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REVIEW ARTICLE

Removal mechanisms of heavy metal pollution from urban runoff in wetlands

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Abstract Solid particles, particularly urban surface dust in urban environments contain large quantities of pollutants. It is considered that urban surface dust is a major pollution source of urban stormwater runoff. The stormwater runoff washes away urban surface dust and dissolves pollutants adsorbed onto the dust and finally discharges into receiving water bodies. The quality of receiving water bodies can be deteriorated by the dust and pollutants in it. Polluted waters can be purified by wetlands with various physical, chemical, and biologic processes. These processes have been employed to treat pollutants in urban stormwater runoff for many years because purification of treatment wetlands is a natural process and a low-cost method. In this paper, we reviewed the processes involved during pollutants transport in urban environments. Particularly, when the urban stormwater runoff enters into wetlands, their removal mechanisms involving various physical, chemical and biologic processes should been understood. Wetlands can remove heavy metals by absorbing and binding them and make them form a part of sediment. However, heavy metals can be released into water when the conditions changed. This information is important for the use of wetlands for removing of pollutants and reusing stormwater.

Keywords wetlands, heavy metal, stormwater runoff, removal mechanisms

1 Introduction

There are many kinds of pollutants on the urban surface, when the precipitation happens and runoff is formed, pollutants can be dissolved and washed away and finally discharged into receiving water bodies (Taebi and Droste, 2004). It is considered that urban stormwater runoff is one of the most prevalent sources of water quality impairment in aquatic ecosystems (USEPA, 1996). Combined with increasing population and water scarcity and rapid urbanization and industrialization, the degradation of aquatic ecosystems has generated increasing interest in the controlling pollution and reusing of urban stormwater (Thurston, 1999; Ngabe et al., 2000; Fletcher et al., 2008). The pollutants in urban stormwater are the barrier to reuse it. So, it is very important to knowledge of the basic pollution processes of urban stormwater runoff.

Among the various non-point sources, urban stormwater runoff is an important source of pollution because it may contain abundant heavy metals such as Cu, Pb, Zn, As, Hg, Cr, and Cd (Makepeace et al., 1995; Sriyaraj and Shutes, 2001). The heavy metals in urban stormwater runoff mostly come from the particulate matter within the surface water systems caused by atmospheric transport and local human activities including resuspended road dust, vehicle emissions, industrial discharges, heating systems, building deterioration, and other anthropogenic activities (Al-Khashman 2004; Faiz et al., 2009; Mulligan et al., 2009; Apeagyei et al., 2011; Khairy et al., 2011). Kinds of heavy metals within stormwater runoff are discharged directly into natural water bodies, these non-biodegradable metals will accumulate in the aquatic environment, causing both short-term (e.g. acute toxicity) and long-term (e.g. carcinogenic damages) adverse effects on human life and other organisms (Wu and Zhou, 2009; Khairy et al., 2011). These adverse effects can be enlarged through taking contamination of drinking water and food (Cheng et al., 2002; Terzakis et al., 2008; Eckley and Branfireun, 2009; Luo et al., 2009; Wu and Zhou, 2009). For example, cadmium can lead to tissue damage and cellular death (Méndez-Armenta and Ríos, 2007). Furthermore, some metals like chromium (VI) are thought to be toxic to organisms such as plants and animals (Richard and Bourg, 1991).

Sedimentation can be taken as one of the principal

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removal mechanisms of heavy metals in water (Reinelt and Horner, 1995; Walker and Hurl, 2002). Sedimentation of suspended solids in water can be influenced by particle size, hydrologic regime, flow velocity, and residence time (Reinelt and Horner, 1995). Wetlands with residence and purification function can eliminate the negative impacts of urban stormwater runoff, because there are dense vegetations and suspended particles (USEPA, 1995). They can serve as a natural purifier for urban stormwater runoff and allow pollutants to be removed from the water by sedimentation or filtration process. For example, Walker and Hurl (2002) found that when the stormwater runoff passed through the wetland, contaminant (Zn, Pb, and Cu) concentrations on sediment decreased 57%, 71% and 48%, respectively. However, some heavy metals such as Cr and As are remained relatively constant or increased. Therefore, this contradiction calls for investigating the removal mechanisms of heavy metals of urban stormwater runoff in wetlands.

The main purpose of this paper is to provide a review on the concentration of heavy metals in urban environment and their removal mechanisms in wetlands receiving urban stormwater runoff, depending on literatures and practical working experiences. Figure 1 illustrates the processes involved heavy metals transport in urban environments. It's very important to understand the basic mechanisms and processes that control the metals removal by wetlands. The knowledge of these can increase the probability of success of the treatment wetland application and the optimization of remediation technologies fitting for polluted wetland can be achieved.

