Transformation processes of metals associated with urban road dust: A Critical Review

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\textbf{Shortened version of the title:} Transformation processes of metals in road dust
Abstract

The fate of metals in stormwater is primarily influenced by the transformation processes that they undergo during build-up on impervious surfaces. These processes result in changes to the bioavailability, mobility, toxicity and persistence levels of metals which can significantly influence stormwater quality. Accordingly, this paper critically evaluates the transformation processes of metals accumulated on road surfaces, namely, adsorption, surface precipitation and oxidation-reduction, and their likely influence on stormwater quality to highlight the key knowledge gaps, and to identify future research needs. Based on the review outcomes, transformation processes of metals are found to be influenced by the fine particle size of road dust, predominantly <150 µm and physio-chemical properties of solids and environmental factors. The review identified knowledge gaps where further research is needed such as in relation to: mobilisation of metal-nitrogen complexes and their impact on stormwater quality, surface precipitation of metals on road dust, conditions favourable for changes in the redox status of road dust, time-dependent transformation characteristics of metals on road surfaces and enhancement of risk assessments by taking into consideration the bioavailability of metals. Research in these areas would benefit decision makers in evaluating the potential environmental risk and for implementing effective stormwater pollution mitigation strategies.

Key words: Surface complexation; Stormwater quality; Stormwater pollutant processes

1. Introduction

Stormwater runoff from urban areas is recognised as a major non-point source of pollution to receiving water environments (Jacobson, 2011). The majority of pollutants transported by stormwater runoff (wash-off) are accumulated (built-up) on impervious surfaces such as roads during dry weather periods as a result of both, natural and anthropogenic activities. Once pollutants are accumulated, their physical and chemical forms undergo dynamic changes (transformations) before being incorporated into stormwater runoff (Gunawardana et al., 2015; Jayarathne et al., 2018b; Sutherland et al., 2012). As a result, their impacts on stormwater quality would be different when compared to the originally deposited pollutants. To safeguard urban water environments, stormwater pollution mitigation strategies need to be designed by understanding the characteristic changes to pollutants.

Metals, one of the key pollutants ubiquitous in urban areas, are particularly important in terms of stormwater quality management due to their potential ecological and human health impacts. Unlike organic contaminants, metals are not biodegradable in nature. Therefore, elevated concentrations of metals in receiving water bodies can cause toxic impacts on aquatic organisms (Tao et al., 2012; Zhao et al., 2012), while the ingestion, inhalation and/or dermal contact of metal contaminated dust particles or stormwater can result in either short or long term human health issues (Ali et al., 2017; Keshavarzi et al., 2015; Li et al., 2017; Ma et al., 2016). The bioavailability, mobility, toxicity and persistence characteristics of metals in the environment are primarily dependent on their physico-chemical forms. For example, free metal ions and weakly bound metals are relatively more toxic and bioavailable compared to complexed or firmly bound metals (Murakami et al., 2009; Violante et al., 2010). This
highlights the importance of understanding the behavioural changes of metals attached to solids in order to predict their environmental fate and consequent water quality impacts. Numerous research studies have been conducted and a significant knowledge base exists in relation to the behaviour of metals associated with various particulate matter such as agricultural soils (Cai et al., 2012; Qiutong and Mingkui, 2017) and freshwater and marine sediments (Horvath et al., 2010; Nemati et al., 2011; Palleiro et al., 2016; Passos et al., 2010). However, only limited studies have been carried out to investigate the physical and chemical transformation processes of metals associated with road dust and their potential stormwater quality impacts. Accordingly, the primary objective of this review was to undertake a critical evaluation of the current-state-of-the-art-knowledge and to identify the key knowledge gaps that exist and future research directions in relation to the transformations of road deposited metals. This review only focuses on the physical and chemical transformation processes.

2. Transformation processes of metals

Metals accumulated on road surfaces are intrinsically associated with a heterogeneous mix of organic and inorganic particulates, which is generally referred to as road dust or road deposited solids (RDS). During dry weather periods, road dust and associated metals are subjected to dynamic processes such as redistribution and resuspension due to vehicular traffic and wind-related turbulence (Abraham et al., 2018; Amato et al., 2013; Patra et al., 2008). At the same time, metals are subjected to different transformation processes, changing their physico-chemical behaviour over dry weather periods. These processes can be complex due to the dynamic nature of changes to influential factors associated with road surfaces. According to past research studies, the key processes governing the changes to the original physical and chemical form of metals are adsorption, surface precipitation and oxidation-reduction (Akpomie et al., 2015; Bradl, 2004; Demirbas, 2008; Ritter, 2002).

2.1. Adsorption mechanism

The primary chemical transformation process that determines the inter-molecular interaction of freely available metals with solids is adsorption (Sposito, 2008; Toth, 2002). As given in Table 1, different reactive groups attached to solid constituents such as organic matter, metal oxides, carbonates and clay minerals (adsorbent) create distributed charge characteristics, influencing the interaction of metal ions.

The interaction of free metal ions to solids results in the formation of electrostatically charged layers (i.e. Stern and diffuse layers) and stable molecular units that are called ‘surface complexes’ around the solid surface (Chen et al., 2013; Harrison, 2007). The formation of positively charged Stern layer due to the attraction of cations to a negatively charged solid surface leading to the creation of surface complexes is illustrated in Figure. 1. Depending on the interaction force involved and the availability of water molecules, metal-surface complexes can be categorised as outer and inner sphere (Harrison, 2007; Huang et al., 2011; Sparks, 2003). Metals that are accumulated on road surfaces can also undergo different surface complexation processes depending on the availability of surface charge sites on different solid constituents.

Ion-exchange and chemisorption are the primary transformation processes in relation to outer-sphere and inner-sphere surface complexation of metals. Past researchers have pointed out that ion-exchange of metals is neither a bond nor an adsorption process (Farquhar et al., 1997). However, in research literature, it is referred to as a nonspecific adsorption or an electrostatic
sorption process which involves weak bonds associated with outer sphere complexation (Bradl, 2004; Inglezakis and Poulopoulos, 2006; Polcaro et al., 2003).

Table 1. Reactive surface functional groups present in common adsorbents (Data from Chorover and Brusseau, 2008 with permission from publisher).

| Adsorbent type                        | Surface functional group/ Reactive sites                  |
|---------------------------------------|----------------------------------------------------------|
| Organic matter                        | Phenolic hydroxyls                                       |
|                                       | Carboxylic                                               |
|                                       | Carbonyl                                                 |
|                                       | Sulphydryl                                               |
|                                       | Aromatic compounds                                       |
|                                       | Aliphatic compounds                                      |
|                                       | Phosphoryl                                               |
| Oxides and Hydroxides (e.g. Al₂O₃, FeOOH) | Surface hydroxyl group                                   |
| Metal carbonates (e.g. calcite, dolomite) | Surface hydroxyls group                                 |
|                                       | Surface metal                                            |
|                                       | Surface carbonate                                        |
| Layer silicates (e.g. clays)           | Siloxane ditrigonal cavity                               |
|                                       | Exchangeable metals                                      |
|                                       | Edge surface hydroxyls                                   |

Figure 1. (a) Formation of the electrostatic layers around a negatively charged solid particle (Adapted from Chen et al., 2013 with permission from publisher); (b) formation of adsorption complexes of metals (Adapted from Chorover and Brusseau, 2008 with permission from publisher).
2.1.1. Ion-exchange of metals

Ion-exchange is a phenomenon that results from the exchange of freely available metal ions with the originally attached ions to the solid surface according to a stoichiometric replacement process (Bleam, 2011; Huang et al., 2011). This means that metals are not subjected to any chemical transformation, but are physically attached to solids by electrostatic interactions. Such reactions can occur at both, permanent and variable charge sites on clay minerals, organic matter and metal oxides (Roberts et al., 2005; Zhuang and Yu, 2002). In terms of chemical properties, metals with higher ionic charge and small hydrated radius (usually called the hydration sphere) have a significant tendency to undergo ion-exchange reactions due to their high charge densities (Bleam, 2011).

