000$  vehicles/day). The speed of the roads were chosen in three categories: low speed 20–50 km/h, medium speed 50–80 km/h and high speed roads  $> 100$  km/h. Road ages, speed and traffic volumes for individual roads were determined using VIC Road Government department data and library collections, State Library of Victoria repository collections and Greater Melbourne street directories editions 1966 to 2012. Samplings for traffic and age characteristics as new age roads-low traffic (NL), new age roads-medium traffic (NM), new age roads-high traffic (NH), medium age roads-low traffic (ML), medium age-medium traffic (MM), medium age-high traffic (MH), old low traffic (OL), old age-medium traffic (OM) and old age-high traffic (OH) were repeated in triplicate; in total there were twenty seven roadside samples. In addition, three sites in parklands were chosen as control sites at locations  $> 0.5$  km away from roads and  $> 1$  km from industry. This gave a total of 30 soil samples.

Top soil (0–10 cm) (Hjortenkrans et al., 2008; Werkenthin et al., 2014), was collected within a 2–5 m distance from road edges using a clean stainless steel spatula and placed in zip-lock polythene bags (approximately 500 g). The immediate road edge up to 1 m was avoided to minimise the risk of sampling refilled or recently disturbed soil from road constructions and upgrades (Werkenthin et al., 2014). Samples were air dried and sieved using a 2 mm sieve. These samples were sealed in zip lock polythene bags and stored at ambient laboratory conditions ( $22 \pm 2$  °C) in the dark until analysed.

## 3. Analytical methods

### 3.1. Soil metal analysis

An aliquot (0.5 g) of each air dried and sieved soil sample was weighed into digestion tubes and 2.5 ml *aqua regia* (HNO<sub>3</sub>: HCl, 1:3) was added. The samples were digested at 105 °C for 2 h followed by the addition of 1 ml 30% H<sub>2</sub>O<sub>2</sub> (w/w). The digestion was continued for a further 15 min at 105 °C. When cooled to room temperature, the final volume was diluted to 50 ml using ultra pure Milli-Q ( $18 \text{ M}\Omega\text{cm}^{-1}$ ) water.

The acid digested extracts were filtered through nylon filter membranes of pore size 0.45  $\mu\text{m}$  and analysed for Ag, As, Cd, Co, Cr, Cu, Mo, Mn, Ni, Pb, Pd, Pt, Sb, Se, Sn Rh, Zn and W using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS: Agilent Technologies 7700 x Analyser). Metal concentrations exceeding 100  $\mu\text{g}/\text{kg}$  were measured using Atomic Absorption Spectrometry (AAS). Reagent blanks, replicates and certified reference materials (DO82-540, ERA) representing 10% of the total sample population were incorporated into the analysis to determine contamination, precision and bias of the analysis. The analytical results showed no signs of contamination and the accuracy was found to be consistently within 10% of the certified values.

Meteorological parameters contributing to metal dispersion and accumulation in roadside soil such as wind velocity, wind direction, rainfall/leaching, weathering, topology were not taken into account.

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