CHAPTER I

Copper in the Urban Water Cycle

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ABSTRACT: Increasingly stringent regulation of wastewater effluents has forced communities to consider control of copper inputs. To aid these efforts, this work identifies the various sources of copper in the urban environment and considers the benefits of each. The work also synthesizes information on the removal of copper in wastewater treatment plants and provides an overview of wastewater regulations. This review will help communities to develop an active, more holistic approach to reducing copper inputs and draw attention to improved copper removal at wastewater plants.

I. INTRODUCTION

Low concentrations of heavy metals such as copper can impact the ecology of natural waters under at least some circumstances. Consequently, regulations for discharge of copper to the environment have recently become more stringent. In some areas deemed to be especially susceptible to environmental harm from copper discharge, such as the San Francisco Bay, the allowable copper concentrations are so low that passive removals obtained in conventional wastewater treatment processes are not sufficient to meet discharge limits. Thus, as a first step in rationally developing strategies to meet the limits, it is useful to consider the sources and sinks of copper in the urban water cycle and the perceived benefits and detriments of each. The collection, treatment and disposal of copper will then be discussed along with corresponding national and international regulations.

As an overview to this cycle, in the urban setting (Figure 1-1) water flows containing copper enter surface waters through one of two primary sources including storm water runoff from transportation areas, lawns, and fields or discharge of treated wastewater. While there is often some intermixing of these waters in a given system, the origin of copper within each is relatively distinct. Water treatment plants use surface waters and, after treatment, distribute water to homes and businesses that use the water and then discharge it as wastewater. While every aspect of this cycle is not present in all urban situations, the presentation does highlight key interdependencies which are important to understanding this complex problem.

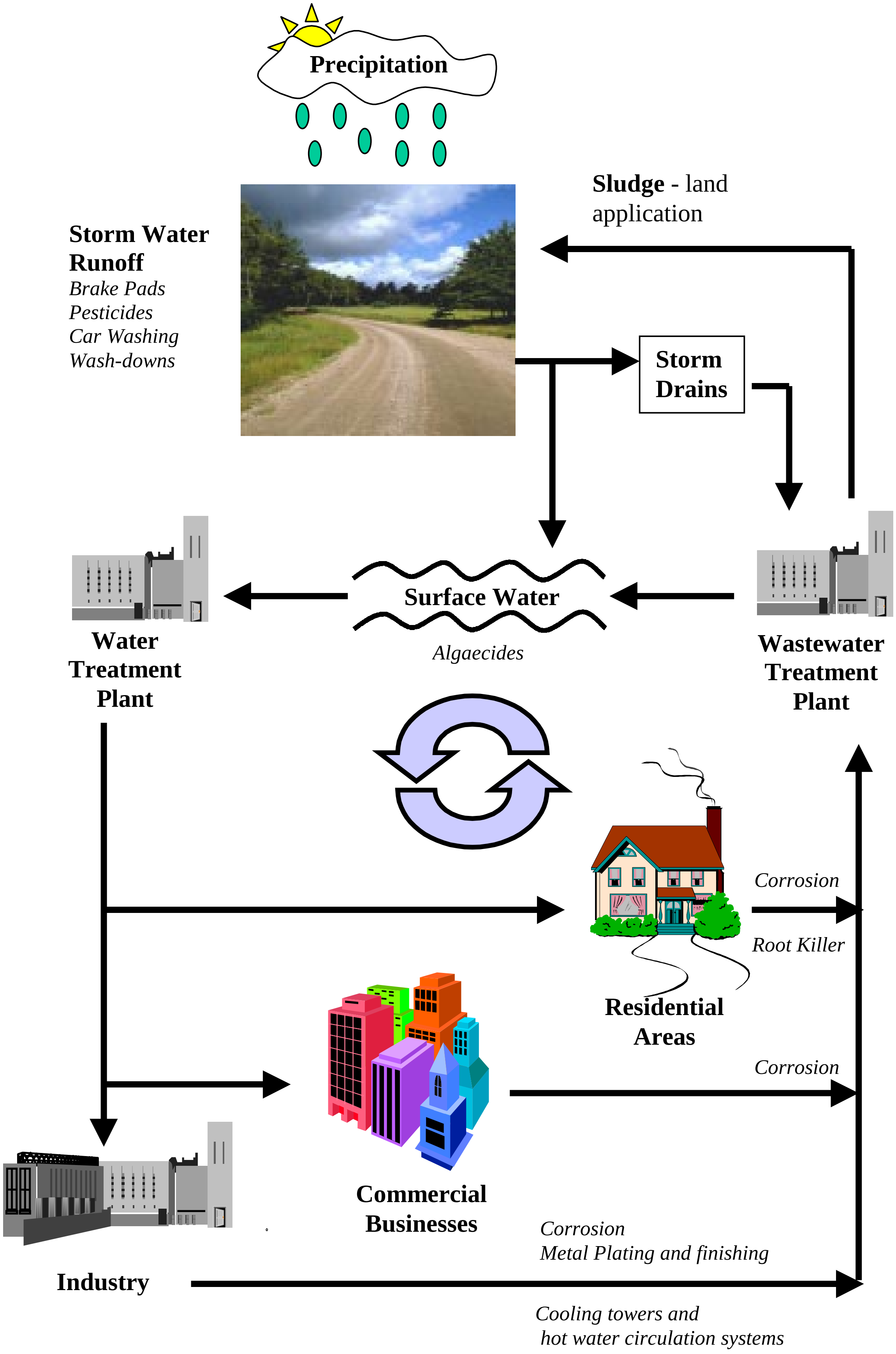


Figure 1-1: Copper in the urban water cycle.

II. SOURCES OF COPPER IN THE URBAN WATER CYCLE

Copper in the urban water cycle is derived from a variety of sources (Table 1-1). For the purpose of this work, industrial sources are defined as businesses that manufacture products while commercial sources sell services and manufactured products. How significant is each source in the context of the urban water cycle? To address this question, several mass balances on influent copper to WWTP's were collected from: Palo Alto, CA; Torrington, CT; Boulder, CO and the Netherlands.

At the outset, it should be noted that the entire process of constructing a mass balance for copper is fraught with uncertainty. While communities know the total amount of copper inputs to the sewage treatment plant with a fairly high degree of precision, they attempt to estimate industrial and commercial inputs through extrapolation of grab sample results. Other inputs are also quantified to the extent possible, for example, in Boulder, the contribution of copper from root killer was determined by sales of these products in local hardware stores. Thereafter, corrosion of plumbing is assumed to account for whatever remains. This result should be viewed with some skepticism.

Table 1-1 Sources of copper in the urban water cycle

Source	Description	Perceived Benefits	Perceived Detriments	References
Industrial	Used in metal plating/finishing, circuit board production, and paint products. Produced through smelting and used in heat transfer applications such as cooling towers.	Unique benefits and characteristics	In rare circumstances can be released to storm sewers	City of Palo Alto (1996), Kennedy Jenks Consultants (1995)
Commercial	In products used by metal fabricators, vehicle service facilities, medical facilities, construction areas, laboratories, automobile parts stores, plumbing businesses, hardware stores and others.	N/A	Can be discharged directly to sewers and storm drains	City of Palo Alto (1996)
Residential	Corrosion of washing machines, present in consumer products, foods, fecal matter and runoff from lawn care and car washing.	Essential in the human diet; sometimes useful in consumer products	Might be deterimental when consumed in very high concentrations (10 – 20 grams)	City of Palo Alto (1996), Von Arx (1996), Petterson (1995)
Plumbing Materials	Corrosion by-product release from copper plumbing.	Pathogen control properties; relatively high resistance to corrosion	Contributes to copper loading through sewer	Gaunt (1995), City of Palo Alto (1996)
Brake Pads	Contain copper which is gradually introduced to the environment in a particulate form through wear.	Unnecessary material in brake pads	Particles washed into storm drains	Engberg (1995)
Algaecides	Algaecides including copper sulfate pentahydrate (blue stone), copper enolate (Cutrine Plus), and copper citrate (Cupeos)	Control of THMs, taste and odor problems	Copper added to drinking water source	Canale et al. (1997), Meister (1996)
Pesticides	Pesticides including copper hydroxide, copper sulfate, copper carbonate, copper oxide and copper oxychlorides	Control of pests in agricultural operations	Runoff into surface waters and storm drains	Meister (1996)
Root Killer	Commercially sold copper sulfate solid dosed to toilets.	Slowly kills roots clogging sewage pipes	Contributes slugs of copper to WWTPs	Tuwiner (1977)

In a majority of the mass balances collected (Figure 1-2), corrosion of drinking water pipes is the primary contributor of copper to the WWTP. Food and industry are also very significant. However, there is considerable variation between communities. For example, in Boulder, CO root killer is the main source while it is not even considered in the other three studies. This is surprising given the widespread availability of root killer, and it is possible that this potential source was overlooked and falsely attributed to corrosion.