Metals that undergo ion-exchange transformations are likely to be more mobile and bioavailable as they are weakly bound to the solid surfaces. This can result in variability in particle-bound metal mobility during both, build-up on urban surfaces during dry weather periods and wash-off by stormwater runoff. The mobility sequences of metals in relation to different geochemical binding forms of road dust have been reported in previous studies. Metals associated with the exchangeable (ion-exchange), reducible (metal-oxide bound), oxidisable (organically bound) and residual (metals incorporated within the lattice structure of minerals) forms have been found to be in the mobility order of Cd > Zn > Pb > Cu (Li et al., 2001), Cd > Zn > Pb > Cu > Ni (Duong and Lee, 2009), Zn > Pb > Cd > Cu > Mn > Co > Ni > Cr > Fe (Zhang and Wang, 2009), Cd > Mn > Zn > Cu > Ni > Pb > Cr > Co (Ozcan and Altundag, 2013) and Cd > Zn > Cu > Pb > Mn > Ni > Cr (Jayarathe et al., 2017). Metals, which specifically undergo ion-exchange transformations are found at the beginning of mobility sequences. Accordingly, metals such as Cd and Zn can significantly influence the quality of stormwater and consequently the receiving water environments due to their high mobility characteristics. The high potential for desorption of Cd and Zn can be attributed to the electronic configuration of Cd$^{2+}$ [4d$^{10}$ 5s$^{0}$] and Zn$^{2+}$ [3d$^{10}$ 4s$^{0}$]. The outer orbit of these metals are completely filled (i.e. have d$^{10}$ configurations). Therefore, they do not form strong bonds with surface functional groups on solids (Gunawardana et al., 2013; Zhang et al., 2016).

Conventional stormwater pollution mitigation strategies commonly aim to remove the solids load from stormwater runoff, ensuring the removal of pollutants associated with solids. However, this may not ensure the removal of pollutants in the mobile (exchangeable) fraction. The readily available (bioavailable) nature of exchangeable metals in stormwater runoff can impose toxic impacts on aquatic environments and human health. This highlights the significance of understanding the role of ion-exchange of metals associated with road dust and their environmental fate over time in order to implement robust stormwater mitigation measures, targeting the readily available metal species. Additionally, risk assessment approaches need to be refined such that the potential risk from metals are specifically evaluated based on their mobility and bioavailability characteristics. This is particularly important for decision makers in evaluating accurate environmental risk, regulating stormwater harvesting and managing the safe use of stormwater. However, as pointed out by Jayarathe et al. (2018), in most risk assessment studies, the risk posed by metals is either overestimated or underestimated without considering their mobility and bioavailability, which is directly linked to the geochemical binding forms of metals, highlighting the importance of further research on geochemical characteristics of metals in stormwater quality analysis.
Other than ion-exchange, metals such as Cu and Zn complex with ligand containing nitrogen to form metal-nitrogen complexes (Ghasemi et al., 2013; Uchimiya et al., 2011). The nitrogen complexes are generally soluble or can be converted to soluble forms due to changes to chemical parameters such as pH (Ziyath et al., 2016). As such, this can potentially increase the mobility and bioavailability of complexed metals in stormwater runoff. The presence of different nitrogen species on urban road surfaces and related stormwater quality impacts have been reported in research literature (Kleinman et al., 2006; Miguntanna et al., 2010; Vaze and Chiew, 2002). However, the interaction of different nitrogen species with metal ions that leads to the formation of metal-nitrogen complexes and their impact on stormwater quality has not been adequately reported. This is particularly important as both, metals and nutrients can potentially impose significant human and ecosystem health risks.

2.1.2. Chemisorption of metals

Metals can be chemically transformed into new phases by exchanging electrons between ions and surface functional groups in solids. This results in the formation of inner-sphere complexes, which is often referred to as ‘chemisorption’ (Inglezakis and Poulopoulos, 2006). Chemisorbed metals are firmly attached to solid particles as the transformation mechanism necessarily involves ionic or covalent bonds (Huang et al., 2011; Sposito, 2008; Worch, 2012). Therefore, such metals are found to be characteristically enriched in the geochemical fractions of either reducible or oxidisable form of road dust (Jayarathne et al., 2017; Świetlik et al., 2015). Gunawardana et al. (2015) further reported that the primary mechanism of Cu, Pb, Cr and Ni adsorption to organic matter and metal oxides associated with road dust is chemisorption, while ion-exchange would be the secondary mechanism. This implies that the variability in transformation processes of metals and their environmental fate are strongly related to their geochemical characteristics.

Unlike ion-exchange, chemisorbed metals have limited opportunities for desorption and become bioavailable as they are in the form of stable inner-sphere complexes. As such, the potentially toxic impacts of exchangeable metals and their bioavailability characteristics can be reduced by increasing the chemisorption ability of metals to solids. However, the mechanisms or processes enhancing the chemisorption properties of metals in stormwater runoff have not received adequate research attention in the context of stormwater treatment. Chemisorption reactions are strongly pH dependent and often occur under low metal concentrations (Cerqueira et al., 2011). However, the variation in chemical conditions over time can desorb chemisorbed metals and later release into the environment, enhancing their bioavailability and toxicity (Charlesworth et al., 2003; Maniquiz-Redillas and Kim, 2014). Consequently, retaining solid particles on road surfaces during dry weather periods or in stormwater for an extended period would cause changes in the bioavailability of chemisorbed metal ions. Therefore, stormwater remediation measures should be implemented by understanding the fate of chemisorbed metals under influential parameters. This highlights the fact that there is an urgent need for further investigations to monitor the long-term behaviour of metals associated with road dust and stormwater. Additionally, research is required to evaluate the practicality of treating stormwater at different physico-chemical conditions such as pH and redox conditions. However, beyond laboratory monitoring, future research should explore in order to understand the behaviour of metals under real environmental conditions.
2.2. Metal precipitation

Metals can also chemically transform into a new solid phase as a result of reactions with anionic chemical agents such as PO$_4^{3-}$ and CO$_3^{2-}$ or due to the removal of OH groups in the solid complexes (Rieuwerts et al., 1998; Scheidegger and Sparks, 1996). However, precipitation becomes dominant when the metal ion loading reaches a threshold, followed by adsorption (Figure 2). This essentially occurs only under high pH and high anionic/cationic concentrations. Under such conditions, common metals that transform to precipitates are Zn(OH)$_2$, Pb$_3$(PO$_4$)$_2$, Pb(OH)$_2$, NiCO$_3$, Cu(OH)$_2$, CuCO$_3$, Ca$_3$(PO$_4$)$_2$, CaCO$_3$, FeOH$_3$ and FePO$_4$ (Djukić et al., 2016).

