CHAPTER II

LITERATURE REVIEW

2.1 Heavy metals in stormwater runoff

Heavy metals in stormwater runoff are mostly from the operation of motor vehicles, direct fallout, and the degradation of road materials. Moreover, related sources of metals include gasoline (Pb), diesel fuel (Cd), exhaust emissions (Pb, Ni), crankcase and lubricating oils (Pb, Ni, Zn), grease (Zn, Pb), tire wear (Cd, Zn), coating on moving part (Cu, Pb), decorative and protective coatings (Al, Cd, Cu, Zn, Ni, Fe), brake lining wear (Cu, Cr, Ni), moving engine parts (Fe, Mn, Cr, Co), and asphalt paving wear (Ni, V). Most metal species, except Cu and Cd, are in particulate form. In general, the quantities of heavy metals in runoff and the forms they exist depend on the physical and chemical properties of the metals themselves (Harper, 1998).

According to the NURP (U.S. EPA, 1983), Cu, Pb, and Zn, are the most commonly found heavy metals in stormwater runoff. On a United States national basis, freshwater acute toxicity criteria for Cu were exceeded in 47 percent of the samples and for Pb in 23 percent of the samples. Freshwater chronic toxicity criteria were commonly violated for Pb (94 percent), Cu (82 percent), Zn (77 percent) and Cd (48 percent) (Harper, 1998).

Table 2.1 shows the concentrations of Cu, Pb, Cd and Zn in runoff from different areas. From Table 2.1, the concentrations of Cu, Pb, Cd and Zn in different areas are different. Even within the same area, the concentrations of these heavy metals vary with land use.

Table 2.1 Heavy metal concentrations in stormwater runoff

References	Concentration (µg/l)			
	Cu	Cd	Pb	Zn
NURP[1]	114	-	653	528
Typical urban storm water[2]	35	8	150	150
Nationwide Statistics[3]				
Mean	34	0.7	140	160
Range	4-560	0.7-30	3-28000	10-5570
San Francisco Bay Area[4]				
Mean	46.6	2.21	114.6	312.8
Range	NA*-46.6	1.66-3.07	51.7-151	188-371
Urban runoff in Paris[5]				
Roof runoff				
Mean	37	1.3	493	3422
Range	3-247	0.1-32	16-2764	802-38061
Yard runoff				
Mean	23	0.8	107	563
Range	13-50	0.2-1.3	49-225	57-1359
Street runoff				
Mean	61	0.6	133	550
Range	27-191	0.3-1.8	71-523	246-3839
Santa Monica Bay Area[6]				
Mean	59.3	-	16.8	2090.3
Range	40-103	-	4-45	1321-2601

NA* - Not available

[1] Pitt and Shawley, 1981

[2] Stanley Associates Engineering, 1992

[3] Horner et al., 1994

[4] BASMAA, 1996

[5] Gronmaire-Mertz et al., 1999

[6] Lau et al., 2001

[7] Coast River Environmental Services Ltd., 2002

2.2 Theory of Heavy Metal Sorption

The adsorption of a metal onto a solid substance is described by:

$$M + S \longleftrightarrow MS \tag{1}$$

where M is the metal sorbate, S is the solid sorbent and MS is the metal-solid sorbent complex. Metal sorbate molecules are held on the surface of the sorbent principally by two mechanisms, chemisorption and physisorption. Chemisorption is a covalent bond between the sorbate and sorbent. Physisorption is a weak, reversible attraction between the sorbate and sorbent. The major sorption mechanism of metals to the carbonaceous sorbents is physical entrapment of the metal into internal pores (i.e., physisorption).

The amount of sorbate that a sorbent can accumulate is determined by generating an equilibrium sorption isotherm, which is a plot of the equilibrium aqueous concentration (Ceq - mass sorbate/volume of solution) versus the corresponding sorbed concentration (Csorb - mass sorbate/mass sorbent). There are several isotherm models used but the most common are the Langmuir and Freundlich adsorption models. Only the Freundlich model is reviewed here since it is used in this study.

The Freundlich adsorption isotherm model is based on sorption on unlimited heterogeneous surface, which has been considered an empirical relationship. It is described by:

$$Csorb = K_f \times Ceq^{n} \tag{3}$$

or

$$\log Csorb = \log K_f + n \log Ceq \tag{4}$$

where K_f is the Freundlich coefficient and n is the nonlinearity constant. The unit of K_f depends on the units of Ceq and Csorb and the value of n (dimensionless). The sorbent capacity is described by K_f, while the strength of the sorbate-sorbent interaction is described by n. Larger K_f values represent a greater sorbent capacity, while smaller n values represent a stronger interaction.