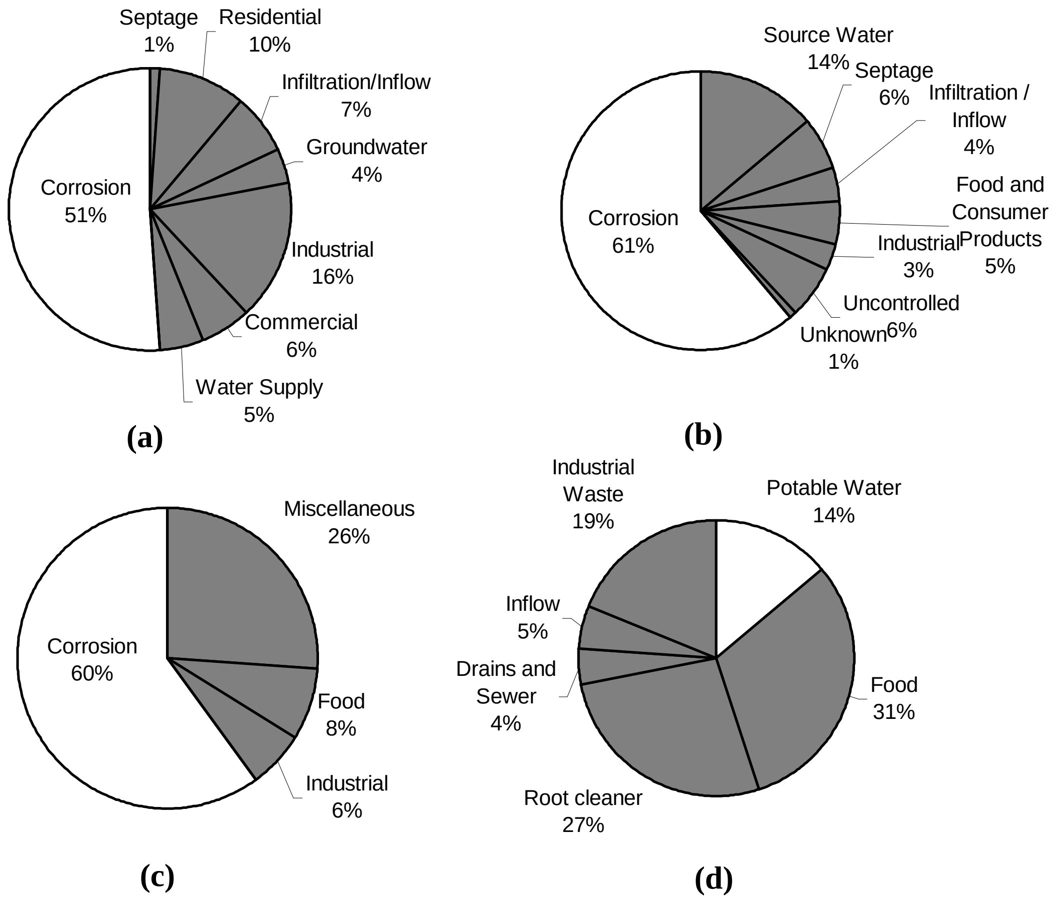
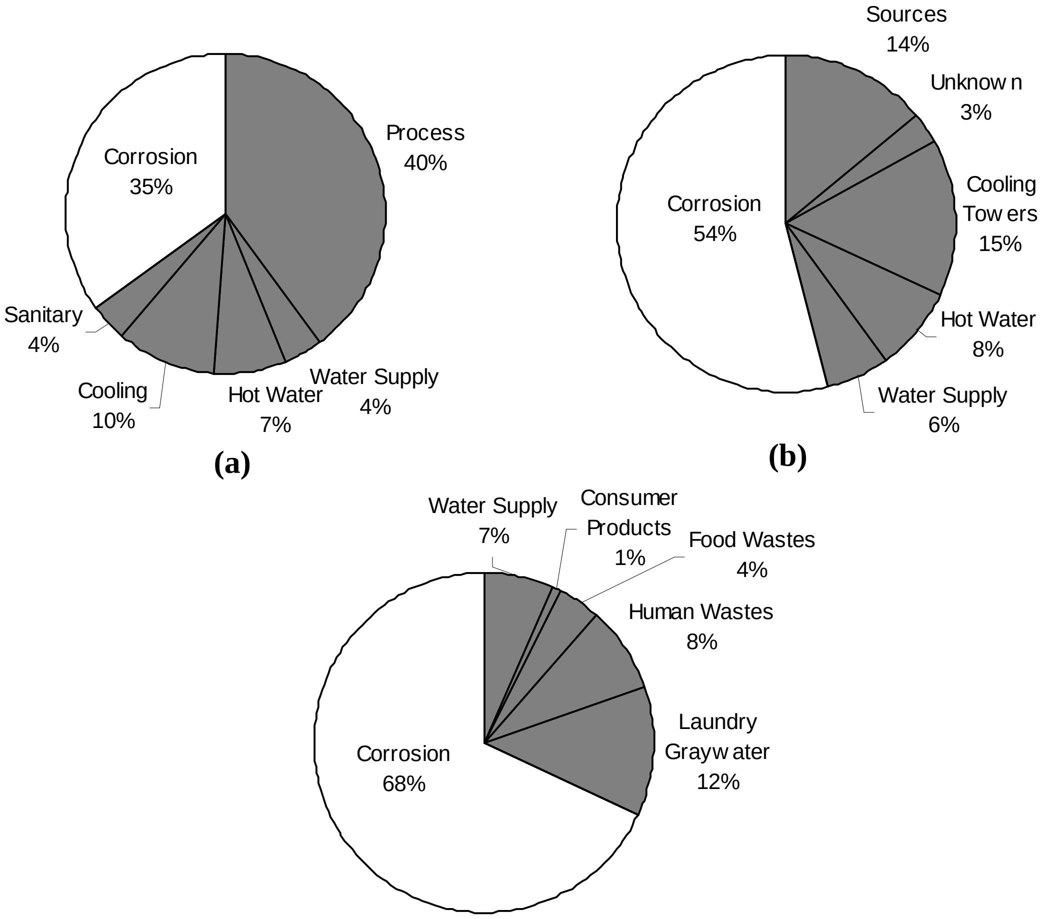


Figure 1-2: Wastewater treatment plant copper sources for: (a) Palo Alto, CA (City of Palo Alto, 1996), (b) Torrington, CT (Curtis et al., 1994), (c) The Netherlands (Van den Hoven et al., 1995), and (d) Boulder, CO (City of Boulder, 1995).

Consistent with the mass balances in Figure 1-2, the Massachusetts Department of Environmental Protection found that corrosion of copper pipe contributed 31%, 34%, 49% and 61% of the total copper influent to four regional WWTPs (Isaac et al., 1997). In combination, these five studies strongly suggest that the corrosion of drinking water pipes is a large contributor of copper to WWTPs.

The City of Palo Alto further broke down its copper contributions into Industrial, Commercial and Residential categories (Figure 1-3). These studies serve to highlight the fact that copper pipe corrosion is a key contributor to the overall commercial and residential categories in the previous figure, further reinforcing the importance of this source.



(a) **(b)**

(c)

Figure 1-3: Breakdown of the wastewater treatment plant copper sources for Palo Alto, CA (a) Industrial, (b) Commercial and (c) Residential.

Viewed from the perspective of copper concentration in sewage influent (Figure 1-4), corrosion contributes as little as 20 ppb to sewage influents in some cities and as much as 130 ppb in others, indicating that corrosion is a highly variable copper source.

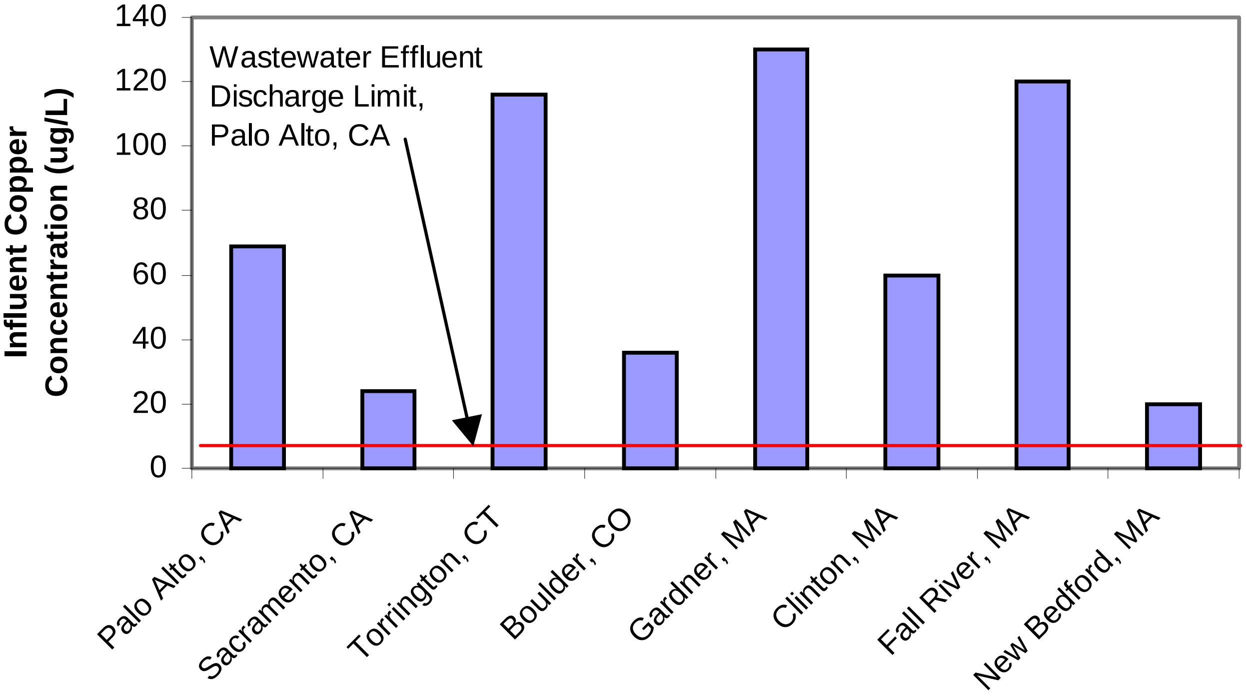


Figure 1-4: Comparison of wastewater treatment plant influent copper concentrations due to corrosion.

