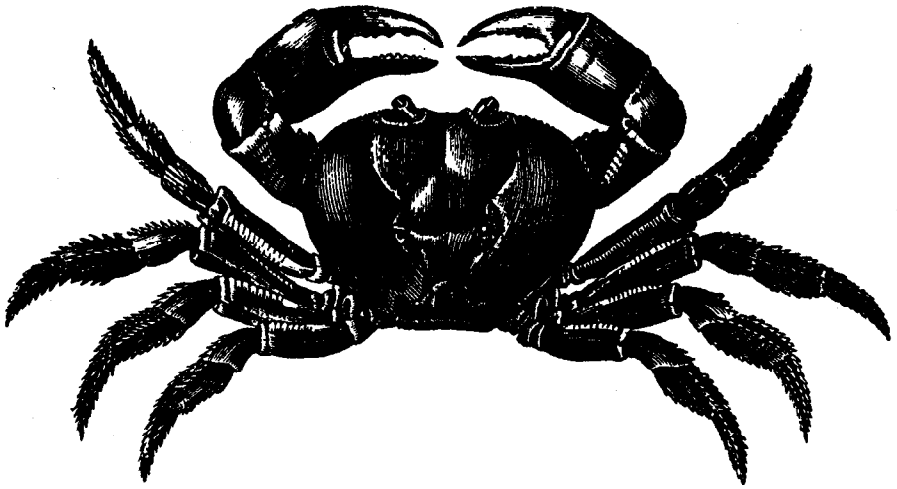
Evaluation of

Copper- and Tributyltin-containing Compounds

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PART ONE — PROGRAM TO REGULATE COPPER AND TRIBUTYLTIN

Nita A. Davidson

Introduction

In February 1994, AB 3394 was introduced by Assembly Member Byron Sher (D, Palo Alto) to address excessive discharges of copper and tributyltin into bays, estuaries, and inland surface waters. The bill would have allowed the California Regional Water Quality Control Boards (Regional Boards) to prohibit the sale, use, and discharge of copper-containing root control compounds, and copper- or tributyltin-containing cooling water additives, once the Regional Boards determined that these compounds 1) interfered with obtaining water quality objectives or 2) prevented compliance with national pollutant discharge elimination system (NPDES) permits. The sponsors of the bill assumed that the Regional Boards have the authority to regulate the sale or use of pesticides on a local basis. However, under current law, the Department of Pesticide Regulation (DPR) has exclusive authority to regulate the sale and use of pesticides throughout California and customarily does so through administrative rather than legislative processes.

After several discussions with Assembly Member Sher, his staff, and representatives from Publicly Owned Treatment Works (POTWs), the California Environmental Protection Agency and DPR determined that an administrative solution would quickly achieve the goals of AB 3394, under DPR's current regulatory authority (Department of Pesticide Regulation, 1994). In August 1994, DPR, along with the cooperation and assistance of the State Water Resources Control Board (State Board) and Regional Boards, established a high-priority program to address the sale and use of copper- and tributyltin-containing pesticides.

The Copper and Tributyltin Program

The copper and tributyltin program was created to develop an administrative solution to concerns raised about the water quality impacts in the San Francisco Bay Area by pesticides containing copper and tributyltin. Staff of the Environmental Monitoring and Pest Management Branch of DPR formed a work group to accomplish the tasks involved in evaluating the copper and tributyltin problem. Based on information at hand, the work group identified the San Francisco Bay Area counties in the Regional Board's San Francisco Bay Region (Region 2) as areas of greatest concern. These counties include (1) San Francisco, (2) Santa Clara, (3) San Mateo, (4) Alameda, (5) Contra Costa, (6) Solano, (7) Napa, (8) Marin, and (9) Sonoma.