2.3 Previous Studies on Heavy Metal Sorption

A large number of adsorbents were tested for the removal of heavy metals from solutions. Coal impregnated with sulfonyl groups (Suneeth Kumar, 1987) and iron oxide coated sand (Benjamin et al., 1996) were some of the examples of low-cost adsorbents studied. Gabaldon et al. (1996) and Leyva-Ramos et al. (1997) investigated the use of activated carbon for removing heavy metals from water. Biosorbents, such as biological aerobic sludges (Chang et al., 1995; Atkinson et al., 1996), *Streptoverticillium cinnamoneum* biomass (Puranik and Panikar, 1997), fungi (Nagendra Rao, 1989; Sharma, 1990), shrimp chitin (Chui et al., 1996), non-living sewage sludge (Solari et al., 1996), chitosan *N*-benzyl sulfonate derivatives (Weltrowski et al., 1996), were tested for their abilities to sorb heavy metals in aqueous solutions.

Natural materials or waste products from industrial or agricultural processes with large adsorptive capacities can be ideal sorbents. They are abundant, require little processing, and can be disposed of in a sustainable manner if necessary (Bailey et al., 1999). These materials include soybean hulls (Nitirach, 2002 and Marshall et al., 1999), peanut shells (Watwoyo et al., 1999), rice husk (Lee et al., 1999), wheat straw (Kumar et al., 2000), apple residues (Lee et al., 1998), and sawdust (Ajmal et al., 1998).

Wood tends to adsorb copper and chromium ions in comparatively equal quantities (1.8 - 3.2 mg/g and 1.5 - 3.2 mg/g, respectively), depending on the wood species. The copper and chromium sorption capacities of wood degraded by white and brown rot fungi are approximately 2-3 times higher than normal wood, while those for wood digested by grub for copper and chromium ions are 3.0 mg/g and 1.0 mg/g, respectively (Iiyama et al., 2001).

U.S. EPA (1997) used tailored compost made from leaves, which has high organic contents, in stormwater filtration system. They are best used for sediment, particulate nutrients, organic carbon, hydrocarbons, and some heavy metal removal (Center for Watershed Protection, 1995/1996). The leaf compost filter removed 88% of zinc, 61% of chromium and 67% of copper (Stewart, 1992).

Lister et al. (2001) used sewage sludge and paper mill waste for biosorption of metals (Cd, Cu, Zn and Pb). Sewage sludge was more effective in removing heavy metal from water. However, 3-month-composted paper mill waste removed heavy metals significantly more than the ordinary paper mill waste.

The compost stormwater filter (CSF) media are pellets of composted leaves with a high sorptive capacity. The composted leaves structure has pore spaces to trap particulate metals and surface area for removal of dissolved metals by ion exchange. The ion exchange property is from humic substances that are produced during the composting process. Thus, Stormwater Management, Inc. (Portland, Oregon) has developed and copyrighted compost filtration in highway and parking lot runoff treatment (Conrad, 1995). Kellems et al. (2003) reported that the CSF media can remove 97% dissolved Cu and 94% dissolved Zn.

Grimes et al. (1999) studied the availability and binding of heavy metals (Cd, Cu, Pb and Zn) in compost derived from household waste. There are two possible sources of strong interaction between metals and compost: (1) the interaction of heavy metals within the inorganic fraction lattice; and (2) complexing interaction with potential ligands in the organic fraction. Moreover, they found that the relative binding of these metals to household waste compost is in the order Pb $>$ Cd $\approx$ Cu $>$ Zn.

2.4 Composting

2.4.1 Definition

Composting is the biological process for decomposition of organic matter to simpler substances under controlled conditions. It depends on microbial activity. Thus, the efficiency of composting is dependent on environmental conditions that affect microorganisms.

2.4.2 Important parameters in aerobic composting

The basic environmental conditions present in composting system are oxygen, pH, temperature, moisture, material disturbance, organic matter and the particle size as well as activity of microbial populations.

2.4.2.1 Particle size

Microbial activity usually occurs on the surface of the particles. Therefore, decreasing particle size increases surface area that encourages microbial activity and promotes the rate of decomposition. However, the excessively small particles pack together too hard and inhibit the air flow through the pile. This decreases the oxygen available to microorganisms within the pile and lessens the rate of microbial activity.