It is notable that drinking water effluent limits for metals are significantly higher than wastewater effluent limits. For example, the U.S. Environmental Protection Agency (EPA)'s drinking water action limit for copper is 1300 ppb while the wastewater effluent limit for Boulder, Colorado is 16 ppb (Edwards et al., 1997) and for Palo Alto, California it is 4.9 ppb (Figure 1-4). In other words, the wastewater effluent standard is 81 times more stringent than the EPA's drinking water action limit in Boulder and 265 times more stringent in Palo Alto. Given that wastewater effluent discharge limits are so low, and copper contributions to WWTP's from plumbing corrosion are relatively high, it may be wise for communities to take a closer look at corrosion control practices when planning to reduce copper in wastewater effluent.

III. PERCEIVED BENEFITS OF COPPER IN THE URBAN WATER CYCLE

To identify potential means of reducing copper in source water, it is useful to carefully examine each source and document its purported benefits (Table 1-1).

A. Root Killer

Root growth in sewage pipes produces a mechanical obstruction leading to odor problems and blocked pipes (Tuwiner, 1977). In order to combat this problem, residents sometimes pour "root killer" into their toilets or municipalities sprinkle it along clogged pipe sections. Most root killers sold in hardware stores consist of water soluble copper sulfate crystals. Recommended doses of root killer for a single household range from 0.70 to 4.0 pounds of product per year, which translates to approximately 0.2 – 1.0 pounds of elemental copper if the root killer is pure copper sulfate (Roebic Laboratories, Inc., 1999). This copper is then directly transported to a wastewater treatment plant.

In addition to concerns over copper loading to the environment, root killers are also not likely to be an immediate solution to a clogged sewer line although copper sulfate can immediately reduce odors due to the breakdown of fungi within the root mass (Tuwiner, 1977). Even if roots are killed, it takes several months for them to decay completely and wash away. It follows that consumer use of root killer as a "quick fix" treatment for clogged sewers is inappropriate.

B. Algaecides and control of disinfection by-product precursors

Copper compounds such as copper sulfate pentahydrate (blue stone), copper enolate (Cutrine plus) and copper citrate (Cupeos) are dosed to source waters as algaecides. Algae and plankton can cause problems for water treatment such as tastes, odors and high turbidity. Blue-green algae produce a toxic compound that is poisonous to cows and pigs that drink water from eutrophic lakes (Horne et al., 1994). Furthermore, reactions between organic matter and certain disinfectants can form carcinogenic disinfectant by-products (DBP's). Organic matter, or the total organic carbon (TOC) in a surface water, consists mainly of material produced by algae, watershed point and nonpoint inputs, and extracellular carbon products from various biological sources within the watershed (Canale et al., 1997). The control of algae, especially in eutrophic waters in which phosphorus levels and subsequent algae growth are high, is therefore important in reducing the formation of DBPs.

Trihalomethanes (THM's) are a type of DBP that forms when organic matter reacts with chlorine. A multiple regression statistical model of THM formation was developed by Canale et al. (1997) and is given by Equation 1-1:

$$THM = a_0 DOC^{a_1} (Cl_2)^{a_2} T^{a_3} pH^{a_4} (Br^-)^{a_5} t^{a_6} \qquad \text{Equation } 1-1$$

where a = model coefficient; DOC = total dissolved organic carbon concentration (mg/L); Cl_2 = chlorine dose (mg/L); T = temperature (^oC); Br^- = bromide ion concentration (ug/L); and t = reaction time (h). This model illustrates the importance of lowering the dissolved organic carbon content in source waters, through processes such as algaecide application, in order to ultimately reduce the formation of DBPs.

A typical copper compound dose for algae control is approximately 100 – 200 ug/L as copper sulfate based on the total reservoir volume (Hoehn, 1998). However, prior to mixing some of the applied copper may be precipitated as a solid such as malachite which can rapidly settle to the bottom of lakes (Horne et al., 1994). Moreover, any copper that remains in solution will be passed on to the water distribution system and eventually the WWTP. A total copper concentration of 100 ug/L is not expected to pose a drinking water problem since the national drinking water action limit is 1300 ug/L. It could, however, be more significant in wastewater effluent compliance since wastewater discharge is typically regulated to the range of 40 to 200 ug/L total copper (Hall, 1997). Therefore, copper dosing for algae control should consider the benefits of algae and THM control and the possible detrimental impact on wastewater compliance.

C. Disinfectant properties of copper tube and pathogen control

Copper is bacteriostatic, or toxic to many bacteria, viruses and cysts. This property makes copper useful in the paint used on ships to prevent fouling by marine growth and in coating pilings used in marine environments (Gaunt, 1995). Indeed, copper was one of the first disinfectants used in drinking water treatment. In fact, two medical maxims used in India around 2000 B.C. advised that water be "treated by boiling and 'by dipping into it a piece of hot copper' and then filtering it" (Baker, 1948). Given this illustrious history, it is not surprising that modern experimentation confirmed that copper piping helps to eliminate unwanted microorganisms from drinking water.

For example, Rogers et al. (1991) tested the growth of *Legionella pneumophila* bacteria on various plumbing materials. Copper inhibited the growth of the Legionellae wheras glass and plastic did not. Although not directly relevant to drinking water, Dr. Phyllis J. Kuhn (1983) compared the relative bactericidal effects of brass (67% copper and 33% zinc) and stainless steel doorknobs. Agar plate studies revealed that the bacteria cultures on the brass doorknobs contained only sparse streptococcal and staphylococcal growth while the cultures on the stainless steel doorknobs contained heavy growth of both gram-positive and gram-negative organisms. In a later study, this researcher exposed innocula of various bacteria species including e-coli to a strip of copper. After exposure to the copper, many of the microbes died within 15 minutes (Kuhn, 1983).

D. Human micro-nutrition

Copper is an essential element of the human diet since it cannot be synthesized by the body. The World Health Organization (WHO) has established acceptable range of oral intake (AROI) data for copper. The lower limit of the AROI is 20 kg/ug/day for adults and 50 ug/kg/day for children (Lagos, 1997). For a 60 kg adult, this figure works out to 1.2 mg/day of copper required for health. This is very close to daily copper intakes compiled by Pettersson (1995) for industrialized countries (Table 1-2), indicating that average copper intake around the world is not excessive compared to dietary needs.

Table 1-2: Daily copper intake in various countries

Country	Sex	Number of participants	Age	Copper intake (mg/d)
U.S.A. (Seattle, WA)	M/F	295	adults	1.3-2.2
Denmark	M	100	30-34	1.2
Sweden	M/F	80	20-55	1.3
Finland	M	40	Middle age	2
Norway	M	20	40-49	1.0

Copper combines with certain proteins to produce enzymes that act as catalysts. Some key functions include synthesis and maturation of red blood cells (prevention of anaemia), the formation of bones, the functioning of the circulatory and central nervous system and biological production of energy within cells. If copper is deficient in the diet, health problems occur such as impaired immunity, ultragrowth and biochemical alterations in lipid metabolism and in the bones. Developing countries, in particular, experience a high frequency of copper deficiency among children (Dieter, 1995).

Foods that are naturally rich in copper include nuts, seeds, chickpeas, liver and oysters (Table 1-3). Other foods that generally provide up to 50% of the required copper intake include cereals, meat and fish.

Table 1-3: Copper content of selected foods and beverages (after The National Academy of Sciences, 1977)

Food	Copper (mg/100 g edible portion)	Food	Copper (mg/100 g edible portion)
Apples, fresh	0.08	Tomatoes, fresh	0.10
Apricots, fresh	0.12	Almonds, dried	0.14
Avocados, fresh	0.4	Brazil nuts	1.1
Bananas, fresh	0.2	Hazelnuts	1.35
Cantaloupe, fresh	0.04	Walnuts	0.31
Dates, dried	0.21	Cornflakes	0.17
Figs, dried	0.4	Oatflakes	0.74
Olives, green	0.46	Wheat germ	1.3
Raisins, dried	0.2	Eggs, whole, raw	0.03
Strawberries, fresh	0.13	Beef liver	2.1
Kidney beans	0.11	Turkey, medium fat	0.2
Lima beans	0.86	Pork, loin or chops	0.09
Carrots, fresh	0.08	Cod	0.5
Lentils, dried	0.70	Haddock	0.23
Lettuce, fresh	0.07	Lobster	2.2
Peas, dried, split	0.80	Oysters	3.6
Potatoes, raw	0.16	Salmon (Atlantic)	0.2
Spinach, fresh	0.20	Shrimp	0.4

E. Animal and Bacterial Nutrition

Many aquatic organisms need a minimal amount of copper in their diet. Crustaceans and molluscs need copper to ensure the proper functioning of the copper-containing haemocyanin, their main oxygen carrying blood protein. A theoretical estimate for the minimum metabolic requirement of copper in molluscs and crustaceans has been calculated to be 26.3 mg copper/kg dry weight (Lagos, 1997).