![Figure 2. Representation of adsorption and surface precipitation as a function of metal concentration.](image)

In relation to metal transformation on road surfaces, surface precipitation is not necessarily a prominent process compared to ion exchange and chemisorption as metal ion concentration in road dust is relatively low. However, variability in dust build-up provides opportunities for forming concentration pockets of metals, which can lead to the formation of metal precipitates. Djukić et al. (2016) attributed surface precipitation as a possible mechanism of interaction between metal ions and solid particles in stormwater runoff over the adsorption process. The absence of a highly developed internal pore system and high specific surface area is less likely to be responsible for adsorption of metals to road dust particles. However, further investigations are needed to confirm whether surface precipitation is a key process that governs metal transformations on road surfaces under both, dry and wet weather conditions. Moreover, further research should be carried out to identify the favourable conditions for metal precipitation on urban roads. Based on the findings of such research, stormwater treatment design guidelines can be developed to reduce the potential risk of toxic metals in stormwater runoff. For example, favourable pH conditions and chemical agents that influence precipitation can be applied as an effective stormwater treatment measure to reduce the metal ion concentration in runoff. As precipitated metals generally have low water solubility (Sparks, 2003), the mobility and bioavailability of metals in stormwater runoff would decrease compared to their original form.
On the other hand, the presence of metal precipitated products would also induce the transformation of other metal ions. Common metals such as Cu, Ni, Cr, Pb, Cd and Zn undergo complexation or chemisorption with carbonates or metal oxides/hydroxides, which have surface functional groups for adsorption (Maiz et al., 2000; Stead-Dexter and Ward, 2004; Sutherland et al., 2012). Complexed or chemisorbed metals with oxides are less like to be mobile and bioavailable due to their strong interaction. In this context, surface precipitation can be identified as an important chemical process that can reduce metal ion concentrations as well as facilitating the transformation of other pollutants. However, the current state-of-the-art knowledge of surface precipitation of metals associated with road dust and its influence on mobility and bioavailability needs to be significantly improved for achieving enhanced outcomes in stormwater treatment.

2.3. Oxidation-Reduction of metals
Metals are chemically transformed through oxidation and reduction reactions by the loss or gain of electrons from their valence shells. The adsorption characteristics, bioavailability and toxicity of metals are influenced by the oxidation state that metal ions exist. For example, Cr (3+) can be oxidised to Cr (6+), which is known to cause significant health problems, including creating cancer risk. Although Cr (3+) undergoes chemisorption reactions with organic matter, the chemisorption ability of Cr (6+) is relatively low (Violante et al., 2010). As such, the bioavailability and mobility of Cr (6+) is significantly high compared to Cr (3+). Similarly, arsenic exists in the forms of +5, +3, 0, and -3 oxidation states, where As (3+) and As (3’) are more bioavailable and toxic than As (5+) (Mohan and Pittman Jr, 2007). Consequently, metals can be transformed into different oxidation states, either decreasing or enhancing their bioavailability and toxicity. As such, the formation of favourable oxidising and/or reducing conditions due to the changes in aerobic and anaerobic conditions on road surfaces can generate oxidised or reduced metal species with different environmental fate. However, unlike in natural soils or sediments (Du Laing et al., 2009; Zhang et al., 2014), the conditions favourable for changes in the redox status of road dust and factors affecting such processes have not been widely investigated. This is particularly important in terms of stormwater treatment, where favourable oxidising and/or reducing conditions can be applied to minimise the potential toxic impact of metals in stormwater runoff by transforming them into less toxic or bioavailable forms.

The formation of different oxidation/reduction products of metals such as Mn and Fe could also significantly influence the transformation of other metals. Mn undergoes three common oxidation states; 2+, 3+ and 4+. Among them, Mn (3+) and Mn (4+) are considered as stable oxidation products and are in the form of oxides and hydroxides such as MnO₂, MnOOH, and Mn₃O₄. In addition, Fe (+2) oxidises to Fe (+3), forming less soluble ion precipitates such as Fe₂O₃ and FeOOH. The presence of Fe-Mn oxides/hydroxides in solids facilitates the oxidation or reduction of other metal ions such as Cr³⁺, Co²⁺, Co³⁺, Cu²⁺, Ni²⁺, Ni³⁺, and Pb²⁺ (McBride, 1994; Sparks, 2003). The difference in bioavailability characteristics of oxidised or reduced metals can cause potentially harmful human and ecosystem health impacts when washed-off by stormwater runoff.

2.4. Time-dependent metal transformation
Residence time is one of the key parameters that determines the environmental fate of metals (Jalali and Khanlari, 2008; Lim et al., 2002). The influence of residence time on metal behaviour is mainly attributed to the differences in their transformation processes,
predominantly adsorption. Metals can be subjected to different adsorption mechanisms, forming either weak or strong complexes depending on the nature of interaction force involved or competition for surface functional groups. However, with the increase in residence time, they can desorb and subsequently re-adsorb by a different complexation process, resulting in changes to the chemical behaviour of metals. Consequently, metals could have different mobility, bioavailability and toxicity characteristics with increasing residence time.

The weakly bound metals in solids favourably transform into more stable chemical forms with increasing residence time. According to Lu et al. (2005), the exchangeable form of Zn, Cu, Pb and Cd added to soils increase in the first three hours and then slowly transform into the oxide and organically bound forms. A similar transformation characteristic has been reported by Jalali and Khanlari (2008) (Table 2). This indicates that the affinity of metals for solids is very rapid during the initial period of adsorption, followed by the gradual transformation from weak to relatively stable adsorption complexes. As such, the mobility and bioavailability of metals can reduce compared to their original form.

Table 2. Time dependent distribution of metals in different geochemical fraction for three types of soils (Data from Jalali and Khanlari, 2008 with permission from publisher).

| Metal | Time | Soil type 1 (Bahar soil) | Soil type 2 (Azandarian soil) | Soil type 3 (Kaboudar ahang soil) |
|-------|------|--------------------------|------------------------------|----------------------------------|
|       |      | EXC | MNO | FEO | OM | EXC | MNO | FEO | OM | EXC | MNO | FEO | OM |
| Pb    |      |    |     |     |    |     |     |     |    |     |     |     |    |
| C     | 0.9  | 2.7 | 2.5 | 7.8 | 2.8 | 4.3 | 2.9 | 9.7 | 3.4 | 4.3 | 21  | 7.6 |
| 3h    | 166  | 158.5 | 56  | 69  | 187 | 148 | 54  | 42  | 71.5 | 24.5 | 306 | 94.5 |
| 3day  | 105.5 | 161.5 | 81  | 85.5 | 132 | 163 | 66.5 | 51  | 43.5 | 31  | 314 | 99  |
| 4wk   | 45   | 169  | 101 | 105 | 105 | 166 | 80  | 67.5 | 11  | 52  | 298.5 | 112.5 |
| Zn    |      |    |     |     |    |     |     |     |    |     |     |     |    |
| C     | 2.1  | 4.2 | 3.6 | 6.5 | 2.4 | 5.6 | 6.1 | 5.3 | 2.3  | 1.9  | 4.7  | 6.2 |
| 3h    | 200.5 | 88.8 | 44.8 | 55.1 | 225.6 | 62.5 | 50.9 | 98.9 | 113.6 | 73.8 | 175.7 | 89.5 |
| 3day  | 144.6 | 95.1 | 59.4 | 118.2 | 185 | 97  | 54.5 | 126.6 | 100.4 | 85.3 | 201.4 | 73.4 |
| 4wk   | 59.5 | 141.1 | 68.6 | 183.2 | 124 | 191.1 | 67.3 | 210.1 | 73  | 115.4 | 236.6 | 51.1 |
| Cd    |      |    |     |     |    |     |     |     |    |     |     |     |    |
| C     | 0.2  | 0.2 | 0.009 | 3.6 | 0.5 | 0.5 | 0.1 | 0.3 | 0.2 | 0.6 | 0.5 | 0.09 |
| 3h    | 3.8  | 3.2 | 1.2 | 3.6 | 8.9 | 4.8 | 9.9 | 1.4 | 2.8 | 2   | 2.2 | 1.6 |
| 3day  | 3.9  | 1.3 | 1.2 | 3.8 | 1.2 | 0.9 | 1.5 | 2.1 | 2   | 2.4 | 1.8 |
| 4wk   | 2    | 1.7 | 2.1 | 3.2 | 2.6 | 1.9 | 1.4 | 2.2 | 1.1 | 2.1 | 2.7 | 2.4 |
| Cu    |      |    |     |     |    |     |     |     |    |     |     |     |    |
| C     | 0.3  | 1.6 | 3.2 | 3.6 | 0.6 | 0.4 | 1.8 | 4.2 | 1.4 | 2.4 | 1.8 | 3.6 |
| 3h    | 5.8  | 84.9 | 55.7 | 38.8 | 242.5 | 92.4 | 30.5 | 16.1 | 204.6 | 41.2 | 92.5 | 47.9 |
| 3day  | 190.3 | 94.5 | 97.8 | 59.7 | 197 | 114.3 | 49.9 | 25.8 | 144.4 | 52.5 | 113.1 | 69.3 |
| 4wk   | 103.1 | 116 | 143.9 | 85.2 | 123.7 | 136.2 | 80.1 | 62.5 | 44.7 | 82.3 | 129.7 | 109.4 |

Note: a Control sample; EXC- exchangeable, MNO- Mn oxide bound, FEO- Fe oxide bound, OXI- organically bound.