2 Heavy metals pollution in urban environment

Solid particles that accumulate on impervious surfaces in urban environments are generally defined as "urban surface dust," which does not stay in place for a long time. Due to the wind and human activities, they are easily re-suspended back into the atmosphere with a large number of pollutants. Precipitation may wash away urban surface dust and form surface runoff, carrying a mass of pollutants, which can dissolve in surface runoff and in receiving water bodies (e.g. metal ions) and become an important component of the suspended particles due to adsorption (Vermette et al., 1991; Ferreira-Baptista and Miguel, 2005).

2.1 Heavy metals concentration in urban surface dust

The mean concentrations of heavy metals in urban surface dust worldwide are listed in Table 1, while the concentrations are slightly similar in cities of China than that in cities abroad. However, they are much higher than their background values in soil of China (Table 1). It can be sure that urban surface dust contains large quantity of heavy metals, which will result in potential hazard of receiving water bodies and human beings.

2.2 Heavy metals concentration in urban stormwater runoff

A number of investigators have studied the characteristics of urban stormwater runoff, therefore, many data have been collected. The most comprehensive study, the Nationwide Urban Runoff Program (NURP), had been accomplished in the early 1980s by the United States Environmental Protection Agency (USEPA, 1983;Taebi and Droste, 2004). An urban runoff pollution loading factor (event mean concentration (EMC)) was produced from the results of NURP (Taebi and Droste, 2004).The EMC of a pollutant can be calculated by the division of the total pollutant mass to the total runoff volume in that event and catchment (Eq. (1)) (Ma et al., 2011). It is described by the following equation:

$$\mathrm{EMC} = \frac{M}{V} = \frac{\int_0^t Q_t C_t \mathrm{d}t}{\int_0^t Q_t \mathrm{d}t} = \frac{\sum Q_t C_t \Delta t}{\sum Q_t \Delta t}, \tag{1}$$

where M is the total mass of pollutants over the entire event duration (g); V is the total volume of flow over the entire event duration (m^3); t represents time (min); C_t is the concentration of a pollutant (mg/L); Q_t is the variable flow (m^3/min); and Δt is a discrete time interval (min), $\Delta t = (t_{i+1} - t_{i-1})/2$. The EMC was computed for the entire runoff duration of each event.

Table 2 contains an overview of heavy metals mean values of the EMCs for urban surface runoff, which include raw roof runoff and road runoff. From Table 2, it may be found that heavy metals mean values of EMCs in runoff, not only in road runoff but also in roof runoff, are more or less lower in China than in other cities around world. Generally, heavy metals in roof runoff are slightly higher than in road runoff, but heavy metals in roof runoff are greatly higher than in road runoff in China. The runoff which contents heavy metals mean values of EMCs is in the order of roof runoff>road>>rainfall.

Some investigators study the dissolution characteristics of urban surface dust in different aqueous media, which are deionized (DI) water (Joshi et al., 2009; Murakami et al., 2008, 2009), acidified DI water (Li et al., 2008c; Murakami et al., 2008; 2009; Joshi et al., 2009) and river water (Joshi et al., 2009). Joshi et al. (2009) studied metals dissolution characteristics in these three aqueous media. This study clearly indicated that dissolution of metals from surface dusts can be influenced by the solution pH in receiving waters. If the rain is becoming acidic, it is likely to leach out large number of dissolving metals from the surface dust. Murakami et al. (2008; 2009) employed