Copper is essential in the diet of livestock. In fact, copper is used as a growth promoter for livestock by mixing copper into animal feed. For example, 35 mg copper per kilogram of feed is added to food fed to pigs the first 16 weeks of life (The National Academy of Sciences, 1977). After excretion, this copper can potentially be washed into a nearby stream as part of the runoff from a rain event. Copper is also necessary for the processes of nitrification and denitrification to occur in wastewater treatment plants since bacterial enzymes concerned with nitrate transformations require the presence of copper (Horne et al., 1994). The approximate copper requirement for bacterial growth in wastewater treatment is 0.02 ug/mg biomass COD formed (Grady et al., 1999).

IV. PERCEIVED DETRIMENTAL IMPACTS OF COPPER IN THE URBAN WATER CYCLE

Despite the numerous benefits of copper in water systems, copper can be toxic to biological organisms at high concentrations. This section will discuss copper toxicity and its effects on humans and aquatic organisms. Aquatic bioavailability of copper will also be reviewed.

A. Copper and Human Toxicity

Toxicity is defined in two ways, acute and chronic (Ariens et. al., 1976). Acute toxicity is toxic effects that are directly related to the ingestion of a poisonous substance and is a short term effect. Chronic toxicity is toxic effects in which there is an ingestion of small quantities of the toxic substance over a long period of time leading to toxic concentrations and thus to symptoms of poisoning. Acute human toxicity which can affect the blood, the liver, the kidneys and the brain generally occurs when 10-20 grams of soluble copper salts are ingested at one time. However, vomiting and abdominal pain have been reported after ingestion of as low as 10-15 mg of copper (Pettersson, 1995).

Chronic toxic effects of copper in humans are rare due to the sophisticated copper overload rejection methods employed by the human body. Some individuals are genetically susceptible to chronic effects including those that suffer from two rare conditions known as Wilson’s Disease and Indian Childhood Cirrhosis (ICC). People with Wilson’s Disease carry an inherited defect that prevents the excretion of copper via the liver, allowing copper to build up to high concentrations. ICC is one of the most common causes of death of young children in India and is similar to Wilson’s Disease (Pettersson, 1985). The main difference between the two diseases is that the onset of ICC is within a year while it usually takes at least five or six years for copper to build up in the liver with Wilson's Disease (Dieter, 1995).

For the general population, exposure to copper comes from three main sources: air, food and water. Air is a relatively small source of copper and is estimated to provide 0.6 ug/day. In the majority of cases, the highest daily copper intake is from food and is approximately 1500 ug/day. While the intake values for air and food are relatively constant, copper intake from water varies considerably depending on the qualities of the water consumed. A typical daily intake of copper in drinking water is 150 micrograms while a very high daily intake is 3000 micrograms (Gaunt, 1995). The range of daily copper intakes from drinking water can greatly influence the distribution of intake sources (Figure 1-5). Accordingly, the intake of copper could become a potential health problem in the few instances where copper in drinking water is high. Drinking water regulations for copper, discussed in a later section, are therefore useful in minimizing potential health problems.

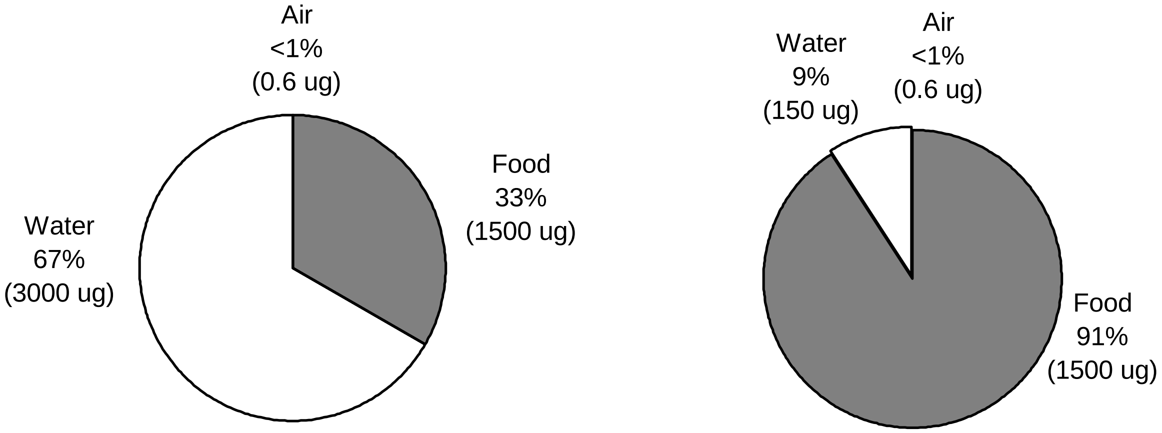


Figure 1-5: (Left) Daily copper intake distribution where the total copper concentration in drinking water is 3000 ug/L; (Right) Typical distribution of copper intakes for the average population.

B. Copper and Ecotoxicity

The toxicity of copper in the aquatic environment has been reviewed extensively by several researchers (Klawiter, 1998; Lagos, 1997; Renner, 1997; Allen, 1997; Sloof et al., 1989; Nriagu, 1988). In general, the toxicity of copper to aquatic species is orders of magnitude higher than it is for humans (Hodson et al., 1979). For example, in soft, fresh water a copper concentration of 0.01 to 0.02 mg/L total copper has been found to be toxic to some fish (The National Academy of Sciences, 1977). Marine invertebrates are even less resistant to copper toxicity in that some species of phytoplankton can be inhibited by as little as 0.006 mg/L total copper (The National Academy of Sciences, 1977).

The magnitude of toxic effect varies greatly among aquatic species. In fact, values of lethal total copper concentrations differ from 5 to 100,000 ug/L (Hodson et al., 1979). Partial lists of copper toxicity values for various freshwater organisms have been documented (Janus et al., 1989; Hall et al., 1997). Low dissolved copper concentrations, on the order of 1-10 ug/L, tend to affect smaller aquatic organisms such as diatoms and invertebrates while higher concentrations, in the range of 100-1000 ug/L dissolved copper, are typically necessary to produce toxic effects in fish (Table 1-4).

Table 1-4: Summary of toxic effects expected for various copper concentrations in waters with moderate to high bioavailablity (after Lagos, 1997)

Total dissolved copper conc. range (ug/L)	Characterization of toxic effects
1-10	Significant effects are expected for diatoms and sensitive invertebrates, notably cladocerans. Effects on fish could be significant in freshwaters with low pH and hardness
10-100	Significant effects are expected on various species of microalgae, some species of macroalgae, and a range of invertebrates, including crustaceans, gastropods, and sea urchins. Survival of sensitive fish will be affected and a variety of fish should have sublethal effects
100-1000	Most taxonomic groups of macroalgae and invertebrates will be severely affected. Lethal levels for most fish species will be reached
>1000	Lethal concentrations for the most tolerant organisms are reached

The variability in toxicity values is partly due to the ability of each organism to regulate internal copper concentrations. For example, adult bivalve mollusks are known to remove and store copper through metabolism with subsequent excretion and sequestering (Greer et al., 1995). The specific effects of copper on aquatic organisms also vary. Some examples are: decrease in respiration in mollusks due to gill damage, greening in oysters, prevention of settling and attachment in barnacles and scallops (Bryan, 1971) and poor growth and increased susceptibility to disease among certain species (Greer et al., 1995).

C. Bioavailability of Copper in Receiving Streams

The toxicity of a given copper concentration in aquatic systems is influenced by many factors including the pH, salinity and temperature of the water, the age and type of the aquatic species, the concentration of mineral and organic matter and whether or not the copper is bioavailable (The National Academy of Sciences, 1977). The latter criterion has recently received a large amount of scrutiny because surface water regulations are based on total copper concentrations rather than bioavailable copper.

Bioavailability is defined as the degree to which chemicals in the environment (e.g., water, sediment, food items) can actually be taken up by organisms (Lagos, 1997). The more bioavailable a chemical, the higher the toxic potential. The bioavailability of metals in aquatic environments is currently a heavily debated topic, mostly due to the fact that metal toxicity appears to be site and species specific. Copper in aquatic environments is routinely classified as particulate and dissolved, with the dissolved fraction further classified as free, inorganically complexed and organically complexed (Figure 1-6).

