# Sources and transport pathways of common heavy metals to urban road surfaces

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## Highlights

- Source of Mn and Pb to urban atmosphere and roads: roadside soil disturbed by wind
- Sources of Cu, Cr and Zn to urban atmosphere and roads: traffic emissions
- Atmospheric deposition is the major pathway for Cu and Zn to road build-up
- Direct deposition is the major pathway for Cr, Mn and Pb to road build-up
- Traffic variables have similar influence on heavy metal transport pathways to roads

**Abstract**
Heavy metals that are built-up on urban impervious surfaces such as roads are transported to urban water resources through stormwater runoff. Therefore, it is essential to understand the predominant pathways of heavy metals to the build-up on roads in order to develop suitable pollution mitigation strategies to protect the receiving water environment. The study presented in this paper investigated the sources and transport pathways of manganese, lead, copper, zinc and chromium, which are heavy metals commonly present in urban road build-up. It was found that manganese and lead are contributed to road build-up primarily by direct deposition due to the re-suspension of roadside soil by wind turbulence, while traffic is the predominant source of copper, zinc and chromium to the atmosphere and road build-up. Atmospheric deposition is also the major transport pathway for copper and zinc, and for chromium, direct deposition by traffic sources is the predominant pathway.

**Keywords:** Atmospheric deposition; Heavy metals; Pollutant build-up; Stormwater pollutant processes; Stormwater quality

## 1. Introduction

Heavy metals, deposited on the urban impervious surfaces such as roads, are washed off to water sources during a rain event, causing adverse impacts on the receiving aquatic ecosystem (Gill et al. 2014; Ladislas et al. In Press; Wicke et al. 2012). Therefore, it is important to control heavy metal pollution of urban water sources (Borne et al. 2013), for which the knowledge of heavy metal transport pathways from the source of origin to the impervious surfaces is essential.

Heavy metals are primarily deposited on urban roads by vehicular traffic via two major pathways: (1) direct deposition; and (2) indirectly, where heavy metals are first emitted to the atmosphere and eventually deposited (Gunawardena et al. 2012). Heavy metals deposited on roads can be re-entrained to the atmosphere due to vehicular, natural and anthropogenic activities induced dust movements. This highlights the complexity of the interaction between pollutants in the atmosphere and road build-up.

Several studies have investigated heavy metal emissions to the urban atmosphere and build-up on urban impervious surfaces. For example, Gunawardena et al. (2012) found that traffic related emissions is the major source of zinc (Zn), copper (Cu) and chromium (Cr) to the urban atmosphere, while soil related sources are responsible for the accumulation of lead (Pb) and manganese (Mn). Similarly, Egodawatta et al. (2013) concluded that Mn and Pb are contributed to urban road build-up via geogenic sources, whereas traffic activities are the primary contributors of Zn and Cu.

However, very limited knowledge is available regarding the linkage between heavy metal accumulation in the atmosphere and build-up on urban roads and, specifically the transport pathways from the atmosphere to road build-up. Furthermore, the influence of traffic activities on heavy metal transport pathways has not been investigated in detail.

This paper presents the outcomes of a research study, which investigated: (1) the sources and transport pathways of common heavy metals from the urban atmosphere to road build-up; and (2) the influence of key traffic variables on heavy metal transport pathways. The study outcomes will contribute to overcoming current knowledge gaps constraining the development of effective strategies to mitigate urban water pollution.

## 2. Materials and methods

### 2.1 Sample collection and testing

Eleven road sites encompassing different traffic and land use characteristics were selected from the Gold Coast, Queensland, Australia, for the study (Fig. 1). Air sampling was conducted over a period of 8 h covering morning and evening traffic peaks, using the high volume polyurethane foam (PUF) sampler designed by USEPA as per Method TO-13A (USEPA, 1999). Road build-up samples were collected from 2.0 m x 1.5 m plot areas in the middle of a traffic lane using a wet and dry vacuuming system. A detailed discussion on air and build-up sampling protocols adopted can be found in Gunawardena et al. (2012) and Herngren et al. (2006), respectively.