Searching the literature and requesting information from interested parties

Staff assembled pertinent literature, collecting in-house publications and reprints of journal articles contributed by the Palo Alto Regional Water Quality Control Plant (RWQCP) (a POTW) and Region 2. To ensure that important references had not been overlooked, staff obtained 169 abstracts on environmental monitoring of copper and tributyltin. Information

compiled from these references is included in parts Two and Three of this report, which describe the fate of copper and tributyltin in the environment.

For the evaluation of the pest management alternatives portion, staff assembled 44 abstracts for copper and 683 for tributyltin. As the alternatives portion was completed, a growing list of contacts contributed even more material. Staff also sent out requests for additional literature to interested parties, including managers of POTWs, County Agricultural Commissioners, University of California Cooperative Extension Horticultural Advisors, and registrants of copper- and tributyltin-containing pesticidal products.

Identifying sites where copper- and tributyltin-containing pesticides are used

Staff identified sites where copper- and tributyltin-containing pesticides are used (e.g., sewers, drains, cooling water systems), and used the sites to search DPR's Pesticide Label Database (PLD) for product labels of copper- and tributyltin-containing pesticides and alternatives that do not contain these compounds. This component was essential to verify products currently registered in California that are specifically used for the identified sites. In addition to gathering product labels and interviewing arborists, public works engineers, and managers of cooling water systems, the pest management team compiled a comprehensive list of copper and tributyltin alternatives. The alternatives to copper are divided into municipal and residential use categories; within these categories, they are further described by duration of effectiveness, major limitations, and approximate cost (Part Four). The analysis prepared for tributyltin describes tributyltin substitutes; lists specific products registered in California; describes limitations of each class of alternative; and provides cost ranges for treatment, maintenance, and cleanup for each product (Part Five).

Administrative options for regulating copper- and tributyltin-containing compounds

Options include promoting a voluntary program among users of copper- and tributyltin-containing products or employing one of three regulatory options (Part Six). These options include 1) canceling copper- and tributyltin-containing products throughout California without regard to regionally specific discharge problems, 2) designating the products as restricted materials to prevent non-licensed users from purchasing and using them, and 3) prohibiting sale and use of the products on a regional basis. This report will provide the basis for a decision to proceed with one of the three options.

Establishing Water Quality Objectives

Water quality objectives are established by the State Board, which evaluates scientific studies of the effects of contaminants on organisms and biological communities (SFBRWQCB, 1992a). Effluent limitations based on water quality objectives are then established for discharges from POTWs; effluent limitations are based on the depth of the water body where the discharge leaves

the POTW. If effluent limitations violate conditions of discharge permits, the Regional Board could fine POTWs up to $25,000 per day.

Water quality objectives for copper

In 1986, Region 2 adopted amendments revising the Water Quality Control Plan for the San Francisco Bay Basin (Basin Plan). This version of the Basin Plan was rescinded in September 1994 and is currently under revision. One amendment included a site-specific water quality objective for copper in the San Francisco Bay. Region 2 received funding from the State Board and the United States Environmental Protection Agency to develop the site-specific objectives for shallow- and deep-water effluent limitations (discharges from POTWs). In October 1992, Region 2 adopted a site-specific water quality objective for total copper in San Francisco Bay of 4.9 micrograms per liter (µg/L) (= parts per billion [ppb]) based on the protection of aquatic life (SFBRWQCB, 1992b). This amendment to the Basin Plan (Resolution 92–128) adopted a deep-water effluent limitation of 37 µg/L, and a 4.9 µg/L limitation for shallow-water discharges. Because concentrations of copper higher than 4.9 µg/L were measured through most of the estuary, Resolution 92–128 established goals for reducing mass emissions of copper by the year 2003 of 20 percent for storm water, and 25 percent for riverine sources and municipal and industrial discharges.