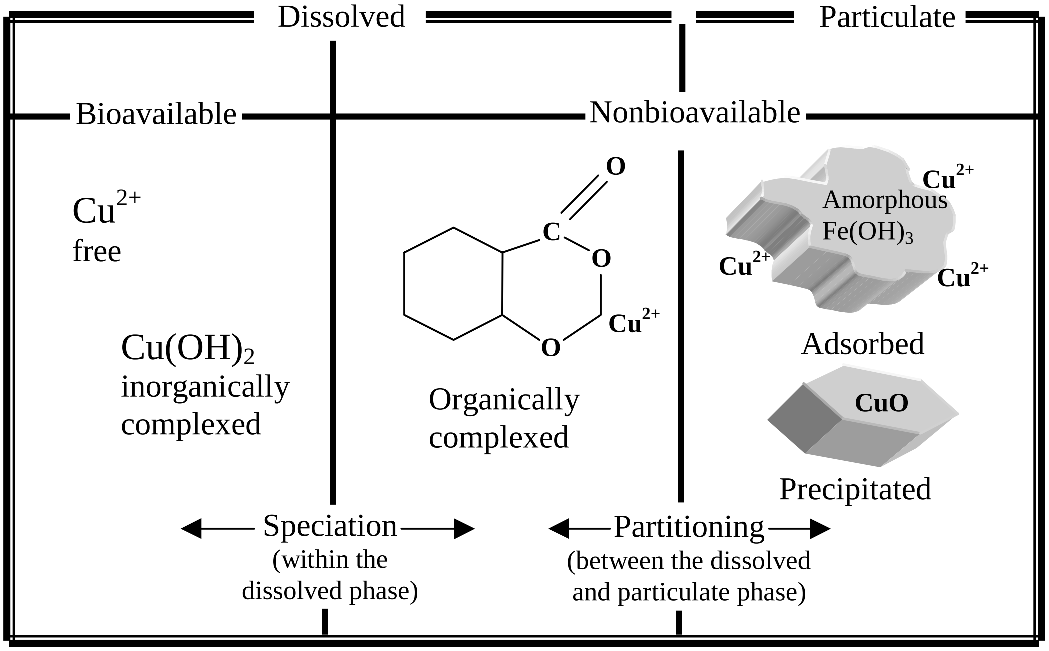


Figure 1-6: Forms of copper present in aquatic environments (after Paulson et al., 1993).

The most widely bioavailable form of copper that is toxic to aquatic life is often referred to as *labile* copper which includes free copper and easily dissociable and exchangeable inorganic complexes (Slooff et al., 1989). However, speciation changes with water quality which can make copper more or less bioavailable.

The chemical and physical properties of a surface water strongly influence copper toxicity. One of the most influential water quality parameters is the amount of complexing material present (Hodson et al., 1979). The more organic matter present, for example, the more bound copper and the lower the copper toxicity. Inorganic complexing material also plays an important role in reducing copper toxicity. For example, high alkalinity waters complex carbonate with copper to form non-toxic complexes (Snoeyink et al., 1980). Because calcium and magnesium ions compete with copper for binding sites on organisms, higher water hardness also tends to reduce copper toxicity.

The pH of a water has a seemingly contradictory effect on copper toxicity. Hydrogen ions compete with copper ions for organism binding sites decreasing toxicity at low pH, but a larger fraction of the copper is free at low pH, increasing toxicity (Klawiter, 1998). Renner (1997) found that the amount of total copper required to kill 50% of fathead minnows increased with pH, indicating that the effect of the cupric ion is dominant over the effect of hydrogen ions competing for binding sites in this case. In general, the more saline the water, the less toxic the copper due to inorganic complexation of copper. However, both increased salinity and increased temperature might also stress aquatic organisms lowering their natural defenses against copper toxicity.

Besides water quality, copper toxicity is also affected by the mode of toxic action in the particular organism. For example, toxic effects experienced by fish depend on the extent to which copper binds to the gills of the fish. Receptor sites on the gill surface, which are negatively charged ligands, bind with organic matter, inorganic ions such as sodium, calcium and magnesium, and metals such as copper. The extent to which gill sites are available for binding with copper will determine the extent of copper toxicity (Allen, 1997).

Although few and far between, some copper toxicity regulations incorporating water quality have been instituted and will be discussed in a later section. Researchers are in the process of developing a new modeling approach to be used in metal toxicity determination and regulation. For example, the International Copper Association has sponsored a group of researchers to develop a model in which metal species in receiving waters are considered to interact competitively between receptor sites on aquatic organisms, ligands and particulate matter in the receiving water. This model would allow for direct incorporation of bioavailability concepts such as metal species variation, pH and hardness (Allen, 1997; Renner, 1997).

V. “SINKS” FOR COPPER IN THE URBAN ENVIRONMENT

Copper in the urban water cycle is collected and treated in various ways in order to reduce copper input to surface waters and drinking waters. Once water containing copper is discharged to a sanitary sewer, it is carefully treated in a wastewater treatment plant before release to the environment. In some cities that have combined storm water and sanitary sewers, all water passes through the same rigorous treatment whether it is flushed down the toilet or collected in street storm drains. However, most cities have separate sewers for storm water runoff which occasionally discharge directly to the environment, usually with some type of pre-treatment.

All types of treatment provide an opportunity for copper removal. However, most existing removal of copper is passive; that is, the primary intent is to achieve other goals such as removal of soluble organic matter, particulates, pathogens and nutrients. Some removal of copper also happens to occur during these processes. This is worth noting because very little research effort has been devoted to identifying conditions that markedly improve copper removal. Moreover, since copper is a conservative substance (cannot be transformed into another substance), all the copper that is removed from a water must appear in some other form elsewhere. In the case of sewage plants, the removed copper is concentrated in the small amount of residual solids that leave a sewage plant as sludge. Depending on its composition and governing regulations, this sludge must ultimately be used as a fertilizer/compost, or properly disposed of in a landfill or hazardous waste site.

A. Removal of Copper in WWTPs

A thorough review of the literature demonstrates that passive removal of copper varies widely from study to study. In this review we classified reported removal based on whether it was a full-scale treatment plant, a smaller scale pilot plant designed to simulate a full scale plant, or a much smaller laboratory scale reactor study. There are a large number of unknown variables that might be influential in the copper removals reported; for example, under ideal conditions percent metal removal has been found to increase linearly with sludge age (Stephenson, 1987). In any case, for the data collected in this review, percentage copper removal was typically highest at full scale plants and lowest in lab scale studies (Figure 1-7).

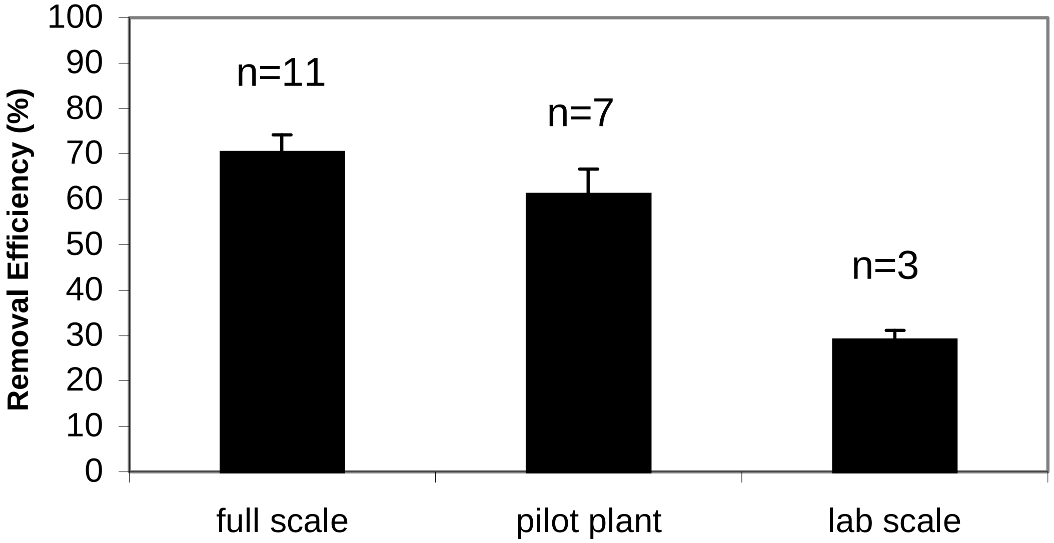


Figure 1-7: Average removal efficiencies achieved by various treatment plants (error bars indicate 95% confidence interval for data compiled from Stephenson (1987), City of Palo Alto (1996), Oliver et al. (1974) and Edwards (1995).

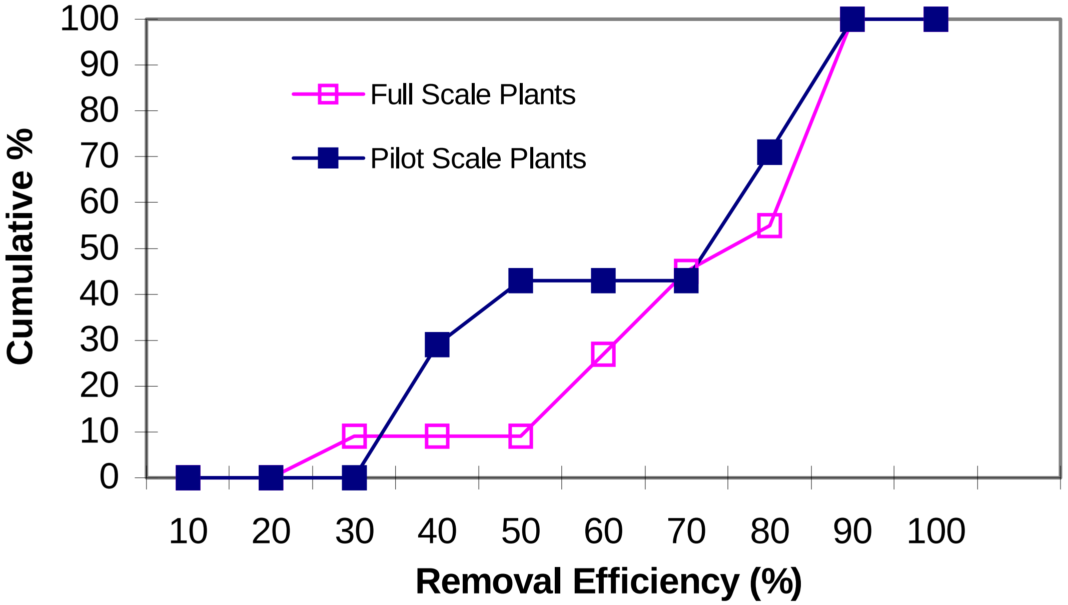


Figure 1-8: Cumulative distribution of removal efficiency data for full scale and pilot scale plants.