Due to the dynamic nature of changes that pollutants accumulated on road surfaces undergo during dry weather periods and the heterogeneous composition of road dust, the transformation characteristics of metals attached to road dust would be different from that of soils. Even though significant studies have been carried out to understand the time dependent transformation characteristics of metals associated with different types of soils under laboratory conditions,
the knowledge in relation to road dust is limited. As road dust is a heterogeneous mix of different organic and inorganic soil constituents that originate from a range of sources such as erosion of soils from surrounding areas, metals associated with road dust would undergo similar transformation characteristics as in soils. In-depth research on time-dependent transformation of metals on road surfaces can strengthen the understanding of characteristic changes to the mobility and bioavailability of metals.

According to a recent study carried out by Jayarathne et al. (2018b), transformation of Zn, Cu, Pb and Cd associated with road dust from less stable to stable geochemical forms do not follow a systematic trend with antecedent dry days, nor reach equilibrium after eleven dry day. However, significant changes in metal distribution were noted during the initial dry weather period, where the rate of transformation was found to be in the order of Pb > Cu > Zn > Cd. This signifies the relatively higher potential of Cd and Zn to be mobilised on road surfaces during dry weather periods.

The presence of organic matter in soil not only acts as an adsorbent, but can also result in the increase in metals in the oxidisable fraction with time (Lu et al., 2005; Qin et al., 2004). Jayarathne et al. (2018b) observed that road dust with high organic matter content enhances the distribution of metals in the organic matter bound form. On the other hand, Murakami et al. (2009) and Zhang et al. (2016) reported that dissolved organic matter (DOM) can enhance the desorption and mobility of certain metal ions such as Cu and Zn from road dust during wash-off, which are then transported to receiving waters by stormwater runoff. This is attributed to the formation of soluble and immobile metal-DOM complexes, rather than being adsorbed to organic matter. This implies that depending on the nature of organic matter available (i.e. particulate or dissolved), metals associated with road dust can be subjected to different transformation processes during dry and wet weather periods. Therefore, further understanding of the leaching behaviour of metals in the presence of organic matter would improve the performance of stormwater treatment strategies to eliminate specific metal ions from stormwater.

3. Influential parameters in relation to transformation processes

Unlike pure substances, solid particles deposited on road surfaces have varying proportions of organic matter, crystalline and non-crystalline mineral components which have different chemical and physical properties. Therefore, changes in the physical properties (e.g. particle size, specific surface area and mineralogy) and chemical properties (e.g. cation exchange capacity) of road dust would exhibit differences in the fate of metals over dry weather periods. Moreover, external parameters such as prevailing environmental conditions would also influence these processes.

3.1. Influential physico-chemical properties of solids

3.1.1. Particle size

The variability associated with particle sizes of road dust due to anthropogenic and natural activities significantly influences the transformation processes of metals, predominantly adsorption. The distribution of metals in different size fractionated road dust particles have been widely reported in many research studies (Ball et al., 1998; Bian and Zhu, 2009; Sansalone and Ying, 2008; Zhao et al., 2017). However, metals are commonly found at high concentrations in fine particles compared to that of coarser particles (Table 3). In fact, fine particles have enriched high surface area and density of surface functional groups available on
the surface, enhancing metal adsorption capacity compared to coarser particles. Once metal ions are transformed by adsorbing to solids, their relative mobility during both, build-up and wash-off are dependent on the mobility of associated solid particles (Kayhanian et al., 2012). Metal contaminated fine particles entrained in stormwater runoff can remain in suspension for a relatively long period of time due to their low settling velocity and can be transported over longer distances compared to coarse particles, posing potential stormwater quality impacts. Accordingly, in order to minimise the influence of potentially toxic metals on receiving water environments, appropriate mitigation measures should be implemented, targeting fine dust particles, predominantly during dry weather periods (Gbeddy et al., 2018; Zhang et al., 2015). Further, a comparative analysis of the contribution of different particle sizes of road dust in transporting transformed metal species can also provide important information for the design of effective stormwater mitigation measures.

Table 3. Metal distribution in the fine fraction of road dust.

| Pollutant | Significant particle size | Reference                        |
|-----------|---------------------------|----------------------------------|
| Metals    | <20 µm                    | Manno et al. (2006)              |
|           | <50 µm                    | Roger et al. (1998)              |
|           | <63 µm                    | Sutherland et al. (2012)         |
|           | <75 µm                    | Zhang et al. (2015)              |
|           | <250 µm                   | Duong and Lee (2011)             |
|           |                            | Liu et al. (2015)                |
|           |                            | Gunawardana et al. (2015)        |
|           |                            | Jayarathe et al. (2017)          |

**3.1.2. Specific surface area**

Specific surface area (SSA), which measures the surface area of a material per unit of mass is an important parameter relating to the metal adsorption ability of solids (Cerato and Luteneggerl, 2002b; Huang et al., 2011). This means that the amount/quantity of metals, which is transformed through different adsorption processes increases with the increase in SSA. Specific surface area is also a function of particle size of solids (Bleam, 2011; Sansalone and Ying, 2008). Based on the study carried out by Gunawardana et al. (2014), total SSA (internal and external) of <75 µm size road dust is six times higher (17.6 m² g⁻¹) compared particles in the 300-425 µm size range (2.86 m² g⁻¹) and the concentration of metals adsorbed is significantly high in <75 µm particles. As such, the variability in SSA of solids can influence the variability in metal transformation characteristics with different particle sizes of solids. On the other hand, minerals such as clays, metal oxides and hydroxides associated with road dust can enhance metal transformation by adsorbing different quantities of metal ions as they have different SSA values (Cerato and Luteneggerl, 2002a; Petersen et al., 1996).

**3.1.3. Mineralogy**

Presence of minerals in road dust can significantly influence transformation processes as they have different charge sites to adsorb metal ions. The favourable charge sites available on minerals to interact with metal ions can result from isomorphous substitution or deprotonation of surface functional groups present in the mineral structure (Filep, 1999; Sparks, 2003). The common primary and secondary minerals found in road dust are quartz, feldspars of albite and
microcline, clay minerals of chlorite and illite, carbonates of dolomite, calcite and siderite and metal oxides of magnetite and gypsum (Djukić et al., 2016; Gunawardana et al., 2012; Roger et al., 1998; Świetlik et al., 2015).

A study carried out by Jayarathne et al. (2018a) found that the adsorption characteristics of metals to different minerals vary depending on the type of metal ion and particle size. Pb adsorption to <150 µm size fraction was found to be influenced by minerals such as chlorite and albite, whilst in the >150 µm size fraction, illite and microcline showed a significant influence on Pb adsorption. Moreover, amorphous matter had a positive correlation with Zn and Cd in the >150 µm size fraction, but not in the <150 µm size fraction. Gunawardana et al. (2015) also reported that Zn, Cu, Pb and Ni in road dust have a positive correlation with clay forming minerals of chlorite, muscovite and albite, and with the cation exchange capacity of solids, implying that the transformation by ion-exchange would be a primary mechanism of metal adsorption to such minerals. The differences in the affinity of metals to different types of minerals are attributed to the variability and availability of favourable charge sites. This could further result in the variability in metal transformation with different particle sizes of road dust. As such, determining the ability of different minerals for effective removal of toxic metals in stormwater runoff is important in terms of stormwater treatment.