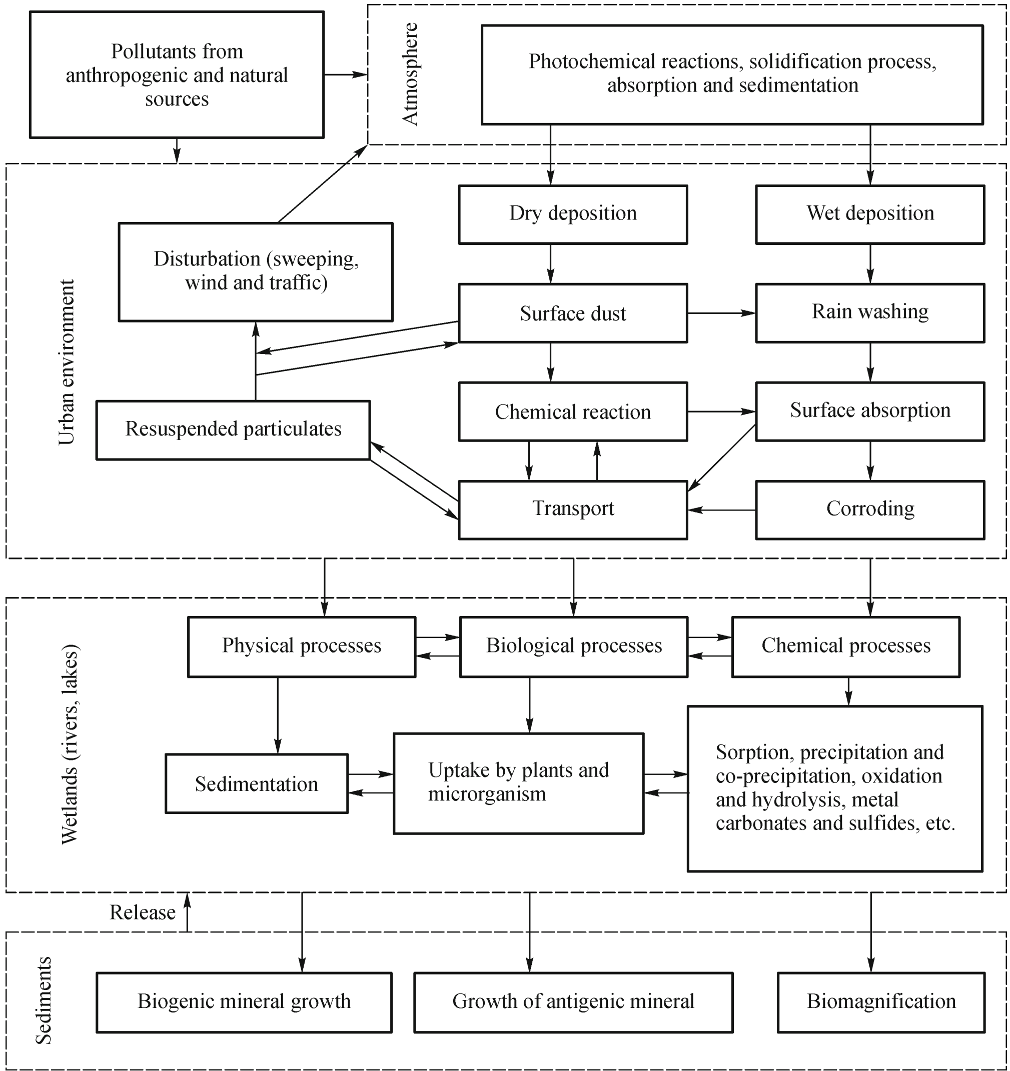

Fig. 1 Flow diagram illustrating the processes involved during pollutants transport in urban environments

artificial road runoff water (road dust leachates) to obtain percolating water from the soakaway sediment to discuss on relationship between the sorption behavior of heavy metal species and the water quality of road runoff. There should be a method that will suggest that the surface dust leachates could be regarded as valid and representative to mimic surface runoff water, which has similar chemical parameters (e.g. heavy metals, DOC and pH) of surface dust leachates with these in dissolved phase of actual surface runoff water.

On the basic of analysis above, stormwater runoff from urban impervious surfaces often contains significant amounts of heavy metals. Because metals do not degrade naturally, high concentrations of them in stormwater runoff flow into receiving waters and can result in pollution in the aquatic environment at levels that are toxic to organisms in surrounding environments. As the limit of time and space of rainfall, there should simulate surface runoff with surface dust leachate to study the pollutants removal process in future.

3 Heavy metal removal mechanism in stormwater wetland

When the urban stormwater runoff, agricultural runoff, and other wastewaters enter or pass through wetlands, various pollutants are removed by several physical, chemical, and biologic processes. More recently, wetlands which have the potential for water-quality improvement are exploited for the treatment of different kinds of wastewaters (Walker and Hurl, 2002; Gopal and Ghosh, 2008; Yeh, 2008; Lizama et al., 2011). To understand the basic processes of the removal, even the potential applications, knowledge of

Table 1 Mean concentrations of heavy metals in urban surface dust

City	Mean concentrations of heavy metals/(mg·kg^{-1})					
	Cd	Cu	Cr	Ni	Pb	Zn
Riyadh[a)]	2.3	61.7	32.5	45.0	2134.0	338.0
Madrid[b)]	Nd	188.0	61.0	44.0	192.7	476.0
Warsaw[c)]	Nd	154.3	100.3	55.7	174.0	1286.7
Ottawa[d)]	0.4	65.8	43.3	15.2	39.1	112.5
Birmingham[e)]	1.6	466.9	Nd	41.1	48.0	534.0
Coventry[e)]	0.9	226.4	Nd	129.7	47.1	385.7
Sydney[f)]	4.4	147.0	83.6	27.2	389.0	657.0
Luanda[g)]	1.1	42.0	26.0	10.0	351.0	317.0
Budapest[h)]	Nd	351.0	235.0	326.0	894.0	1608.0
Jordan[i)]	6.4	91.9	65.5	Nd	59.5	639.8
Xi’an[j)]	Nd	95.0	167.3	Nd	230.5	421.6
Chongqing[k)]	5.0	79.4	87.3	22.2	75.6	169.7
Shanghai[l)]	1.0	257.6	264.3	66.4	236.6	753.3
Urumqi[m)]	Nd	81.1	109.7	Nd	82.7	549.0
Baoji[n)]	Nd	123.2	126.7	48.8	433.2	715.3
Xianyang[o)]	0.1	177.2	Nd	Nd	52.7	Nd
Shenyang[p)]	4.4	81.3	Nd	Nd	106.3	334.5
Jinhua[q)]	Nd	142.1	219.8	44.4	161.8	758.7
Hangzhou[r)]	1.6	116.0	51.3	25.9	202.2	321.4
Guangzhou[s)]	2.4	176.0	78.8	23.0	240.0	586.0
Background values in soil of China	0.1	22.6	61.0	26.9	26.0	100.0