Plotting the data as a cumulative distribution better illustrates the range of removals that have been reported (Figure 1-8). At full scale plants, 50% of all plants achieved less than 70% copper removal efficiency and 50% of all plants achieved better removal. Meanwhile, 50% of the pilot scale plants achieved greater than 68% removal efficiency and 50% achieved less. The reported removals varied from 25% to 90% for full scale plants and 33% to 83% for pilot scale plants.

What can account for this extremely wide variation in copper removal? Some researchers have attributed the variability in copper removal efficiencies to differences in process configurations within different WWTPs. For example, some plants that achieve very high removal efficiencies treat their sludge by direct vacuum filtration and sludge incineration rather than digestion. The process of sludge digestion concentrates some of the copper into a supernatant that is pumped back to the headworks of the WWTP. Metals concentrations in supernatants have been noted to be 10-300 times more concentrated than the influent heavy metals concentration (Brown, 1973). In other words, at plants that employ sludge digestion, the copper is removed from the water, but a significant portion is put back after treatment. Vacuum filtration and sludge incineration processes do not allow this.

Other researchers have emphasized the importance of an efficient secondary treatment process. A recent study by Edwards (1995) tracked the speciation of copper as it traveled through a wastewater plant. Although a significant portion of copper is removed during primary settling processes, most copper is removed through adsorption to microbial flocs (particulate biomass) used in the activated sludge process (Figure 1-9). Because the biomass is recycled continually to treat the sewage, particulate copper levels build up in this stage of treatment to the milligram per liter level.

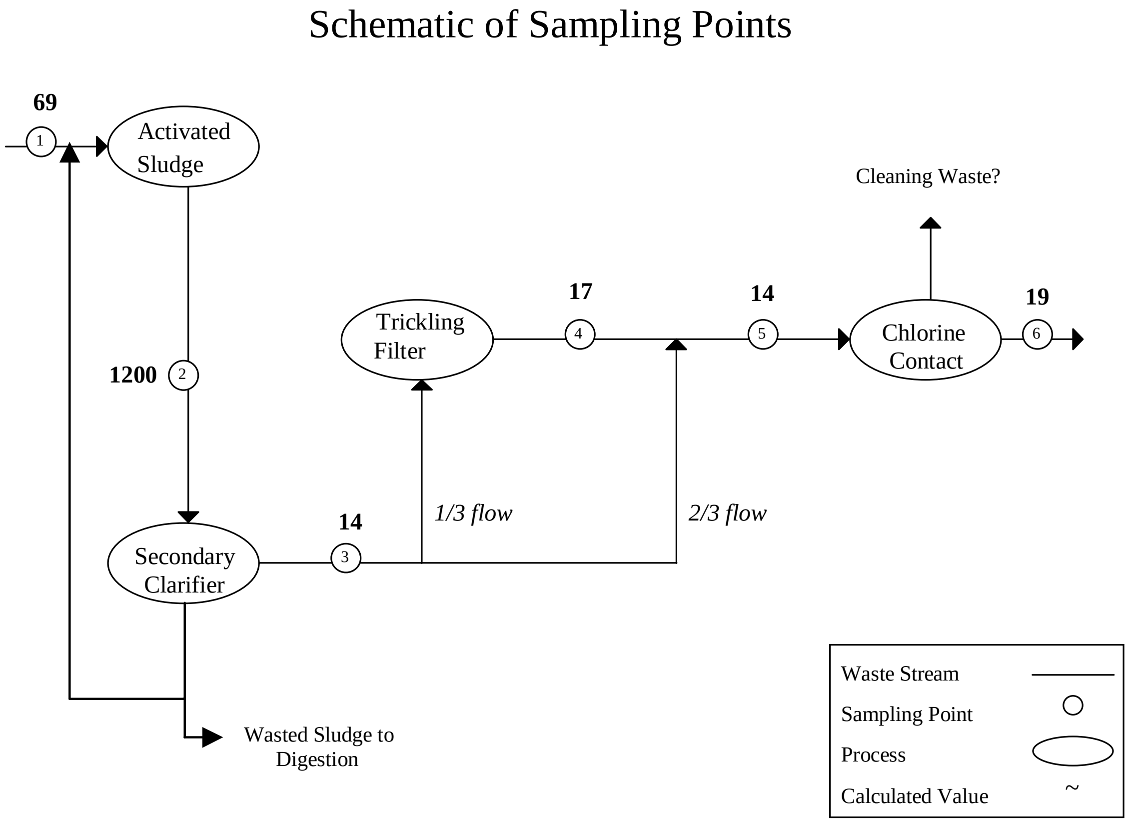


Figure 1-9: Summary of copper sampling results through the Boulder WWTP (Edwards et al., 1996). Inflow and outflow values are expressed in µg/L total copper.

After the activated sludge process, the particulate copper in the biomass is settled from the water, leaving behind relatively clean wastewater for discharge to the environment. However, what if this solid liquid separation is not working with 100% efficiency? In the case of Figure 1-9, the particulate copper concentration is about 1200 ppb. If the solid liquid separation is 99% effective, which is quite good, then 12 ppb of particulate copper will be discharged from the secondary clarifier. If the separation is only 95% efficient then 60 ppb of particulate copper will be discharged. Even though the speciation of this copper could be altered after chlorination, sulfite quenching of the chlorine or subsequent mixing with the surface water, it is clear that effluent copper concentrations can be strongly dependent on settling efficiency in the secondary clarifiers.

Examining the literature on copper removal at various stages of wastewater treatment, percent copper removal during primary treatment varies from 20-45% while the removal during secondary treatment varies from 40-80% (Figure 1-10). This is probably because primary treatment processes can only remove particulate copper (Lester, 1979), whereas secondary treatment allows soluble copper uptake into the biomass of growing microorganisms. This discussion strongly indicates that copper speciation in the sewage as it enters the plant can alter the site and mechanisms of removal.

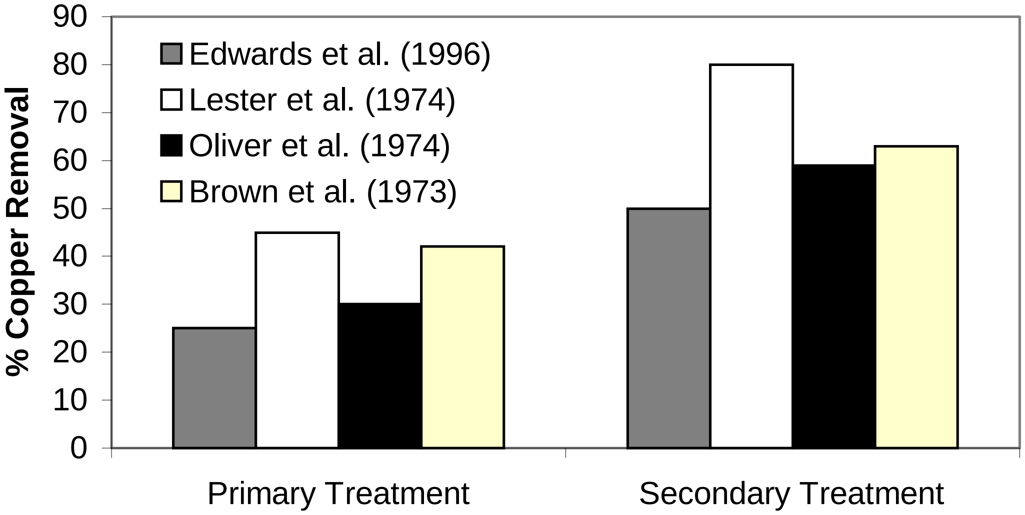


Figure 1-10: Copper removal in different stages at wastewater treatment plants (Edwards, 1995), (Edwards et al., 1996).

One study found that most of the copper in wastewater effluent is in a soluble form (passed through a 0.45 µm pore size filter) and suggested that this fact should be reflected in treatment processes (Oliver et al., 1974). This finding was confirmed by Lester, 1983, who determined soluble copper by passage through a 0.40 µm filter. In contrast, another study concluded that between 30 and 80% of the copper in the wastewater effluent at Boulder, Colorado WWTP was in the particulate form not passing through a 0.45 µm pore size filter (Edwards et al., 1996). The variability noted in the Edwards study support the notion that effluent copper is highly dependent on small variations in the sludge settling process, water quality and other factors. In support of this assertion, Keiding et al. (1996) found that when activated sludge is diluted, bacterial flocs sometimes quickly release soluble extracellular polymeric substances (EPS) in the wastewater. Since soluble EPS can bind soluble species such as copper, an increase in soluble EPS could result in an increase in soluble copper in the wastewater effluent. Future research should determine whether heavy rain events increase soluble copper concentrations via this mechanism.