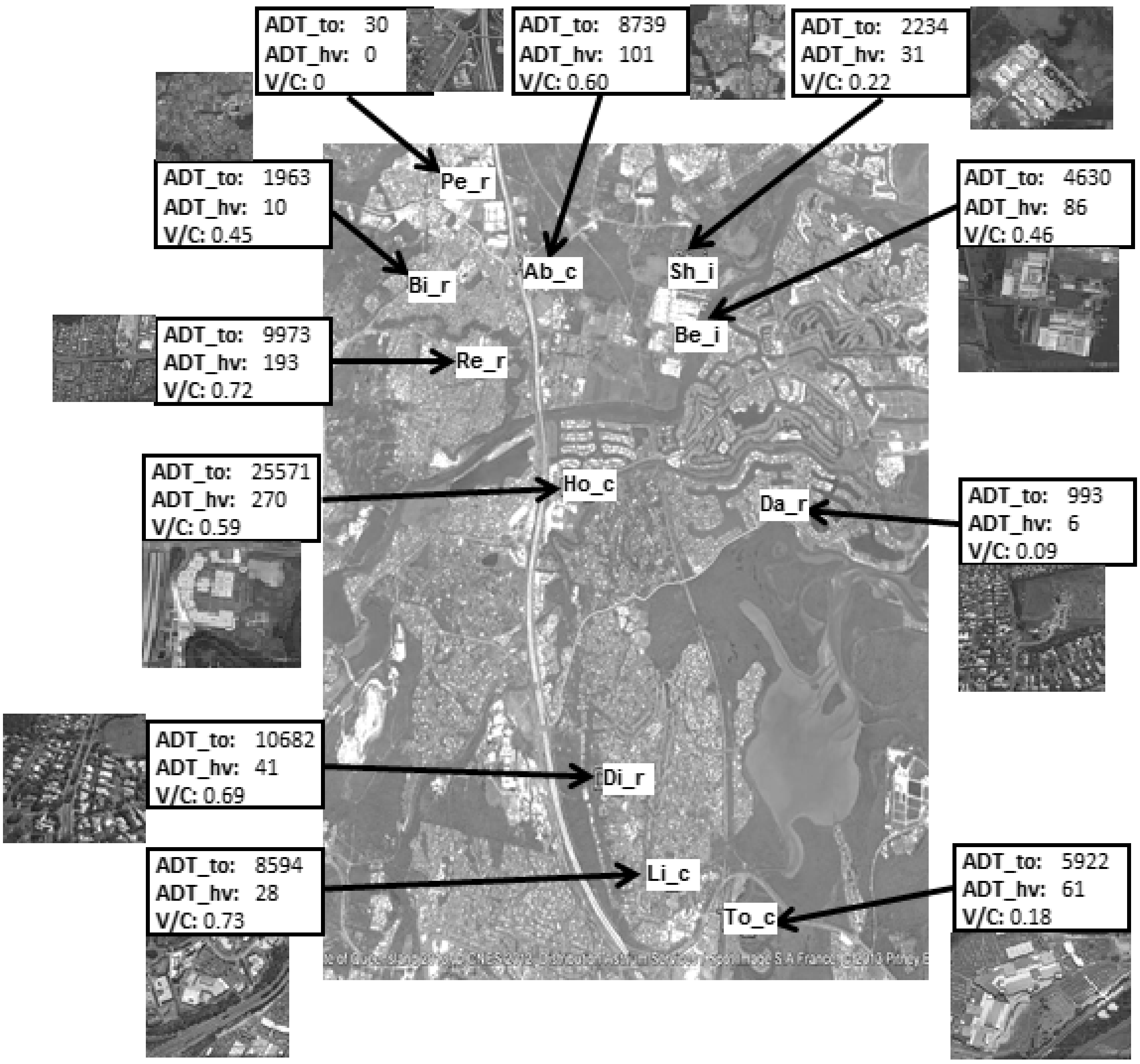



**Fig. 1:** Study sites (Legend: ADT_to - Annual average daily traffic volume; V/C - Volume to capacity ratio; ADT_hv - Total heavy traffic volume; r – residential site; c – commercial site; i – industrial site) (Adapted from Gunawardena et al. 2014b)