2.4.2.2 Carbon-to-nitrogen (C/N) ratio

Microorganisms need carbon and nitrogen for their growth. Organic carbon provides energy and cellular building. Nitrogen is an important component of the proteins, nucleic acids, amino acids and enzymes. In general, materials that are green and moist tend to be high in nitrogen, and those that are brown and dry are high in carbon.

2.4.2.3 Moisture content

Microorganisms needs water in their activity, so decomposition occurs fast in the liquid film on the surface of particles. Too little moisture inhibits microbial activity while too much moisture obstructs the diffusion of air into the pile.

2.4.2.4 Temperature

Decomposition occurs most rapidly during the thermophilic stage of composting (40-60°C), which lasts for several weeks or months. This stage also is important for destroying thermal sensitive pathogens, fly larvae, and weed seeds. Most species of microorganisms cannot survive at temperatures above 60-65°C. After the thermophilic phase, the compost temperature drops, and at this point, decomposition is taken over by mesophilic microbes through a long process of curing or maturation.

2.4.2.5 Air requirements

Oxygen is essential for the metabolism and respiration of aerobic microorganisms. During composting, the oxygen concentration falls and the carbon dioxide concentration increases. Anaerobic conditions will occur if the oxygen concentration drops below 5%. Mixing and turning promotes aeration by loosening up and increasing the porosity of the compost ingredients.

2.4.2.6 pH

As microorganisms decompose organic matter, they release organic acids. In the early stage of composting, these acids accumulate and make pH drop. The low pH encourages the growth of fungi and the breakdown of lignin and cellulose. The organic acids become further broken down during the composting process and as the compost matures it will approach a neutral pH of 7. If the system becomes anaerobic, acid accumulation can make pH drop to 4.5, limiting microbial activity. However aeration is enough to return the compost pH to acceptable ranges.

Table 2.2 presents the proper values of important parameters in aerobic composting. However, it is difficult to define the optimal course of composting as it depends on utilization aims.

2.4.3 Composting time

The composting process can take from 2 months to 2 years, depending on effort involved. A number of factors are important in controlling the composting process and the time that the process takes. These factors are the important parameters in aerobic composting above (temperature, moisture, oxygen, particle size, the carbon-to-nitrogen ratio of the waste and the degree of mixing or turning). In general, the more actively these factors are controlled, the faster the process.

Table 2.2 Optimum design considerations for aerobic composting process (adapted from Tchobanoglous et al., 1993).

Parameter	Comment
Particle size	The suitable size should be between 25 and 75 mm (1 and 3 in).
Carbon-to-nitrogen (C/N) ratio	The optimum carbon to nitrogen ratios (by mass) should be between 25 and 50 for aerobic composting. Nitrogen may be a limiting nutrient at higher ratios, while at lower ratios, ammonia is emitted and biological activity is also slowed.
Moisture content	The optimum moisture content should be between 50 and 60 percent during the composting process.
Mixing/turning	During composting, material should be mixed or turned to prevent drying and air absent. Frequency of mixing or turning is dependent on composting operation type.
Temperature	Temperature should be maintained between 122 and 131°F (50 and 55°C) for the first few days and between 131 and 140°F (55 and 60°C) for the remainder of the active composting period. If temperature is above 151°F (66°C), biological activity is decreased.
Air requirements	For optimum results, air with at least 50 percent of the initial oxygen concentration remaining should pass all parts of the composted material.

Table 2.2 Optimum design considerations for aerobic composting process (adapted from Tchobanoglous et al., 1993) (Cont.)

Parameter	Comment
pH control	The optimum pH for aerobic decomposition should be at 7 to 7.5. To reduce the loss of nitrogen in the form of ammonia gas, pH should not rise above 8.5.

Tiquia et al. (2002) used 63 composting days to study dynamic of yard trimmings composting. Barrington et al. (2002) determined the effect of carbon source on compost nitrogen and carbon losses by composting pine shavings alone and with soybean and long grass supplements, hay alone and with urea and long wheat straw supplements, and chopped oat straw for 21 days. Kulcu and Yaldiz (2004) investigated the kinetics and optimal aeration rate for composting a mixture of agricultural wastes consisting of grass (54%), tomato (10.6%), pepper (20%), and eggplant (15.4%).