A later amendment (Resolution 93–61) to the Basin Plan established a mass-based approach to determine copper loading for the San Francisco Bay (SFBRWQCB, 1993). Because copper levels exceeded mass-loading limitations throughout the South Bay, one POTW, Palo Alto RWQCP, which discharges to shallow water, was told to reduce its copper load by 32 percent. (The load reduction for the two other shallow-water dischargers, San Jose and Sunnyvale, remained at 25 percent.) In annual mass loading, this is equivalent to 720 pounds, 32 percent less than the 1,060 pound baseline discharge.

In 1993, Region 2 issued a Cease and Desist Order (CDO) to the Palo Alto RWQCP upon renewal of its NPDES permit because violations of the new copper discharge limitations were anticipated. The CDO set up a three-year schedule for compliance with the mass limit and a five-year schedule for concentration limit compliance for Palo Alto and similar schedules for San Jose and Sunnyvale. The conditions of the CDO generated a comprehensive outreach program targeted toward public, commercial, and industrial sectors.

Water quality objectives for tributyltin

In 1992, Region 2 adopted a shallow-water effluent limitation for tributyltin of 5 parts per trillion (ppt) (= 0.005 µg/L) for the San Francisco Bay. In studies conducted by the State Board in the late 1980s, high levels of organic tin compounds (butyltins) were found in river and lake marinas (see Part Three, this report). The high concentrations of butyltins were attributed to the use of tributyltin-containing antifouling hull paints on boats.

From 1992 to 1994, samples from discharges in Palo Alto (RWQCP) exceeded the effluent limit of tributyltin (Kelly D. Moran, pers. comm.). Staff of the Palo Alto RWQCP searched for various tributyltin sources and ruled out antifouling hull paints. They found that tributyltin-containing discharge from cooling water systems was the most obvious source in their service areas (RWQCP, 1993; RWQCP, 1994).

Sources of copper and tributyltin for South Bay POTWs

Loading of metals for the three POTWs that discharge south of the Dumbarton Bridge (Palo Alto, San Jose, and Sunnyvale) is exacerbated by the shallow water and slow replenishment of fresh water in the South Bay (Lacy, 1993). Sources of copper from municipal and industrial discharge in the South Bay make up 25% of the annual average loading of copper. Sources of copper discharge via sewers, storm drains, and rivers include abandoned mines, drinking water pipes, brake linings, copper-containing root control compounds, human wastes, food wastes, and laundry graywater (Larry Walker Associates, 1994). The Palo Alto RWQCP monitored residential, industrial, and commercial wastewater to establish the source of metals in their effluent (RWQCP, 1994). They also studied specific discharge sources, such as machine shops, vehicle service facilities, and cooling towers.

Two studies identified copper sulfate root control compounds as contributing three to ten percent of copper recovered in the effluent of POTWs (Larry Walker Associates, 1994; SRI International, 1991). In Martinez, the Central Contra Costa Sanitary District (CCCSD) initiated a research and implementation project to identify and quantify sources of trace metals in residential wastewater (Larry Walker Associates, 1994). The study found that of all metals evaluated, copper should be given high priority for control, and residential source control efforts should focus on reducing use of copper-containing root control compounds. In Palo Alto, residential use of copper sulfate for tree roots in 1990 accounted for 36 to 42 pounds of elemental copper, approximately 10 percent of the total copper loading (SRI International, 1991).

Unlike copper, potential sources of tributyltin are entirely pesticidal. They include biocidal cooling water systems additives, antifouling paints and stains, protective wood treatments, disinfectant commercial toilet bowl cleaners, and disinfectant carpet and upholstery cleaners (Department of Pesticide Regulation, 1993). In Palo Alto, RWQCP staff determined from surveys that the lack of boat maintenance facilities and tributyltin-containing paints or disinfectants pointed to cooling water systems as the single source of tributyltin (Moran, 1994). Staff calculated that one gallon of 2 percent tributyltin solution discharged to the sewer and treated with other wastewater at the RWQCP would contaminate more than 2.4 billion gallons of the effluent, exceeding the 5 ppt tributyltin effluent limitation. Even very small discharges from one or two cooling towers using tributyltin-containing products could put the City of Palo Alto in violation of their discharge permit (Moran, 1994).