The study investigated Cr, Cu, Pb, Zn and Mn, which are common heavy metals present in the urban environment. The laboratory analyses were undertaken according to Method 200.8 for inductively coupled plasma-mass spectroscopy (US-EPA, 1994) with TraceSELECT (Product No. 54704) as the certified reference material.

## 2.2 Data analysis

As traffic volume, congestion and vehicle mix have been found to exert influence on heavy metal build-up (EPASGV, 1999), annual average daily traffic volume (ADT_to), volume to capacity ratio (V/C) and total heavy traffic volume (ADT_hv) were used as surrogates, respectively. Volume to capacity ratio (V/C) is the ratio between the actual volume of traffic and the theoretical traffic capacity of a road. Hence, a V/C ratio above 1.0 suggests that the road capacity is exceeded and the road is congested.

Data analysis was conducted using factor analysis and multi-criteria decision making methods, Preference Ranking Organization Method for Enrichment Evaluation (PROMETHEE) and Geometric Analysis for Interactive Aid (GAIA). Factor analysis was performed using StatistiXL software (v. 1.8, 2008, StatistiXL, Broadway–Nedlands, Australia). The factors were extracted from the raw data matrix, consisting of metal build-up loads and atmospheric metal concentration (Table 1), using principal component extraction method based on the initial eigenvalue criteria ≥ 1. The factor rotation was performed using the orthogonal VARIMAX rotation technique to simplify the interpretation of a complex data set by making each variable to primarily associate with a specific factor (Abdi 2003; Egodawatta et al. 2013).

**Table 1: Data matrix used in the study**

| Site ID | Build-up Metal Loads ($mg/100m^2$) | | | | | Atmospheric Concentration ($\mu g/m^3$) | | | | | Traffic Variables | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Mn | Cu | Zn | Pb | Cr | Mn | Cu | Zn | Pb | ADT_to | ADT_hv | V/C |
| Di_r | 2.17 | 7.20 | 83.4 | 222 | 41.7 | ND | 0.002 | ND | 0.001 | 0.001 | 10682 | 41 | 0.69 |
| Ab_c | 2.38 | 26.5 | 102 | 233 | 33.0 | 0.001 | 0.110 | 0.003 | 0.205 | 0.008 | 8739 | 101 | 0.60 |
| Re_r | 19.5 | 43.2 | 157 | 256 | 16.2 | ND | 0.036 | 0.002 | 0.116 | 0.022 | 9973 | 193 | 0.72 |
| Be_i | 1.11 | 6.99 | 90 | 158 | 32.0 | ND | 0.007 | 0.001 | 0.118 | 0.021 | 4630 | 86 | 0.46 |
| Ho_c | 2.75 | 48.2 | 119 | 247 | 30.3 | 0.034 | 0.022 | 0.001 | 0.076 | 0.007 | 25571 | 270 | 0.59 |
| Bi_r | 0.86 | 39.9 | 143 | 351 | 42.0 | 0.022 | 0.033 | 0.014 | 0.155 | 0.031 | 1963 | 10 | 0.45 |
| Li_c | 2.74 | 5.47 | 216 | 209 | 63.7 | 0.086 | 0.031 | 0.022 | 0.320 | 0.059 | 8594 | 28 | 0.73 |
| To_c | 1.15 | 3.52 | 77.3 | 141 | 33.4 | 0.024 | 0.381 | 0.013 | 0.210 | 0.129 | 5922 | 61 | 0.18 |
| Da_r | 2.90 | 190 | 118 | 177 | 69.3 | 0.025 | 0.028 | 0.014 | 0.110 | 0.043 | 993 | 6 | 0.09 |
| Pe_r | ND | 10.6 | 75.0 | 107 | 12.5 | ND | 0.002 | ND | 0.001 | 0.001 | 30 | 0 | 0.00 |
| Sh_i | 1.38 | 39.8 | 245 | 317 | 82.9 | 0.000 | 0.007 | 0.001 | 0.118 | 0.021 | 2234 | 31 | 0.22 |

Notes: ND: not detected; The raw data was partially obtained from Gunawardena et al. 2014b.