### 3.1.4. Cation Exchange Capacity

Cation Exchange Capacity (CEC) is an important chemical parameter that represents the ability of a solid particle to adsorb positive ions in an exchangeable form (Rayment and Lyons, 2011). This implies that solids with different CECs can facilitate transformation of metals, primarily ion-exchange. On the other hand, it leads to the variability in metal interaction in terms of different particle sizes of solids. As reported by Gunawardana et al. (2015), CEC of road dust varies with the highest value being for < 75 µm size fraction (9.44 meq 100g⁻¹), followed by 75-150 µm size fraction (7.46 meq 100g⁻¹).

The capability of a solid surface to exchange metal ions is an indicator of the net negative charged sites (either permanent or variable charges) available on that surface (Bleam, 2011; Huang et al., 2011). Accordingly, the amount/quantity of permanent and variable negative charge sites developed on solid surfaces influences the amount of metals that are transformed through either ion-exchange or chemisorption. According to a study carried out by Zhuang and Yu (2002), the amount of pH-dependent negative charge development on clay minerals of kaolinite and montmorillonite coated with Fe and Al oxides, increases with increasing pH, while at low pH, positive charges are prominent (Figure. 3). However, clay minerals coated with organic matter are characterised by pH-dependent negative charge development rather than positive charges at both, low and high pH. Similarly, road dust with high organic matter and clay content can facilitate the transformation of metals, adsorbing relatively high amounts of metal ions.

### 3.2. Environmental factors

The discussion below highlights the importance of moisture content and temperature as environmental factors, on metal transformation. Though the influence of these factors in relation to metals accumulated on road surfaces has not been investigated in-depth, the significance of environmental factors on metal behaviour has been discussed in soil related studies. As road dust is a heterogeneous mixture of soils, the knowledge acquired by such studies can be used to identify the potential influential factors on metal transformation on road
surfaces. However, further research studies are required to understand the influence of a range of environmental factors on metal behaviour in road dust, for detailed understanding of the fate of metals on road surfaces.

Figure 3. pH-dependent surface charge development for kaolinite (Kt) and montmorillonite (Mt) coated and uncoated with Fe oxide, Al oxide and organic matter (Adapted from Zhuang and Yu, 2002 with permission from publisher).

Hydration/hydrolysis is a natural phenomenon common to pollutants when they are present in a water-saturated environment. Metal ions, for example, can hydrate by attracting polarized water molecules (Grzybkowski, 2006; Wulfsberg, 1991). Hydrated metal ions (M\(^{n+}\)) generally arrange as an octahedral molecule by sharing six or twelve water molecules as; M(H\(_2\)O\(_n\)\(^{n+}\) or M(H\(_2\)O\(_n\)M(H\(_2\)O\(_n\)\(^{n+}\) or M(H\(_2\)O\(_n\)M(H\(_2\)O\(_n\)\(^{n+}\) (Grzybkowski, 2006). Similarly, metals accumulated on road surfaces can become hydrated when they come in contact with water or moisture during their build-up. The hydrated radius is a governing parameter for the selectivity of metals for ion-exchange transformations as reported in Section 3.1.

Temperature is also positively correlated with the transformation characteristics of metals, predominantly adsorption. The effect of temperature on metal adsorbed to well-characterised solids such as clays and oxide minerals under laboratory conditions have been widely
investigated in order to understand the endothermic (i.e. a reaction accompanied by heat adsorption) and exothermic (i.e. a reaction which transfers energy to the surroundings as heat) nature of the adsorption process (Akpomie et al., 2015; Sarı et al., 2007; Sharma, 2008). However, there is a dearth of knowledge in research literature relating to the effect of temperature on metal adsorption to road dust. Even though temperature cannot be controlled in a real-world environment such as a road surface, investigating the influence of temperature on pollutant processes is important in order to understand the fate of metals under different environmental conditions.

The adsorption ability of metals increases with increasing temperature. Xing et al. (2011) observed that the amount of Zn, Cu and Pb adsorbed to loess at 40°C is high compared to that at 25°C, where Zn and Cu undergo endothermic reactions, whilst Pb adsorption is exothermic. Sangiumsak and Punnattanasin (2014) also reported that metal adsorption to different types of clay, including lean clay, fat clay, silty clay, clayey sand and silty sand increases with increasing temperature (20°C to 40°C). The pore size of solids and negative charge development on solid surfaces generally increase with increasing temperature, leading to relatively higher metal adsorption capacity (Meena et al., 2008).

The geochemical behaviour of metals is also found to be influenced by the variation in temperature. According to Dho and Lee (2003), in a single metal adsorption system, the amount of Cu associated with the exchangeable fraction of natural clays is high at temperature below 25°C, whereas at temperature above 40°C, Cu is largely associated with the carbonate bound fraction. Zn is mainly present in the exchangeable fraction at both, high and low temperatures (15°C-55°C). In a competitive adsorption environment, Cu is associated with the carbonate bound fraction at all temperatures, whilst Zn is mainly in the exchangeable fraction. Similar metal behaviour could be expected on road surfaces with temperature changes. Accordingly, the mobility and potential bioavailability characteristics of Zn can be highlighted at both, low and high temperatures.

4. Influence of transformations on pollutant processes

It can be hypothesised that primary pollutant processes, build-up and wash-off, are closely related to pollutant transformations. Build-up process influences pollutant transformations as well as the wash-off process, while transformation processes influence both, build-up and wash-off processes either, directly or indirectly (Figure. 4). Therefore, the interactive influence of pollutant processes and transformation characteristics needs to be recognized in-depth in order to understand the characteristic changes in mobility and bioavailability of metals and their potential stormwater quality impacts.

The sizes of road dust particles changes over the dry weather period as natural and anthropogenic activities physically break them down. This results in changes to the physico-chemical properties of solids such as specific surface area and cation exchange capacity (Gunawardana et al., 2015; Lau and Stenstrom, 2005). Consequently, size-dependent variation in transformation characteristics of pollutants can be expected over the build-up period. This further enhances the variability associated with pollutant build-up in terms of their loads and composition. Moreover, as the transformed pollutants can have different mobility and bioavailability characteristics, the potential inconsistencies between mobility and bioavailability of pollutants associated with different particle sizes of solids can be expected.
**Figure 4.** Conceptual relationship between pollutant processes and transformation of pollutants.

During pollutant transformations, different chemical forms can be released into the environment depending on the processes that they undergo. For example, during ion-exchange, metals that are originally attached to solid surfaces can be released in a new chemical form. Furthermore, metals undergo surface precipitation forming new metal-precipitated products, which have different chemical and physical characteristics. Therefore, pollutant species with different chemical composition would accumulate on the road surfaces, implying a relationship between transformation of metals and pollutant build-up in terms of species composition. During rainfall, a considerable fraction of build-up pollutants that have already been subjected to different transformations, is detached from their original surfaces and subsequently washed-off with stormwater runoff (Amato et al., 2012; Murphy et al., 2015). The wash-off pollutant load is primarily influenced by the initially available pollutant build-up load. This further implies that the load and composition of pollutants associated with different particle sizes of road dust can influence the changes in the load and composition of wash-off pollutants associated with different size fractions (Wijesiri et al., 2015).