Notes: Nd = no data available; a) Al-Raihi et al. 1996; b) Miguel et al. 1997; c) Lisiewicz et al. 2000; d): Rasmussen et al. 2001; e) Charlesworth et al. 2003; f) Chattopadhyay et al. 2003; g) Ferreira-Baptista and Miguel, 2005; h) McAlister et al. 2006; i) Jaradat et al. 2004; j) Han et al. 2006; k) Li et al. 2006; l) Shi et al. 2010; m) Liu et al. 2009; n) Lu et al. 2010; o) Shi and Wang, 2009; p) Li et al. 2008a; q) Li et al. 2008b; r) Zhang and Wang, 2009; s) Duzgoren-Aydin et al. 2006

benefits and limitations of wetland treatment systems are extremely helpful for designing constructed wetlands to improve the water quality.

3.1 Physical removal processes

In natural or constructed wetlands, there are many processes like filtration, adsorption, plant uptake and chemical transformation in the removal of heavy metals from water (Walker and Hurl, 2002), however, sedimentation with suspended particles has long been recognized as the primary process in the removal of heavy metals from stormwater runoff (Mays and Edwards, 2001). In practice, wetlands have been considered most often for the treatment of urban stormwater runoff (Reinelt and Horner, 1995; Thurston, 1999). They will be significant benefits and low cost of purifying water and supplying the groundwater (Shutes, 2001; Liang and Wong, 2003). This purification is depended on the reduction of suspended particles, nutrients and heavy metals. Once heavy metals enter into a wetland, whether the water is stagnant or mobile, a number of removal processes may occur (Zoppou, 2001). Heavy metals in wetlands tend to be combined with suspended particles and more easily with the finer particles. So it is considered that heavy metals in wetlands may be transported from water to the sediment or biota or vice versa, which can be easily filtered and accumulated in wetlands (Walker and Hurl, 2002).

Sedimentation rate of suspended particles depends on water flow rate in wetlands. The roots and floating plants will make surface water typically move very slow or calm through wetlands. Through a variety of physical, chemical and biochemical processes, roots and floating plants ultimate contribute to purification of wastewater by sedimentation (Khan et al., 2009). Particles are more or less dense than water, sedimentation will happen only after floc formation (Yao and Gao, 2007). Sedimentation rate is proportional to the particle settling velocity and water residence time in wetlands (DeBusk, 1999). In the process of floc formation, suspended particles may also be combined with other types of fine particles like heavy metals which will be removed from water. In wetland ecosystems, flocculation is influenced by pH, concentration of suspended particles, ionic strength and microorganism concentration (Droppo et al., 1997; Matagi et al., 1998; Sheoran and Sheoran, 2006). Sedimentation is rather than a

Table 2 Heavy metals mean values of EMCs in runoff water

City	Wastewater type	Heavy metals/($\mu g \cdot L^{-1}$)					
		Cd	Cu	Pb	Zn	Cr	Ni
Nantes[a)]	Raw runoff	1.0	45.0	58.0	356.0	Nd	Nd
Paris[b)] (median)	Roof runoff	1.3	37.0	493.0	3422.0	Nd	Nd
	Yard runoff	0.8	23.0	107.0	563.0	Nd	Nd
	Street runoff	0.6	61.0	133.0	550.0	Nd	Nd
Isfahan[c)]	Urban runoff	Nd	Nd	278.0	342.0	Nd	Nd
Genoa[d)]	Road runoff	Nd	19.4	13.2	81.1	Nd	Nd
	Roof runoff	Nd	10.0	5.1	446.7	Nd	Nd
Cremona[e)]	Road runoff[1)]	Nd	1397.0	34.0	222.0	1.5	7.4
	Road runoff[2)]	Nd	469.0	11.0	156.0	Nd	Nd
	Road runoff[3)]	Nd	826.0	18.8	260.0	7.0	Nd
	Road runoff[4)]	Nd	1683.7	19.8	528.3	8.5	10.1
Macau[f)]	Road runoff[5)]	Nd	13.4	10.0	43.0	Nd	Nd
	Road runoff[6)]	Nd	33.3	81.0	288.0	Nd	Nd
Guangzhou[g)]	Road runoff	26.5	0.1	100.6	1.9	52.7	26.5
	Road runoff	11.9	0.0	51.3	0.5	8.7	11.9
	Road runoff	0.7	0.0	70.5	0.3	4.3	7.6
	Rainfall	0.2	0.0	0.2	0.1	n.d.	n.d.
Shanghai[h)]	Roof runoff[7)]	6.0	36.0	44.0	688.0	14.0	Nd
	Roof runoff[8)]	6.0	33.0	36.0	1129.0	11.0	Nd
	Roof runoff[9)]	6.0	28.0	47.0	1035.0	14.0	Nd
Shanghai[i)]	Road runoff	4.0	0.1	0.1	1.0	0.3	0.3
Nanjing[j)]	Road runoff	0.8	0.1	40.4	0.5	Nd	Nd