PROMETHEE and GAIA analysis was undertaken using Visual PROMETHEE software to complement the factor analysis outcomes. A detailed description of these methods can be found in Behzadian et al. (2010). In the GAIA biplot, two variables are considered positively correlated if their corresponding vectors form an acute angle, negatively correlated if they form an obtuse angle and uncorrelated if they are orthogonal as per the interpretation rules outlined by Espinasse et al. (1997).

PROMETHEE was used as a data pre-treatment method prior to GAIA analysis. The data matrix used consisted of 13 variables (build-up metal loads, atmospheric metal concentrations and traffic parameters) and 11 objects (study sites) as shown in Table 1. The PROMETHEE algorithm requires the definition of three modelling parameters, namely a ranking sense, weighting and specific preference function, for each variable. For the ranking sense, the 'maximum' option was chosen for each variable in order to identify transport pathways that lead to high heavy metal pollution on urban roads. The weight was selected as 1 to ensure all variables have equal significance in the analysis. The V-shaped preference function was selected since this has been found to be applicable for environmental analysis (Gunawardena et al. 2012).

# 3. Results and discussions

## 3.1 Factor dnalysis

Outcomes of the factor analysis are presented in Table 2. Only factor loadings > 0.5 are presented since < 0.5 is not considered significant (Harrison et al. 2003; Gunawardena et al. 2014a). The communality, which is analogous to the coefficient of determination in regression analysis, is generally greater than 0.6 and the mean communality is greater than 0.7 suggesting that the factor analysis outcomes are reliable (Egodawatta et al. 2013).

**Table 2: VARIMAX rotated factor loadings for atmospheric and road build-up**

| [a]Metals | Factor1 | Factor2 | Factor3 | Communalities |
|---|---|---|---|---|
| Cr-A | 0.95 | | | 0.90 |
| Mn-A | | 0.59 | 0.53 | 0.64 |
| Cu-A | 0.93 | | | 0.93 |
| Zn-A | 0.80 | | | 0.78 |
| Pb-A | | 0.83 | | 0.76 |
| Cr-B | | -0.63 | | 0.52 |
| Mn-B | | | -0.78 | 0.60 |
| Cu-B | 0.87 | | | 0.94 |
| Zn-B | | -0.73 | | 0.72 |
| Pb-B | 0.81 | | | 0.91 |

[a]A and B stand for atmosphere and road build-up, respectively.

Cr, Cu and Zn in the atmosphere (Cr-A, Cu-A and Zn-A) and Cu and Pb in road build-up (Cu-B and Pb-B) have positive loadings on Factor 1, which corresponds to traffic emissions since these heavy metals are generally associated with traffic activities (Gunawardena et al. 2014a). Pb-B having a positive loading indicates that it is influenced by traffic activities, though leaded fuel has been phased out in Australia over a decade ago. Therefore, the positive loading is primarily attributed to the re-suspension of Pb from past emissions from fuel combustion deposited in soil and its disturbance by traffic activities. However, Friend et al. (2011) have shown that there is still some contribution of Pb to the atmosphere, which may not have originated from re-suspension of soil particles. Additionally, both Cu-A and Cu-B are associated with the same factor suggesting a close relationship between atmospheric and build-up loads. Therefore, factors influencing Cu concentration in the atmosphere and build-up would be the same.