Consequently, transformed pollutants are removed during the wash-off process, which will dictate the impacts on receiving waters, including the first flush phenomenon (Alias et al., 2014; Bach et al., 2010; Murphy et al., 2015). As emphasized in this review, bioavailability and mobility of pollutants in stormwater runoff are influenced by the transformation processes that they undergo over dry weather periods. Though the influence of pollutant processes on stormwater quality has been widely discussed in research literature, the important role that pollutant transformations play influencing pollutant processes and consequent stormwater quality has not been explored in-depth. As such, further investigation on transformation characteristics of pollutants associated with road dust is required for informed decision making in stormwater quality analysis.
5. Conclusions

This critical review has evaluated the current knowledge in relation to the transformation processes of metals attached to road dust and factors influencing such processes. As identified in research literature, ion-exchange and chemisorption play significant roles when determining the fate of metals on road surfaces. Ion-exchange is the primary mechanism for the association of metals with clay forming minerals, whilst metals are preferentially adsorbed to organic matter and metal oxides through chemisorption. However, transformation characteristics of metals can vary with the increase in residence time, changes to chemical conditions and physico-chemical properties of associated solids.

The review has further highlighted that the transformation processes of stormwater pollutants and pollutant processes are closely related. Changes in chemical and physical characteristics of solids during their build-up will eventually influence pollutant transformations and consequently, stormwater quality. Therefore, comprehensive research on transformation processes are essential in order to accurately identify the potential stormwater quality impacts in order to enable the implementation of technically robust stormwater pollution mitigation measures.

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References

Abraham, J., Dowling, K., and Florentine, S. (2018). Assessment of potentially toxic metal contamination in the soils of a legacy mine site in Central Victoria, Australia. *Chemosphere, 192*, 122-132.

Akpomie, K. G., Dawodu, F. A., and Adebowale, K. O. (2015). Mechanism on the sorption of heavy metals from binary-solution by a low cost montmorillonite and its desorption potential. *Alexandria Engineering Journal, 54*(3), 757-767.

Ali, M. U., Liu, G., Yousaf, B., Abbas, Q., Ullah, H., Munir, M. A. M., and Fu, B. (2017). Pollution characteristics and human health risks of potentially (eco)toxic elements (PTEs) in road dust from metropolitan area of Hefei, China. *Chemosphere, 181*, 111-121.

Alias, N., Liu, A., Goonetilleke, A., and Egodawatta, P. (2014). Time as the critical factor in the investigation of the relationship between pollutant wash-off and rainfall characteristics. *Ecological Engineering, 64*, 301-305.

Amato, F., Schaap, M., Denier van der Gon, H. A. C., Pandolfi, M., Alastuey, A., Keuken, M., and Querol, X. (2012). Effect of rain events on the mobility of road dust load in two Dutch and Spanish roads. *Atmospheric Environment, 62*, 352-358.

Amato, F., Schaap, M., van der Gon, H. A. D., Pandolfi, M., Alastuey, A., Keuken, M., and Querol, X. (2013). Short-term variability of mineral dust, metals and carbon emission from road dust resuspension. *Atmospheric Environment, 74*, 134-140.

Bach, P. M., McCarthy, D. T., and Deletic, A. (2010). Redefining the stormwater first flush phenomenon. *Water Research, 44*(8), 2487-2498.
Ball, J., Jenks, R., and Aubourg, D. (1998). An assessment of the availability of pollutant constituents on road surfaces. *Science of The Total Environment, 209*(2), 243-254.

Bian, B., and Zhu, W. (2009). Particle size distribution and pollutants in road-deposited sediments in different areas of Zhenjiang, China. *Environmental Geochemistry and Health, 31*(4), 511-520.

Bleam, W. F. (2011). *Soil and Environmental Chemistry*: Elsevier Science.

Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science, 277*(1), 1-18.

Cai, L., Xu, Z., Ren, M., Guo, Q., Hu, X., Hu, G., Wan, H., and Peng, P. (2012). Source identification of eight hazardous heavy metals in agricultural soils of Huizhou, Guangdong Province, China. *Ecotoxicology and Environmental Safety, 78*, 2-8.

Cerato, A. B., and Luteneggerl, A. J. (2002a). Determination of surface area of fine-grained soils by the ethylene glycol monoethyl ether. *Geotechnical Testing Journal, 25*, 315-321.

Cerato, A. B., and Luteneggerl, A. J. (2002b). Recommended method for determining surface area of fine-grained soils. *Geotechnical Testing Journal, 31*-321.

Cerqueira, B., Covelo, E. F., Andrade, L., and Vega, F. A. (2011). The influence of soil properties on the individual and competitive sorption and desorption of Cu and Cd. *Geoderma, 162*(1–2), 20-26.

Charlesworth, S., Everett, M., McCarthy, R., Ordóñez, A., and de Miguel, E. (2003). A comparative study of heavy metal concentration and distribution in deposited street dusts in a large and a small urban area: Birmingham and Coventry, West Midlands, UK. *Environment International, 29*(5), 563-573.

Chen, M.-h., Fang, H.-w., and Huang, L. (2013). Surface charge distribution and its impact on interactions between sediment particles. *Ocean Dynamics, 63*(9-10), 1113-1121.

Chorover, J., and Brusseau, M. L. (2008). Kinetics of Sorption—Desorption. In S. L. Brantley, J. D. Kubicki and A. F. White (Eds.), *Kinetics of Water-Rock Interaction* (pp. 109-149). New York: Springer.

Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: A review. *Journal of Hazardous Materials, 157*(2), 220-229.

Dho, N. Y., and Lee, S. R. (2003). Effect of Temperature on Single and Competitive Adsorptions of Cu(II) and Zn(II) onto Natural Clays. *Environmental Monitoring and Assessment, 83*(2), 177-203.

Djukić, A., Lekić, B., Rajaković-Ognjanović, V., Veljović, D., Vulić, T., Djolić, M., Naunovic, Z., Despotović, J., and Prodanović, D. (2016). Further insight into the mechanism of heavy metals partitioning in stormwater runoff. *Journal of Environmental Management, 168*, 104-110.

Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., and Tack, F. M. (2009). Trace metal behaviour in estuarine and riverine floodplain soils and sediments: a review. *Science of The Total Environment, 407*(13), 3972-3985.

Duong, T. T. T., and Lee, B.-K. (2009). Partitioning and mobility behavior of metals in road dusts from national-scale industrial areas in Korea. *Atmospheric Environment, 43*(22), 3502-3509.

Duong, T. T. T., and Lee, B.-K. (2011). Determining contamination level of heavy metals in road dust from busy traffic areas with different characteristics. *Journal of Environmental Management, 92*(3), 554-562.

Farquhar, M. L., Vaughan, D. J., Hughes, C. R., Charnock, J. M., and England, K. E. R. (1997). Experimental studies of the interaction of aqueous metal cations with mineral substrates: Lead, cadmium, and copper with perthitic feldspar, muscovite, and biotite. *Geochimica et Cosmochimica Acta, 61*(15), 3051-3064.
Filep, G. (1999). *Soil Chemistry: Processes and Constituents*: International Specialized Book Services.

Gbeddy, G., Jayarathne, A., Goonetilleke, A., Ayoko, G. A., and Egodawatta, P. (2018). Variability and uncertainty of particle build-up on urban road surfaces. *Science of The Total Environment, 640–641*, 1432-1437.

Ghasemi, S., Khoshgoftarmanesh, A. H., Afyuni, M., Hadadzadeh, H., and Schulin, R. (2013). Zinc–amino acid complexes are more stable than free amino acids in saline and washed soils. *Soil Biology and Biochemistry, 63*, 73-79.

Grzybowski, W. (2006). Nature and properties of metal cations in aqueous solutions. *Polish Journal of Environmental Studies, 15*(4), 655.