Many approaches have been noted to improve copper removal. Bethel (1995) found that copper removal could be enhanced by minimizing the mixed liquor concentration in order to maximize biological growth and uptake of copper. Other suggestions for more efficient copper removal in WWTP's have been made including Sterritt et al.'s recommendation of an approximate 15 day sludge age (Sterritt, 1980). The City of Palo Alto modified their filter backwash procedures by ceasing pre-chlorination before backwashing, since the chlorine was apparently solubilizing the copper. If plant operators wish to stray from strictly conventional treatment, one researcher found that co-precipitation of copper by ferric coagulation could improve copper removal substantially (Karthikeyan et al., 1997). This was further confirmed by a survey of 20 wastewater treatment plants revealing that many of the plants using ferric chloride coagulation achieved superior copper removal (City of Palo Alto, 1994).

B. Discharge of Copper in Storm Waters

Storm water runoff is a significant source of copper to the environment. One study reported that storm drain discharges from Santa Clara County, California contained more than five times the amount of copper discharged by the three WWTPs in the South Bay, California area (Engberg, 1995). Another study in which first flush samples were collected from 10 industrial sites concluded that the most common metals found in the runoff were copper and zinc (Line et al., 1996). The main industrial contributors of copper found in this study were textile and food production industries. Other sources of copper in storm water runoff include leaks from automobiles, accidental spills, road debris, roof runoff and agricultural pesticides.

The fate of copper in urban storm water can follow several paths (Figure 1-11.) To illustrate, in a combined sewer system copper is contributed to the wastewater treatment plant influent by both wastewater (32%) and runoff water (68%). In the sewer lines, 5% of the copper is lost from leaks in the pipe while 71% is incorporated into sludge and 24% is discharged to surface water.

The copper that is incorporated into the sludge is often deposited on agricultural soil as a fertilizer.

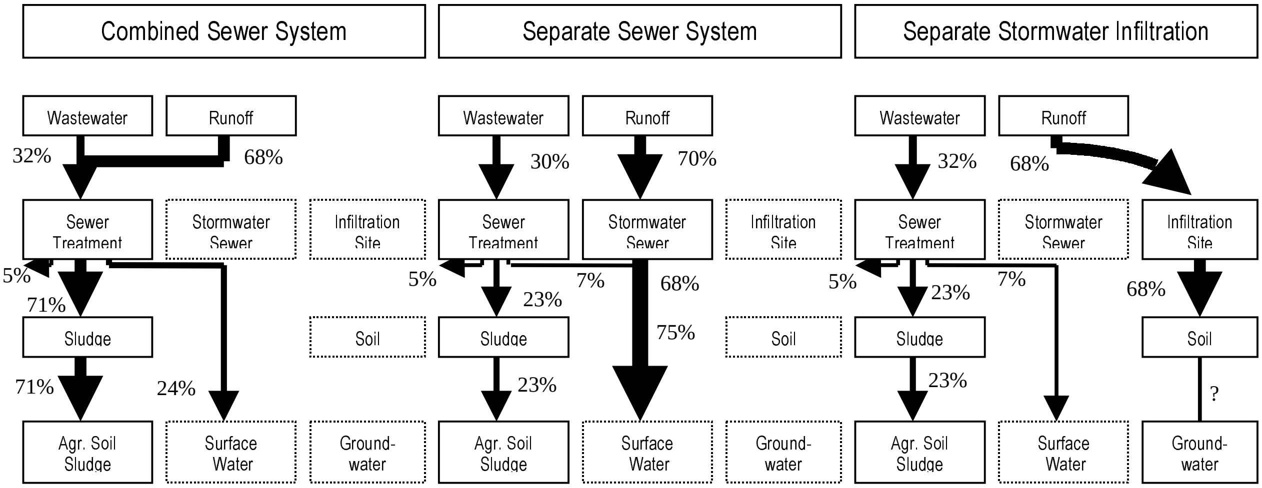


Figure 1-11: Three potential urban drainage systems [after (Boller, 1997)]. Percentages show relative mass flow of copper.

In the case of a combined sewer system, most of the copper is transferred to sewage sludge. In contrast, separate sewer systems do not allow for the collection of runoff. The runoff is instead allowed to directly enter surface water bodies. In these systems, copper accumulates in stream and lake sediments. A more conventional urban stormwater system might include provisions for storm water infiltration. These systems incorporate artificial infiltration areas that concentrate the runoff by a factor of 5-100 depending on the infiltration structure and soil permeability. When separate stormwater infiltration systems are used, copper is concentrated in the infiltration site which can be controlled and managed.

VI. REGULATIONS ON COPPER INPUT TO THE URBAN WATER CYCLE

The previous section examined ways in which copper is collected, treated and discharged to the environment. Before discharge can occur, there are numerous regulations in place that must be adhered to. This section will summarize regulations on drinking water, secondary sewage effluent and secondary sewage sludge.

A. Drinking Water Regulations

Countries around the world have established a range of guideline values for copper in drinking water at the treatment plant and at the consumer's tap (Table 1-5). For example, France has a very conservative guideline of 0.05 mg/L total copper leaving the water treatment plant, while Sweden is more liberal with a guideline value of 1.0 mg/L total copper. Some countries, such as the United States, only regulate copper at the tap due to the heavy contribution of copper from corrosion in water distribution systems. Guideline values at the tap range from 1.0 mg/L in Finland to 3.0 mg/L in The Netherlands and the United Kingdom.

Table 1-5: Summary of Guidelines for Recommended and Maximum allowable Total Copper at the Plant and at the Tap (Hedberg, 1996)

Country	**Recommended/ Maximum**	**At plant (mg/l)**	**At tap (mg/l)**
Denmark	Recommended		
	Maximum	0.1	3*
Finland	Recommended		
	Maximum		1.0
France	Recommended	0.02	
	Maximum	0.05	
Germany	Recommended		
	Maximum		3*
The Netherlands	Recommended		
	Maximum	0.1	3.0
Norway	Recommended	0.1	1*
	Maximum	0.3	
Sweden	Recommended	0.05	
	Maximum	0.3-1	0.2-1; 2*
United Kingdom	Recommended		
	Maximum		3.0
U.S.A.	Action Level		1.3
	Recommended		1.0
1995 Proposal for EU directive	Recommended		
	Maximum		2.0

*sample is taken after a 12 hour stagnation time

As evidenced by the apparent variability in world-wide drinking water regulations for copper, there is no clear universal consensus on a health-based drinking water guideline value for copper. In fact, it has been suggested that existing guideline proposals are based on incomplete information from unpublished reports and that these guidelines should be reassessed (Fitzgerald, 1995). In 1993, the World Health Organization (WHO) set a health-related guideline value of 2.0 mg/L total copper based on a provisional mean tolerance daily intake (PMTDI) of 0.5 mg/kg body weight. This figure is stated as being “based on a rather old study in dogs.”

The “dog study” was conducted in 1971 by the Warner Lambert Research Institute in New Jersey. During the 6 to 12 month study, beagle dogs were exposed to copper-gluconate diets at levels of 3, 15 and 60 mg/kg/day. Only 1 out of the 12 dogs suffered from elevated copper in the liver when subjected to the highest copper dose. Therefore, the no effect level was 15 mg/kg/day copper gluconate even though the summary of the report misstates this level as 5 mg/kg/day copper gluconate. Furthermore, because copper comprises only 14% by weight of copper gluconate, the doses in the study are significantly over-estimated and therefore the no effect level should have been 2.1 mg/kg/day Cu (Fitzgerald, 1995).

Even though the no effect level found in the study was 5 mg/kg/day, a safety factor of 10 was apparently imposed because the PMTDI value used to calculate the copper guideline value is 0.5 mg/kg/day Cu. In order to calculate the guideline value, drinking water is assumed to contain 10% of the PMTDI and the average person is assumed to weigh 60 kg and ingest 2 liters of water per day. The calculation is then:

$$Guideline\ Value = \frac{0.5\ mg/kg/day \times 60\ kg \times 10\%}{2\ liters/day} = 1.5\ mg/liter$$

This figure was then rounded to 2 mg/L total copper and is now the WHO’s guideline value for copper in drinking water.

Another questionable study forming the basis of a copper guideline value is the one used as the basis of the U.S. EPA’s maximum contaminant level goal (MCLG) of 1.3 mg/L total copper (U.S. EPA, 1988). This figure is based on a “party incident” in 1957 during which women ingested whisky cocktails that had been left for 2 hours in copper-containing shakers (Wyllie, 1957). The results of the study state that 10 of the 15 women involved in the study experienced symptoms of acute copper toxicity in the form of nausea, vomiting and diarrhea ½ to 1 hour after consuming the cocktails. Copper levels within the cocktails were determined in a repeat trial and the U.S. EPA claims that, based on this study, 5.3 mg is the lowest observed adverse effect level for copper. The figure of 1.3 mg/L is obtained by applying a safety factor (S.F.) of 2 and assuming that the average person consumes 2 liters of water per day resulting in the following calculation:

$$MCLG = \frac{5.3 mg/L \div 2\ (S.F.)}{2\ L/day} = 1.3\ mg/L$$

The questionable nature of this study is the assumption that consuming alcohol that contains copper (on an empty stomach) produces the same effects in people as consuming drinking water containing copper. In fact, further analysis suggests that some of the women in this study may have been intoxicated after drinking the whisky cocktails. This conclusion is based on the fact that the women in the study consumed up to 4.5 fl oz of whisky during the study (Wyllie, 1957), whereas only 3.5 drinks are required to raise blood alcohol levels to 0.10 for a 120 lb woman (legal intoxication in most states) (SEA Medical Services, Inc., 1999). It is therefore possible that the resulting intoxication caused nausea and vomiting.