In the case of Factor 2, atmospheric Mn and Pb have positive loadings, while build-up Cr and Zn have negative loadings indicating that the sources contributing Mn and Pb to the atmosphere are different to those of Cr and Zn to road build-up. Since traffic activities are considered as the predominant source of Cr and Zn to road build-up, it can be concluded that traffic is not a primary source of Mn and Pb in the atmosphere. Consequently, it can be further concluded that Mn and Pb are contributed to the atmosphere by the surrounding soil disturbed by natural and traffic induced turbulence. The negative association of Mn-A and Pb-A with Cr-B and Zn-B could be due to traffic induced re-distribution of road deposited metals, where it influences atmospheric Mn and Pb, while negatively influencing road surface build-up of Cr and Zn.

In case of Factor 3, Mn-A has a positive loading, while Mn-B has a negative loading. This suggests that atmospheric deposition is not a major transport pathway, confirming that direct soil inputs are the predominant pathway of Mn to road build-up.

### 3.2 PROMETHEE and GAIA analysis

Though factor analysis identified the transport pathways of some heavy metals, it was not clear for the rest of the heavy metals investigated. Hence, PROMETHEE and GAIA analysis was performed to further investigate the transport pathways of heavy metals to road build-up and to complement the factor analysis outcomes. Fig. 2 (a) shows the relative positions of study sites in a GAIA plot. As evident from the figure, a clear pattern could not be distinguished according to the land use characteristics. This suggests that land use has limited influence on pollutant deposition pathways.

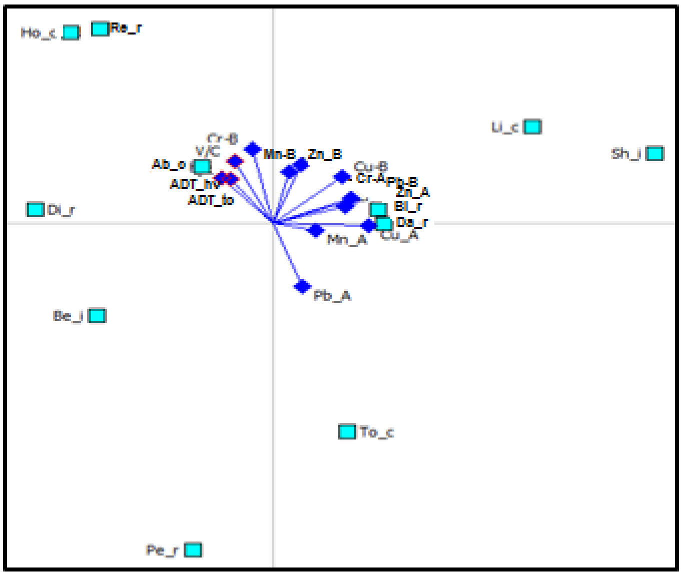
Accordingly, the study sites were removed from the GAIA plot in order to improve the clarity of the relationship among the variables as shown in Fig. 2 (b). As evident from Fig. 2 (b), the vectors corresponding to Cr, Mn and Zn in build-up have a strong correlation with traffic variables suggesting that traffic is a major factor influencing build-up. This further supports the argument that Cr and Zn are contributed to road build-up by traffic sources (Section 3.1). Furthermore, turbulence induced by traffic activities will result in the movement of soil, which is a major source of Mn to road build-up. Therefore, it could be concluded that traffic characteristics play a key role in influencing heavy metal build-up.

Pb in build-up is independent of traffic suggesting that the present traffic activities do not have a significant impact. Therefore, it is hypothesized that Pb contributed to soil from past traffic activities reaches road build-up with the disturbance of soil due to traffic induced turbulence. However, as shown by Friend et al. (2011), there could be some contribution of Pb to atmosphere, which may not originate from soil (Section 3.1).