Notes: Nd = no data available; n.d. = not detected; 1–4) stand for the 4 storm events during 26/09/2007, 24/10/2007, 22/11/2007 and 30/01/2008, respectively. 5) and 6) stand for the 2 storm events during 21/06/2005, 17/08/2005, respectively. 7–9) stand for roof types of concrete, aluminum and glass, respectively. a) Legret and Pagotto, 1999; b) Gromairemertz et al. 1999; c) Taebi and Droste, 2004; d) Gnecco et al. 2005; e) Papiri et al. 2008; f) Huang et al. 2006; g) Gan et al. 2007; h) Chang et al. 2009; i) Wang and Li, 2009; j) Li et al. 2009

simple physical reaction. Some other chemical processes like sorption, precipitation and co-precipitation have to occur first, and then sedimentation becomes possible only after suspended particles aggregate heavy metals into particulate solids large enough to sink (Walker and Hurl, 2002). In this way heavy metals are removed from stormwater runoff and trap in the wetland sediments, thus protecting the ultimate receiving surface and groundwater bodies (Sheoran and Sheoran, 2006).

Wetlands can provide highly efficient physical removal of contaminants in the polluted water by sedimentation (DeBusk, 1999). For example, Windom et al. (1991) reported that an average of approximately 40%, 62%, 80% and 92%, of the total amounts of Cu, Cd, Zn and Pb are carried by suspended solids in rivers on the east coast of the USA. Mulligan et al. (2009) addressed that the level of heavy metal removal is 98.9% due to the heavy metal combines with the suspended solids. Hares and Ward (2004) also found a high level of removal of heavy metals by sedimentation, filtration and bioaccumulation processes in the high reed biomass wetlands in 39-month study.

Therefore, to some degree, the principal role in suspended particles removal is to restrict resuspension of settled particulate matter. Overall, sedimentation is usually considered as a reversible process, which will accumulate particles and associate contaminants on the wetland soil/sediment surface and release contaminants with the environmental change (DeBusk, 1999). Sediment can resuspension and reenters into waters due to wind-driven turbulence and bioturbation (disturbance by animals and humans). The heavy metal contents in water will be increased accordingly. Thus, the turbulence should be decreased. Removal of contaminants from water by wetlands is a sustainable method of environmental management and low cost pollution treatment approach (Shutes, 2001).

3.2 Biologic removal processes

There is other removal process-biologic removal, which is one of the most important methods for contaminant removal in wetlands. Plant uptake is proved to be the most widely recognized biologic process for contaminant removal in wetlands (DeBusk, 1999). Meanwhile the plants absorb some of the pollutants directly in water. The plants can supply oxygen to the microorganisms within the wetland around the rhizosphere.

3.2.1 Metals mobility in the rhizosphere

As an important interface of soil and plant, rhizosphere plays an important role in the wetland system. Under reducing condition, many of the metal pollutants are associated with carbonates and sulfides in the sediments. However, wetland plants can oxidize the sediments in the rhizosphere through the transfer of oxygen downwards (Moorhead and Reddy, 1988; Quan et al., 2007). This oxidation can remobilize the metal pollutants, thus resolving the metals in sediment in wetlands and increasing the content of them in surface water (Lacerda et al., 1993; Weis and Weis, 2004). Plants increase the amount of iron oxyhydroxides in the sediments through oxidation of the rhizosphere to retention of metals in wetlands (Otte et al., 1995). This process is strongly dependent on season. It is believed that plants affect the biogeochemical dynamics of wetland sediments via evapotranspiration-induced advection, which increases the loading of dissolved pollutants into the rhizosphere (El-Shatnawi and Makhadmeh, 2001).

There is combination of intense microbial activity in wetland sediments with the oxygen released by plant roots, which creates both anaerobic and aerobic zones, hence both reductive and oxidative reactions take place simultaneously in the interface of soil and plant (Sobolewski, 1999). These processes are composed mostly of Fe and Mn hydroxides and other coprecipitated metals, and are often referred to as “iron plaque.” Some other metals are released from the anoxic sediments and accumulated in the oxidized rhizosphere (Doyle and Otte, 1997). Their concentrations can reach 5–10 times than that in the surrounding sediments (Sundby et al., 1998). A notable characteristic of roots of some wetland plants is the emergence of metal-rich rhizoconcretions or plaque on the roots (Weis and Weis, 2004).