Gunawardana, C., Egodawatta, P., and Goonetilleke, A. (2014). Role of particle size and composition in metal adsorption by solids deposited on urban road surfaces. *Environmental Pollution, 184*, 44-53.

Gunawardana, C., Egodawatta, P., and Goonetilleke, A. (2015). Adsorption and mobility of metals in build-up on road surfaces. *Chemosphere, 119*, 1391-1398.

Gunawardana, C., Goonetilleke, A., and Egodawatta, P. (2013). Adsorption of heavy metals by road deposited solids. *Water Science and Technology, 67*(11), 2622-2629.

Gunawardana, C., Goonetilleke, A., Egodawatta, P., Dawes, L., and Kokot, S. (2012). Source characterisation of road dust based on chemical and mineralogical composition. *Chemosphere, 87*(2), 163-170.

Harrison, R. M. (2007). *Principles of Environmental Chemistry*: RSC Publishing.

Horvath, M., Bokova, V., Heltai, G., Florian, K., and Fekete, I. (2010). Study of application of BCR sequential extraction procedure for fractionation of heavy metal content of soils, sediments, and gravitation dusts. *Toxicological & Environmental Chemistry, 92*(3), 429-441.

Huang, P. M., Li, Y., and Sumner, M. E. (2011). *Handbook of Soil Sciences: Properties and Processes, Second Edition*: Taylor & Francis.

Inglezakis, V., and Poulopoulos, S. (2006). *Adsorption, Ion Exchange and Catalysis: Design of Operations and Environmental Applications*: Elsevier Science.

Jacobson, C. R. (2011). Identification and quantification of the hydrological impacts of imperviousness in urban catchments: A review. *Journal of Environmental Management, 92*(6), 1438-1448.

Jalali, M., and Khanlari, Z. V. (2008). Effect of aging process on the fractionation of heavy metals in some calcareous soils of Iran. *Geoderma, 143*(1), 26-40.

Jayarathne, A., Egodawatta, P., Ayoko, G. A., and Goonetilleke, A. (2017). Geochemical phase and particle size relationships of metals in urban road dust. *Environmental Pollution, 230*, 218-226.

Jayarathne, A., Egodawatta, P., Ayoko, G. A., and Goonetilleke, A. (2018a). Intrinsic and extrinsic factors which influence metal adsorption to road dust. *Science of The Total Environment, 618*, 236-242.

Jayarathne, A., Egodawatta, P., Ayoko, G. A., and Goonetilleke, A. (2018b). Role of residence time on the transformation of Zn, Cu, Pb and Cd attached to road dust in different land uses. *Ecotoxicology and Environmental Safety, 153*, 195-203.

Kayhanian, M., McKenzie, E. R., Leatherbarrow, J. E., and Young, T. M. (2012). Characteristics of road sediment fractionated particles captured from paved surfaces, surface run-off and detention basins. *Science of The Total Environment, 439*, 172-186.

Keshavarzi, B., Tazarvi, Z., Rajabzadeh, M. A., and Najmeddin, A. (2015). Chemical speciation, human health risk assessment and pollution level of selected heavy metals in urban street dust of Shiraz, Iran. *Atmospheric Environment, 119*, 1-10.
Kleinman, P. J. A., Srinivasan, M. S., Dell, C. J., Schmidt, J. P., Sharpley, A. N., and Bryant, R. B. (2006). Role of rainfall intensity and hydrology in nutrient transport via surface runoff mention of trade names does not imply endorsement by the USDA. *Journal of environmental quality*, 35(4), 1248-1259.

Lau, S.-L., and Stenstrom, M. K. (2005). Metals and PAHs adsorbed to street particles. *Water Research, 39*(17), 4083-4092.

Li, H.-H., Chen, L.-J., Yu, L., Guo, Z.-B., Shan, C.-Q., Lin, J.-Q., Gu, Y.-G., Yang, Z.-B., Yang, Y.-X., Shao, J.-R., Zhu, X.-M., and Cheng, Z. (2017). Pollution characteristics and risk assessment of human exposure to oral bioaccessibility of heavy metals via urban street dusts from different functional areas in Chengdu, China. *Science of The Total Environment, 586*, 1076-1084.

Li, X., Poon, C.-s., and Liu, P. S. (2001). Heavy metal contamination of urban soils and street dusts in Hong Kong. *Applied Geochemistry, 16*(11), 1361-1368.

Lim, T.-T., Tay, J.-H., and Teh, C.-I. (2002). Contamination time effect on lead and cadmium fractionation in a tropical coastal clay. *Journal of environmental quality, 31*(3), 806-812.

Liu, A., Liu, L., Li, D., and Guan, Y. (2015). Characterizing heavy metal build-up on urban road surfaces: Implication for stormwater reuse. *Science of The Total Environment, 515–516*, 20-29.

Lu, A., Zhang, S., and Shan, X.-q. (2005). Time effect on the fractionation of heavy metals in soils. *Geoderma, 125*(3–4), 225-234.

Ma, Y., Egodawatta, P., McGree, J., Liu, A., and Goonetilleke, A. (2016). Human health risk assessment of heavy metals in urban stormwater. *Science of The Total Environment, 557–558*, 764-772.

Maiz, I., Arambarri, I., Garcia, R., and Millán, E. (2000). Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis. *Environmental Pollution, 110*(1), 3-9.

Maniquiz-Redillas, M., and Kim, L.-H. (2014). Fractionation of heavy metals in runoff and discharge of a stormwater management system and its implications for treatment. *Journal of Environmental Sciences, 26*(6), 806-812.

Manno, E., Varrica, D., and Dongarrà, G. (2006). Metal distribution in road dust samples collected in an urban area close to a petrochemical plant at Gela, Sicily. *Atmospheric Environment, 40*(30), 5929-5941.

McBride, M. B. (1994). *Environmental chemistry of soils*. New York: Oxford University Press.

Meena, A. K., Kadirvelu, K., Mishra, G. K., Rajagopal, C., and Nagar, P. N. (2008). Adsorptive removal of heavy metals from aqueous solution by treated sawdust (Acacia arabica). *Journal of Hazardous Materials, 150*(3), 604-611.

Miguntanna, N. P., Goonetilleke, A., Egodowatta, P., and Kokot, S. (2010). Understanding nutrient build-up on urban road surfaces. *Journal of Environmental Sciences, 22*(6), 806-812.

Mohan, D., and Pittman Jr, C. U. (2007). Arsenic removal from water/wastewater using adsorbents—A critical review. *Journal of Hazardous Materials, 142*(1–2), 1-53.

Murakami, M., Fujita, M., Furumai, H., Kasuga, I., and Kurisu, F. (2009). Sorption behavior of heavy metal species by soakaway sediment receiving urban road runoff from residential and heavily trafficked areas. *Journal of Hazardous Materials, 164*(2), 707-712.

Murphy, L. U., Cochrane, T. A., and O'Sullivan, A. (2015). Build-up and wash-off dynamics of atmospherically derived Cu, Pb, Zn and TSS in stormwater runoff as a function of meteorological characteristics. *Science of The Total Environment, 508*, 206-213.
Nemati, K., Bakar, N. K. A., Abas, M. R., and Sobhanzadeh, E. (2011). Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. *Journal of Hazardous Materials, 192*(1), 402-410.

Ozcan, N., and Altundag, H. (2013). Speciation of heavy metals in street dust samples from Sakarya I. Organized industrial district using the BCR sequential extraction procedure by ICP-OES. *Bulletin of the Chemical Society of Ethiopia, 27*(2), 205-212.

Palleiro, L., Patinha, C., Rodríguez-Blanco, M. L., Taboada-Castro, M. M., and Taboada-Castro, M. T. (2016). Metal fractionation in topsoils and bed sediments in the Mero River rural basin: Bioavailability and relationship with soil and sediment properties. *CATENA, 144*, 34-44.