The vectors corresponding to Cr build-up and atmospheric Cr have a weak correlation suggesting that the contribution to build-up from atmospheric deposition is very limited compared to the direct deposition of Cr due to traffic activities. This is because relatively lower solubility of Cr can hinder wet deposition, which generally brings down a larger quantity of heavy metals compared to dry deposition (Morselli et al. 2003). Dry deposition is likely to be the predominant deposition pathway of Cr since the relatively larger diameter of Cr can facilitate this phenomenon (Samara and Voutsa, 2005).

In contrast, vectors corresponding to Mn and Pb in the atmosphere and road build-up are at right angles suggesting that atmospheric deposition is not a predominant pathway to road build-up. This is attributed to the predominance of direct deposition of Mn and Pb on the roads from soil (Section 3.1). Additionally, Gunawardena et al. (2013) have noted that Pb is associated with relatively smaller particles, facilitating the suspension of Pb in the atmosphere for a longer time period. This can be another reason for limited contribution of atmospheric deposition to Pb build-up.

**(a)**




**(b)**

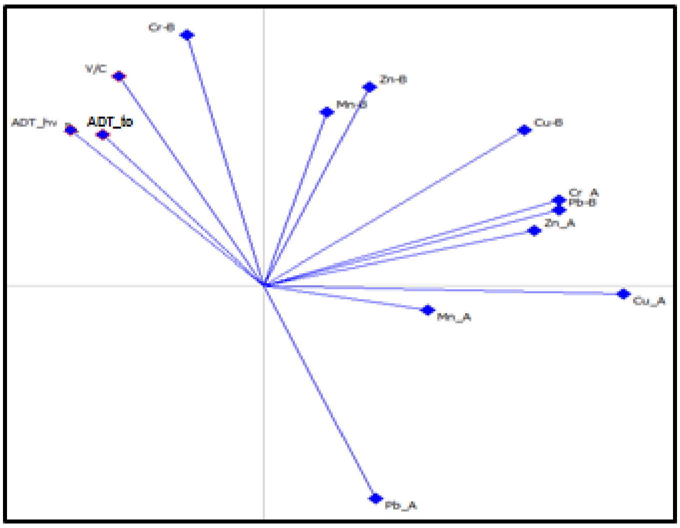



**Fig. 2:** GAIA biplots: (a) Original biplot and (b) Biplot after removing the study sites to improve clarity (Legend: Total traffic volume - ADT_to; Total heavy duty traffic volume – ADT_hv; Congestion – V/C; Subscripts B and A correspond to build-up and atmosphere, respectively)

Cu and Zn show a strong correlation between their respective vectors corresponding to build-up loads and atmospheric concentrations indicating that atmospheric deposition is a major pathway to road build-up. Zn is associated with larger particles in the atmosphere (Gunawardena et al. 2013) facilitating its dry deposition on road surfaces. Similarly, as Cu has a relatively larger diameter (Samara and Voutsa 2005), it is expected to have a relatively high dry deposition rate. Additionally, Zn and Cu are highly soluble in water (Morselli et al. 2003) leading to the deposition of higher quantities on roads via wet deposition. Therefore, it can be hypothesized that atmospheric deposition is a primary transport pathway of Zn and Cu to road surfaces. Furthermore, the vectors corresponding to traffic variables, namely ADT_to, ADT_hv and V/C, have strong correlations with each other suggesting that the influence of traffic variables on heavy metal transport pathways are similar.

## 4. Conclusions

The primary conclusions derived from this study are:

- Mn and Pb are contributed to road build-up and the atmosphere by the roadside soil disturbed by natural and traffic induced wind. Direct deposition is the major pathway of Mn and Pb to the roads compared to atmospheric deposition.
- Cu and Zn are predominantly contributed to the atmosphere and road build-up by traffic emissions. The major pathway to road build-up is atmospheric deposition.
- Traffic sources are the primary contributor of Cr to the atmosphere and road build-up. Though atmospheric deposition is a pathway of Cr to road build-up, it is not the primary source compared to direct deposition.
- Traffic volume, vehicle mix and congestion exert similar influence on heavy metal transport pathways.

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