B. Regulations on Discharges to Surface Waters

Aquatic organisms are more sensitive than people to copper toxicity, as was discussed in an earlier section. This fact is reflected in the regulations for surface waters. The Clean Water Act of 1972 required the U.S. EPA to publish water quality criteria (WQC) on 65 pollutants, evaluating scientific knowledge of health and welfare effects. The criteria are based on an extrapolation of acute toxicity test results to chronic toxicity values. A summary of the method used to determine WQC is provided by Allen (1997). For copper, the saltwater criteria are 4.0 ug/L total copper as a 24 hour average, and not to exceed 23 ug/L total copper at any time. The freshwater criteria are 5.6 ug/L total copper as a 24 hour average, and not to exceed:

$$Cu_{\max} \leq e^{(0.94(\ln(hardness))-1.23)} \qquad \text{Equation } 1-2$$

ug/L total copper at any time (U.S. EPA, 1985). Water hardness is expressed as mg/L $CaCO_3$ and is included in the freshwater criteria because higher water hardness tends to reduce copper toxicity.

Since 1983 U.S. regulations have included a provision for incorporating water quality into toxicity limits. This provision is called the Water Effects Ratio (WER) and it involves determining the ratio of metal toxicity in side-by-side tests using site and laboratory water (U.S. EPA, 1994). The ratio of toxicities obtained is used as a multiplier to adjust the National WQC, resulting in a more site-specific WQC. The WER allows for consideration of the bioavailability of copper and often results in much higher discharge limits but it is very expensive to implement. The U.S. EPA also issued an interim guidance in 1993 stating that *dissolved* metals can be used to set and measure compliance with water quality standards. However, a drawback of the interim guidance is that it relies on site specific information to describe toxicity effects without explaining the mechanisms that influence the toxicity such as metal speciation and partitioning (Paulson et al., 1993.)

C. Regulations on Copper in Secondary Sewage Effluent

As noted earlier, wastewater treatment plants (WWTP's) typically achieve approximately 75% removal of copper (this work). Since this percentage removal tends to stay relatively constant, the higher the copper in the influent to a WWTP, the higher the copper in the effluent (Isaac et al., 1997). Because wastewater effluents sometimes make up a significant fraction of the total flow in surface waters, the copper content of wastewater effluent can greatly influence the toxicity of a stream. As an extreme example, at certain times of the year in certain localities of the U.K., wastewater effluent may represent 90% of the flow in surface waters (Lester, 1983).

In the United States, municipal and industrial wastewater discharges are regulated by the Clean Water Act with National Pollutant Discharge Elimination System (NPDES) permits. NPDES permits are site specific and depend on the flow rate and concentration of a contaminant already in the receiving stream. In the simplest case, the downstream concentration of a contaminant is chosen based on the WQC for that receiving stream and the allowable contaminant concentration in the effluent is calculated based on the following formula (Allen, 1997):

$$C_{dr} = \frac{Q_{ur}C_{ur} + Q_{ef}C_{ef}}{Q_{ur} + Q_{ef}} \qquad \text{Equation } 1-3$$

where Q is the flow rate and C is the concentration of the contaminant. The subscripts dr, ur and ef stand for down river, up river and effluent, respectively. The NPDES permits require treatment plants to use total recoverable copper for effluent limitations. The discharge permit limit is then set such that the discharge will cause an exceedence of the WQC no more than once in three years.

Because the EPA allows water quality standards to be measured as dissolved copper, a chemical translator is required to distinguish the relationship between particulate and dissolved metal concentrations (U.S. EPA, 1996). The translator is based on the partition coefficient, K_d :

$$K_d = \frac{C_p}{C_d \times TSS} \qquad \text{Equation } 1-4$$

Where C_p is the concentration of particulate metal, C_d is the concentration of dissolved metal, and TSS is the concentration of total suspended solids. K_d has been found to be site specific (Allen, 1997).

Since the concentration of total recoverable copper, $C_{T,}$ is equal to the sum of C_p and C_d, the final translator equation is then:

$$\frac{C_T}{C_d} - 1 = K_d \times TSS \qquad \text{Equation } 1-5$$

Realizing that copper toxicity will vary from site to site, and in an effort to give dischargers some regulatory relief, the EPA offers three options in implementing water quality criteria (U.S. EPA, 1992):

1. The simplest method is to measure the total recoverable copper in the ambient water body and compare this measurement to national or state-wide criteria.

2. Instead of total recoverable copper, dissolved copper can be measured, which is thought to be more representative of biologically available copper. The dissolved copper measured would then be compared to criteria appropriate for dissolved metal. This method is more complicated than the first because effluent discharge permits must be expressed as total recoverable copper. Therefore, the chemical translator, referred to above, must be used to go between total copper in the effluent and the dissolved concentration in the ambient water.

3. The most accurate means of implementing a WQC representative of bioavailable copper is the water–effect ratio (WER) discussed previously. This method involves comparing the toxicity of copper in site water to the toxicity of copper in laboratory-produced water for two or more aquatic species. The ratio of toxicities obtained is used as a multiplier to adjust the National WQC, resulting in a more site-specific WQC. WER values have been reported as high as 15 (Allen, 1997).

The use of methods 2 and 3 could allow for regulatory relief when a discharge permit is subsequently calculated from a more site-specific WQC. However, these methods also require more effort and financial investment. Since most of the parameters used to calculate discharge permit limitations are specific to the site of the discharge, permit limits vary greatly. Typically, permit limits for copper are in the range of 40 to 200 ug/L total copper as was stated previously.

D. Regulations on Copper in Secondary Sewage Sludge

Besides aqueous effluents, dischargers also produce sludge effluents. Many WWTPs find it economical to sell sewage sludge to farmers for use in agricultural applications. Although some amount of copper is useful for agricultural nutrition, pollution of nearby waterways due to runoff may occur if a sludge contains too much copper.

The median copper content of dried wastewater sludge is 800 mg/kg, although copper contents range from 84 to 17,000 mg/kg of dried sludge (Tchobanoglous et al., 1991). Regulations are in place to ensure that the copper content of land-applied sludge is not detrimental to the environment. As with other regulations, those for sewage sludge vary around the world (Table 1-6). The Netherlands has the most strict allowance of only 75 mg of copper per kg of dried sludge. The United States, on the other hand, allows up to 4300 mg of copper per kg of dried sludge.

Table 1-6: Regulations for maximum allowed metal concentrations in sewage sludge used as a soil improvement agent in agriculture (after Hedberg, 1996)

Country	Cu (mg/kg dry sludge)
EU	1000-1750
United States	1500-4300
Denmark	1000
Germany	800
Finland	600
France	1000
The Netherlands	75
Norway	1000-1500
Sweden	600

U.S. regulations for sludge disposal via land application are fairly complex. The rule 40 CFR Part 503 regulates the quality of the sludge as well as the application practices. There are four important limits in the rule (Table 1-7).

Table 1-7: U.S. Requirements for Land Application of Sludge (after Sieger et al., 1993)

Requirement #	Limitation	Concentration
1	Pollutant Ceiling Concentration (mg Cu/kg dry sludge)	4,300
2	Cumulative Pollutant Loading Rate (kg dry sludge/ha)	1,500
3	Pollutant Concentration (mg Cu/kg dry sludge)	1,500
4	Annual Pollutant Loading Rate (kg dry sludge/ha-year)	75

In an attempt to encourage the production of high quality biosolids, the EPA made a provision that the higher the sludge quality, the fewer the limitations on land application. For example, if the sludge contains less copper than is specified in requirement 3, is below limitations for other metals, and meets certain pathogen requirements, it can be land applied to agricultural land, forests, public contact sites, reclamation sites, rangeland, pastures and lawns or home gardens. This type of sludge may also be sold or given away in bags for subsequent land applying. If the sludge contains higher copper concentrations then it may not be applied to lawns and home gardens and might not be allowed to be sold in bags. Sieger et al. (1993) provides a helpful, more in-depth summary of U.S. sludge regulations in regards to land application.

VII. CONCLUSIONS

As wastewater effluent discharge permits become more stringent, communities will need to develop effective plans for the reduction of potential surface water pollutants like copper. Isolating pollutant sources and determining the benefits and detriments of each is an important first step. In the case of copper, there are numerous potential sources, although corrosion of drinking water pipes is suspected to be key. Copper is both beneficial and detrimental to the urban water cycle. It is an essential element, necessary in the diet of humans, plants and animals. It is also useful in the control of roots, algae and pathogens. However, excessive copper concentrations can cause detrimental effects such as human and aquatic toxicity. Recently, the issue of biavailability of copper in the environment has greatly affected the way in which copper is regulated. In order for ecologic and economic harmony to exist, a balance must be struck so that benefits can be realized without threat of detrimental effects.

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