2.4.4 Effects of composting parameters on compost properties

Jeris and Regan (1973), Stentiford (1996), and McCartney and Tingley (1998) reported that moisture content is the critical design and operating factor of engineered compost systems because the decomposition of organic matter depends on the presence of water to support microbial activity.

Liang et al. (2003) studied the influence of temperature and moisture content regimes on the aerobic microbial activity of a biosolids composting blend. Both moisture content and temperature influenced the microbial activity of biosolids blends; however, moisture content was more influential than temperature. Fifty percent moisture content seems to be the minimal requirement for rapid increase in microbial activity. On the other hand, a range of 60–70% provided maximum activities. In the range of 30–60% moisture content, the higher the moisture content the higher the microbial activities. Sixty percent moisture content seemed to be the optimal for biosolids composting.

Schloss et al. (2000) used the analysis of variance (ANOVA) to assess the influence of mixing during composting of dog food (Big Red Puppy Food, Pro-Pet Inc., Syracuse, NY). The mixing affected temperature, moisture content and effluent oxygen. It decreased the compost temperature by releasing heat. It reduced the rate of moisture loss. It promoted the constant rate of oxygen use in microorganisms but had no effect on the total amount of oxygen used.

Tiquia et al. (1996) evaluated the effects of three moisture levels, 50% (pile A), 60% (pile B) and 70% (pile C) on the composting process of spent pig-manure and sawdust litter. The results showed that the moisture content influenced the microbial activity and temperature. In pile C, the high moisture content restricted gas diffusion that leaded to confining microorganisms' oxygen use. Moreover, the decomposition process in pile C was slower while there were insignificant differences between pile A and B. This indicated that between 50 and 60% moisture content were suitable for microbial activity of spent litter. The microbial parameters stabilized after 60 days. Thus, 2 months would be adequate for composting the spent litter to be mature.

Nelson et al. (2003) investigate the effects of moisture content on the composting process and final composted product of feedlot manure. The mass reduction of the 40 and 50% MC were significantly more than the 60 and 70% MC. The final volume measurement was taken when the material was still in windrow form and thus contained a pore structure with free air space. The 40 and 50% treatments show low volume.

Lei and VanderGheynst (2000) studied microbial community structure during composting of grape pomace and rice straw. They investigated the effects of inoculation and pH adjustment. The result of initial pH adjustment (4.11-5.98) showed that higher pH made the compost material more suitable for colonization by thermophilic bacteria. Thus, initial pH adjustment increased the time composting process was exposed to thermophilic temperature. Based on this and above studies, initial pH adjustment and moisture content are significant factors that can affect the quality and characteristics of the final compost.

2.4.5 Composter

Composter is a reactor used for composting process. The Cornell Waste Management Institute designed a two-can bioreactor (Figure 2.1) to be used as small-scale indoor composting units for families and a classroom educational tool. The bioreactor consists of two different size garbage cans. The smaller can is drilled sufficient holes and placed inside the bigger one. A brick or some other object is placed at the bottom of the bigger can to separate the leachate from the compost.

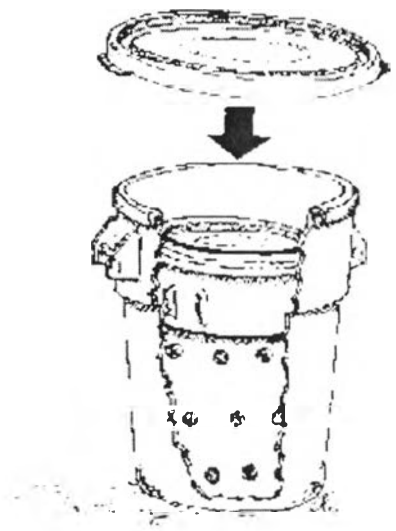

Figure 2.1 A two-can bioreactor developed by the Cornell Waste Management Institute.

2.5 Cation exchange capacity

Cation exchange capacity (CEC) is defined as the amount of positive charges that materials can hold. It is commonly used to represent the degree to which a soil can adsorb and exchange cations including heavy metals. CEC is expressed in milliequivalents per 100 grams (meq/100g) of soil or centiequivalents per 1 kg (ceq/kg) of soil. The larger this number, the more cations the soil can hold. Organics in soils are the main source of CEC. Increasing the organic matter content of any soil will help to increase the CEC. A clay soil, usually richer in organics, therefore tends to have larger CEC than a sandy soil.