Heavy metal remobilisation may be caused by the excretion of plant exudates (Xu and Jaffé, 2006). For example, root exudates significantly change in species and quantity under heavy metal stress (Dong et al., 2007). Root exudates can activate heavy metals in soil, and enhance their bioavailability by dissolving (Xu et al., 2006). The presence of microbial symbionts can affect the accumulation of metals in wetlands such as mycorrhizae (Weis and Weis, 2004). Mycorrhizae provide an interface between the roots and the soil. They can increase the absorptive surface area of root hairs (Meharg and Cairney,1999).

3.2.2 Metals uptake by plants

Wetlands are highly productive systems and support globally large biodiversity (from microorganisms to mammals). There usually contain a large number of plants. MacFarlane et al. (2003) and Weis and Weis (2004) showed that metal accumulation in plants is element- and plant-specific. They found the level of accumulation in leaves change on the basis of the metals. Some heavy metals like Zn can be accumulated in leaves. The concentrations in leaves are relevant to the concentrations in sediment around the plant. However, lead levels in leaves are different, which accumulate in roots and shoots (Weis and Weis, 2004). Deng et al. (2004) investigated that the concentrations of Pb, Zn, Cu and Cd accumulate by many perennial wetland plants. The results showed that metal accumulation is differed among tissues of wetland plants, which are mostly accumulated in root tissues, and then in their shoots. Many factors include metal concentrations, pH, temperature and nutrient levels in the surroundings can influence metal accumulation in wetland plants. There are two kinds of heavy metals accumulated into plants, which are essential micronutrients such as Zn, Ni, Cu, and Mn, and non-essential toxic heavy metals, such as Cd, As, Hg and Pb (Kabata-Pendias and Pendias, 2001; Papoyan et al., 2007). Essential micronutrients are basic components of plants, they are also potentially toxic heavy metals as high content. However, if plants absorb the non-essential toxic heavy metal via the transport systems, which are not only toxic for plant growth but also can limit the uptake of essential micronutrients (Kabata-Pendias and Pendias, 2001; Papoyan et al., 2007).

The transfer ability of pollutants from root to aboveground is dependent on plant species, metals, and physical conditions, for eample pH, redox potential (Eh), and temperature (Weis and Weis, 2004; Reboreda and Caçador, 2007). Besides, other factors, such as sediment organic matter content, grain size, nutrients, microbial biomass, and the other ions concentrations may also influence metals uptake by wetland plants (Dong et al., 2007; Reboreda and Caçador, 2007). In the future, more research attention should go to mechanisms of metal transfer from intermittent wetting and drying wetland soils/sediments to vegetation, as well as their spatial and temporal dynamics.

3.3 Chemical removal processes

Besides, there are a series of chemical processes which referred to the removal of heavy metals in wetlands.

3.3.1 Sorption

Sorption is regarded as the most important chemical removal process in wetland soils/sediments, which can remove many contaminants by short-term retention or long-term immobilization. Sorption is a group of processes that transfer ions (molecules with positive or negative charges) from the solution phase (water) to the solid phase (soil/sediment). These processes include adsorption and precipitation reactions (Sheoran and Sheoran, 2006).

Heavy metals in sediments are adsorbed to the solid particles by either cation exchange or adsorption. Malandrino et al. (2006) reported that clays with high cation exchange capacity and high specific surface area can remove pollutants from aqueous solutions. Some researchers found that the inorganic matter with high adsorption capacity which usually use as sorbents for the removal of metals from various waters due to particularly abundant and inexpensive (Celis et al., 2000; Alvarezayuso and García-Sánchez, 2003; Malandrino et al., 2006). Heavy metal pollution adversely affects in the soil/sediment is long-term because they are being strongly adsorbed by the organic matter or clay. Besides, this harmful effect may last hundreds of years or more, while they will remain as metals, although changes in their speciation or valence state may take place with the time and the sediment conditions change (Groudev et al., 1999; Wieβner et al., 2005; Kalavrouziotis and Koukoulakis, 2009). Many wastewater and runoff contain cations, including ammonium ion (NH_4^+) and most trace metals, such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+} and Cd^{2+}. The capacity of soils/sediments for retention of these cations generally increases with certain substrates such as clay colloids and organic matter content, which refer to as cation exchange capacity (CEC) (Locke et al., 1997).