Passos, E. d. A., Alves, J. C., dos Santos, I. S., Alves, J. d. P. H., Garcia, C. A. B., and Spinola Costa, A. C. (2010). Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. *Microchemical Journal, 96*(1), 50-57.

Patra, A., Colville, R., Arnold, S., Bowen, E., Shallcross, D., Martin, D., Price, C., Tate, J., ApSimon, H., and Robins, A. (2008). On street observations of particulate matter movement and dispersion due to traffic on an urban road. *Atmospheric Environment, 42*(17), 3911-3926.

Petersen, L. W., Moldrup, P., Jacobsen, O. H., and Rolston, D. (1996). Relations between specific surface area and soil physical and chemical properties. *Soil science, 161*(1), 9-21.

Polcaro, A. M., Mascia, M., Palmas, S., Vacca, A., and Tola, G. (2003). Competitive sorption of heavy metal ions by soils. *Environmental Engineering Science, 20*(6), 607-616.

Qin, F., Shan, X.-q., and Wei, B. (2004). Effects of low-molecular-weight organic acids and residence time on desorption of Cu, Cd, and Pb from soils. *Chemosphere, 57*(4), 253-263.

Qiutong, X., and Mingkui, Z. (2017). Source identification and exchangeability of heavy metals accumulated in vegetable soils in the coastal plain of eastern Zhejiang province, China. *Ecotoxicology and Environmental Safety, 142*, 410-416.

Rayment, G. E., and Lyons, D. J. (2011). *Soil Chemical Methods: Australasia*: CSIRO Publishing.

Rieuwerts, J., Thornton, I., Farago, M., and Ashmore, M. (1998). Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. *Chemical Speciation & Bioavailability, 10*(2), 61-75.

Ritter, K. S., Paul Sibley, Ken Hall, Patricia Keen, Gevan Mattu, Beth Linton, Len. (2002). Sources, pathways, and relative risks of contaminants in surface water and groundwater: a perspective prepared for the Walkerton inquiry. *Journal of Toxicology and Environmental Health Part A, 65*(1), 1-142.

Roberts, D., Nachtegaal, M., and Sparks, D. L. (2005). Speciation of metals in soils. *Chemical Processes in Soils*(chemicalprocess), 619-654.

Rogier, S., Montrejaud-Vignoles, M., Andral, M. C., Herremans, L., and Fortune, J. P. (1998). Mineral, physical and chemical analysis of the solid matter carried by motorway runoff water. *Water Research, 32*(4), 1119-1125.

Sangiumsak, N., and Punrattanasin, P. (2014). Adsorption Behavior of Heavy Metals on Various Soils. *Polish Journal of Environmental Studies, 23*(3).

Sansalone, J., and Ying, G. (2008). Partitioning and granulometric distribution of metal leachate from urban traffic dry deposition particulate matter subject to acidic rainfall and runoff retention. *Water Research, 42*(15), 4146-4162.
Sari, A., Tuzen, M., and Soylak, M. (2007). Adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay. *Journal of Hazardous Materials, 144*(1), 41-46.

Scheidegger, A., and Sparks, D. (1996). A critical assessment of sorption-desorption mechanisms at the soil mineral/water interface. *Soil science, 161*(12), 813-831.

Sharma, Y. C. (2008). Thermodynamics of removal of cadmium by adsorption on an indigenous clay. *Chemical Engineering Journal, 145*(1), 64-68.

Sparks, D. L. (2003). *Environmental Soil Chemistry*: Elsevier Science.

Sposito, G. (2008). *The Chemistry of Soils*: Oxford university press.

Stead-Dexter, K., and Ward, N. I. (2004). Mobility of heavy metals within freshwater sediments affected by motorway stormwater. *Science of The Total Environment, 334–335*, 271-277.

Sutherland, R. A., Tack, F. M., and Ziegler, A. D. (2012). Road-deposited sediments in an urban environment: A first look at sequentially extracted element loads in grain size fractions. *Journal of Hazardous Materials, 225*, 54-62.

Świetlik, R., Trojanowska, M., Strzelecka, M., and Bocho-Janiszewska, A. (2015). Fractionation and mobility of Cu, Fe, Mn, Pb and Zn in the road dust retained on noise barriers along expressway – A potential tool for determining the effects of driving conditions on speciation of emitted particulate metals. *Environmental Pollution, 196*, 404-413.

Tao, Y., Yuan, Z., Xiaona, H., and Wei, M. (2012). Distribution and bioaccumulation of heavy metals in aquatic organisms of different trophic levels and potential health risk assessment from Taihu lake, China. *Ecotoxicology and Environmental Safety, 81*, 55-64.

Toth, J. (2002). *Adsorption*: CRC Press.

Uchimiya, M., Klasson, K. T., Wartelle, L. H., and Lima, I. M. (2011). Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations. *Chemosphere, 82*(10), 1431-1437.

Vaze, J., and Chiew, F. H. S. (2002). Experimental study of pollutant accumulation on an urban road surface. *Urban Water, 4*(4), 379-389.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A., and Pigna, M. (2010). Mobility and bioavailability of heavy metals and metalloids in soil environments. *Journal of soil science and plant nutrition, 10*(3), 268-292.

Wijesiri, B., Egodawatta, P., McGree, J., and Goonetilleke, A. (2015). Influence of pollutant build-up on variability in wash-off from urban road surfaces. *Science of The Total Environment, 527–528*, 344-350.

Worch, E. (2012). *Adsorption technology in water treatment: fundamentals, processes, and modeling*: Walter de Gruyter.

Wulfsberg, G. (1991). *Principles of Descriptive Inorganic Chemistry*: University Science Books.

Xing, S., Zhao, M., and Ma, Z. (2011). Removal of heavy metal ions from aqueous solution using red loess as an adsorbent. *Journal of Environmental Sciences, 23*(9), 1497-1502.

Zhang, C., Yu, Z.-g., Zeng, G.-m., Jiang, M., Yang, Z.-z., Cui, F., Zhu, M.-y., Shen, L.-q., and Hu, L. (2014). Effects of sediment geochemical properties on heavy metal bioavailability. *Environment International, 73*, 270-281.

Zhang, J., Hua, P., and Krebs, P. (2015). The build-up dynamic and chemical fractionation of Cu, Zn and Cd in road-deposited sediment. *Science of The Total Environment, 532*, 723-732.

Zhang, J., Hua, P., and Krebs, P. (2016). The influences of dissolved organic matter and surfactant on the desorption of Cu and Zn from road-deposited sediment. *Chemosphere, 150*, 63-70.
Zhang, M., and Wang, H. (2009). Concentrations and chemical forms of potentially toxic metals in road-deposited sediments from different zones of Hangzhou, China. *Journal of Environmental Sciences, 21*(5), 625-631.

Zhao, H., Wang, X., and Li, X. (2017). Quantifying Grain-Size Variability of Metal Pollutants in Road-Deposited Sediments Using the Coefficient of Variation. *International Journal of Environmental Research and Public Health, 14*(8), 850.

Zhao, S., Feng, C., Quan, W., Chen, X., Niu, J., and Shen, Z. (2012). Role of living environments in the accumulation characteristics of heavy metals in fishes and crabs in the Yangtze River Estuary, China. *Marine Pollution Bulletin, 64*(6), 1163-1171.

Zhuang, J., and Yu, G.-R. (2002). Effects of surface coatings on electrochemical properties and contaminant sorption of clay minerals. *Chemosphere, 49*(6), 619-628.

Ziyath, A. M., Egodawatta, P., and Goonetilleke, A. (2016). Build-up of toxic metals on the impervious surfaces of a commercial seaport. *Ecotoxicology and Environmental Safety, 127*, 193-198.