Adsorption represents a stronger binding force than cation exchange. Metal ion adsorption on both non-specific and specific sorbents depends upon the medium, as this medium affects the solubility of metals in solution, as well as the metals binding sites onto medium surface (DeBusk et al., 1996; Gevao et al., 2000; Zouboulis et al., 2004). According to St-Cyr and Campbell (1996), metals like Zn can combine with Fe through absorption and co-precipitation, and thus, if these mobilized metals come near the iron compounds formed on the plant roots, they become adsorbed on the root surface. More than 50% of the heavy metals can be easily adsorbed onto particulate matter and sediment in wetland (Yao and Gao, 2007). Studies suggested that there is competition for organic adsorption sites among Fe, Cu, Zn and Mn, for example, iron and Cu appear to be more strongly adsorbed than Zn and Mn (Tam and Wong, 1996). The adsorption of metals has changed along with the fluctuation of pH in water (Machemer and Wildeman, 1992; Sheoran and Sheoran, 2006). Some experiments showed that competitive adsorption among metals increases the mobility of metals, which highly depend on sediment properties such as CEC and particles surface area (Seo et al., 2008; Oh et al., 2009). Their works showed that Pb in the multimetal adsorption column lose its adsorption capacity significantly as the result of competition with other metals.

Infiltration of rainfall is an attractive practice not only to attenuate excessive flow during storm events but also to reduce the content of pollutants and even sustain groundwater resources (Boller, 1997). Heavy metals in stormwater runoff cause by rainfall are in colloidal, particulate, and dissolved phases (Rangsivek and Jekel, 2005). Removal processes of heavy metals in soil/sediment and other media are known to be related to the speciation of metals (Almas et al., 2006). For example, Murakami et al. (2008; 2009) suggested that sediment in infiltration facilities act as sorbent during infiltration the road runoff. They found that Cu predominantly exists as organic compounds and carbonates in road dust leachates, whereas some heavy metals (e.g., Mn, Zn, and Cd) are found to exist in the form of ions and carbonate.

3.3.2 Precipitation and co-precipitation

The proportion of insoluble heavy metals in sediments is one of factors that limits the bioavailability and toxicity of heavy metals to many aquatic ecosystems. Therefore, precipitation and co-precipitation are a major removal mechanism of heavy metals in wetlands (Yao and Gao, 2007). There are the various treatment methods which employed to remove heavy metals in wastewater, precipitation is the most general method of removing heavy metals. For example, heavy metals are removed by adjust the pH in water to the minimum solubility of heavy metals (Zhou et al., 1999). The heavy metals adsorbed on the precipitation can be removed by sedimentation and filtration (Zhou et al., 1999).

Heavy metals in wetland sediments can be removed by precipitation-adsorption phenomena (Yao and Gao, 2007). Much of the removable fraction of potentially toxic metals such as Pb, Zn, Cd, Cu, and As, can be co-precipitated with pyrite, form insoluble sulfides, and become unavailable to biota (Morse, 1994). In addition, zinc forms insoluble sulfide and carbonate compounds, and also zinc is co-precipitated with Fe and Mn oxides, which is also reported to be co-precipitated in iron plaques and adsorbed on the surface of plant roots (Otte et al., 1995; Kröpfelová et al., 2009). Under acidic conditions, ferric hydroxide surfaces will be positively charges and they will be negatively charges under alkaline conditions. So there should be conducted under acidic conditions to facilitate adsorption and removal of cationic metals such as As, Sb, and Se, Fe and alkaline conditions for co-precipitation of cationic metals (e.g., Cu, Zn, Ni and Cd) (EPRI, 1990; Yao and Gao, 2009). Heavy metals may be associated with iron and manganese oxides as a result of precipitation and co-precipitation phenomena.

3.3.3 Oxidation and hydrolysis of metals

Heavy metals may be released from anoxic sediments (sinks for pollutions) when environmental conditions change (e.g. pH, redox potential) and sediments are exposed to air, at this time sediments can act as a source of pollutants (van den Berg et al., 1999; Wilson and Chang, 2000; Hartley and Dickinson, 2010). So drying and aeration of the wetland sediment lead to falling pH and increase mobility of heavy metals (Hartley and Dickinson, 2010). Generally speaking, it is accepted that the change of redox potential in sediments is also one of the most major factors controlling heavy metal mobility (Salomons and Stigliani, 1995; Zoumis et al., 2001). With the increase of redox potential in sediment, the oxidization rate of metal sulfides and the degradation rate of organic matter will increase correspondingly, which can accelerate the release of the heavy metals adsorbed (Calmano et al., 1993). Heavy metals may form sulphide in anoxic conditions, but they can form more soluble sulphates under oxidized conditions (Singh et al., 1998; Stephens et al., 2001). *Acidithiobacillus ferrooxidans* are able to catalyze the oxidation of ferrous to ferric iron under acidic conditions. The reaction can be expressed as: $4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+$. The release of H^+ ions into pore water will decrease the pH of sediment, the resulting acid conditions affect the solubility of iron hydroxide and then cause a secondary release of heavy metals ($Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O$) (Küsel, 2003; Hartley and Dickinson, 2010). Some of this release material will be re-adsorbed onto the mobile binding compounds. For example, with increase of redox potential in sediment, a stable Cd compound will decrease from 65% to 30% and form a more labile mobile form (Zoumis et al., 2001; Kelderman and Osman, 2007; Peng et al., 2009).

Therefore, with the annual variations of water levels (flooding), wetting and drying variations of the sediment markedly affect the heavy metal presents seasonal release and fixation (Zoumis et al., 2001; Hartley and Dickinson, 2010). Therefore, in the developing and constructing process of wetlands, for decreasing the release of metal from sediment, oxidation of sediment should be avoided (Peng et al., 2009). These situations are very significant in some seasonally flooding rivers. For example, in Woolston Canal, arsenic has been removed 88% of the total from the original sample after wetting and drying (oxygenation) in the laboratory conditions, a substantially higher proportion than other elements. While the removal of Fe, Ni, Zn, Cu, Cr and Pb mobility are 39%, 29%, 16%, 13%, 5% and 5%, respectively (Hartley and Dickinson, 2010).

3.3.4 Metal carbonates and sulfides

According to the previous researches, the heavy metals may remove in the form of carbonates together with their hydroxides. Suspended particles adsorb both of heavy metal carbonates and heavy metal hydroxides and form their components. Carbonates can be significant in initially sinking metals. Although carbonates are less stable than sulphides, they may be transformed to more stable forms following the initial formation (ITRC 2003; Sheoran and Sheoran, 2006). Most metals cations can combine with CO_3^{2-} and S^{2-} forming slightly soluble carbonates and sulfides compounds. A great amount of Cu and Mn carbonates have accumulated in some natural wetland sediment (Sobolewski, 1999). Water quality can be improved through the precipitation of metal carbonates and sulphides as decreasing the acidity of environment waters (Sheoran and Sheoran, 2006; Cao et al., 2009). Copper forms very insoluble compounds with sulphion, including both cupric (CuS) and cuprous (Cu_2S) sulfides (Sobolewski, 1999). In addition, in wetlands, Cu may be intercepted by complexation with plant litter or other organic matters (Dulaing et al., 2006). Lead can form insoluble compounds (e.g., PbS) under anaerobic conditions.

4 Conclusions

Heavy metals in urban environments (including surface dust, soil and waters) have adverse effects on environment and human life health. Urban stormwater runoff is regarded as one of the most prevalent sources of water quality impairment in the estuaries and lakes, which transfers pollutants from urban surface to waters. Toxicities and bioavailabilities of heavy metals in urban stormwater runoff are very complex and dependent on many interrelated chemical, biologic, and physical processes. These processes may vary over time, environment condition and among microorganisms, plants, animals and human beings. Using wetlands to treatment urban stormwater runoff is an effective and low-cost management strategy. High metal removal rates in both natural and constructed wetlands are more than 95% for some special heavy metals. Therefore, it’s very important to understand the basic mechanisms and processes control the metal removal by wetlands, which can increase the probability of success of the treatment wetland application.

Stormwater runoff from the urban impervious surfaces continues to be an important cause of degradation to freshwater. The urban impervious surfaces accumulate a large number of dry and wet deposition pollutants which will dissolve and release heavy metals when they meet waters. Then pollutants (e.g. heavy metals) can be removed by physical, chemical and various biologic processes which involve sedimentation, filtration, sorption, precipitation, co-precipitation.

Under certain circumstances, more than 99% of heavy metal entering into aquatic environment can be stored in wetland sediments in different forms. While sediments act as adsorbents that adsorb heavy metals from water in wetlands. Sediments with a high heavy metal content risk being entered into aquatic environments as well as releasing metal ions by desorption. Hence it is very important to study the sorption and desorption behavior of heavy metal by wetland sediment receiving urban stormwater runoff. However there are some barriers which are time constraints and a lack of reproducibility that using actual urban runoff in sorption experiments is not practical. Some investigators prepared artificially urban stormwater runoff water which is artificial percolating water from surface dust by deionised water, diluted nitric acid deionised water or river water. In the future studies, actual urban runoff can be mimic artificial urban runoff, which make the urban runoff allowing the setup of a reproducible, reliable and constraint-free experimental scheme.

Therefore, an applying knowledge of the entire mechanism from living to non-living components of the ecosystem can provide valuable insight into the overall wetland function and structure. Understanding this mechanism is surely going to be more helpful to evaluate heavy metal removal performance of the constructed and natural wetlands and to assess the functional integrity of anthropogenic influenced, restored and mitigations wetlands and the optimization of remediation technologies fitting for polluted wetland.

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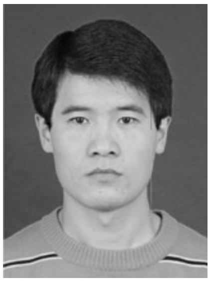

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