Existing local programs for reducing sources of copper and tributyltin

Educational outreach to limit discharges of copper and tributyltin

Since 1990, Palo Alto RWQCP has conducted an aggressive pollution prevention program to comply with discharge limits. Their Clean Bay Business program recognizes local plumbers no longer using copper sulfate for root control, and hardware stores that cooperate by voluntarily not selling these products. RWQCP staff also published a list of auto shops that adopted environmentally sound practices. As of February 1994, RWQCP had published four technical documents on best management practices (BMPs); four user-friendly booklets on BMPs; 11 technical reports; 16 public relations items (including flyers, coupons, door hangers, and buttons); and 40 fact sheets. Only some of these address copper-containing root control compounds, but most deal with the idea of source reduction. As a result of the plant's outreach efforts, cooperation of area businesses and residents, and improved copper-removal efficiency the average annual effluent copper concentration has decreased from 150 µg/L in 1979 to approximately 10 µg/L in 1993. RWQCP's regulatory programs currently address the sewer and storm water discharges of approximately 85 major industrial facilities and more than 1,000 commercial businesses.

The RWQCP created the Cooling Water Systems Program in 1992 to collect information about cooling water systems, develop and promote BMPs for operating and maintaining cooling water systems, and distribute the BMPs to cooling tower users within RWQCP's service area (RWQCP, 1994a). Participants in the program held several public meetings to request input from the regulated community and treatment chemical suppliers. In 1993, the RWQCP developed BMPs that promote appropriate operation and maintenance of cooling water systems to reduce the amount of metals discharged into the Bay while also lowering cooling system costs.

Other governmental agencies in the San Francisco Bay Area besides the Palo Alto RWQCP have published educational material on proper disposal of toxics, some with an emphasis on root control and cooling water systems (San Francisco Bay Area Pollution Prevention Group, 1994). Examples include the City of San Jose Environmental Services Department, the City and County of San Francisco Department of Public Works, Central Contra Costa Sanitary District, and the Sunnyvale Water Pollution Control Plant. A brochure on copper sulfate root killers was developed in April 1994 by 25 Bay Area POTWs and distributed to over 200,000 households throughout the region.

Local ordinances imposed by the cities of Palo Alto and San Jose

Advocates of outreach programs have complained that the task of reducing the amount of metals entering municipal sewers is monumental because effluent limitations are so low—on the level of parts per billion or trillion. For example, the Palo Alto RWQCP calculated that the small volume of tributyltin-containing discharge that causes the plant to violate its effluent limitation makes it impractical to identify and eliminate all the small sources of tributyltin through an inspection and education program (Moran, 1994a).

In response to continued violations of effluent limitations, the City of Palo Alto passed an ordinance in February 1992 that banned the discharge of copper-containing root control compounds containing greater than five percent copper by weight to the sanitary and storm sewer systems. The RWQCP found that banning discharge rather than sale of these products made enforcement of the ordinance difficult; although monitoring the sale of products from retail outlets and plumbers is achievable, monitoring the discharge of copper-based root killers from every household is impossible. RWQCP recognized a loophole with their outreach program when the owner of a chain retail outlet in their service area chose not to participate in a local-government–sponsored program until getting more information from his parent company or professional association (Moran, 1994b).

Following Palo Alto's example, San Jose adopted an ordinance in September 1992 that regulated the sale, use, and discharge of copper-containing root control compounds. San Jose City Council supported the ordinance based on state and federal laws that they believed stated that the City may exercise control over users of its storm drain and sewer systems, and may adopt regulations relating to all substances discharged into these systems, including pesticides. DPR responded that authority to regulate pesticides resides with DPR, pursuant to Food and Agricultural Code § 11501.1, which states that "[n]o ordinance or regulation of local government, including, but not limited to, an action by...a city council...may prohibit or in any way attempt to regulate any matter relating to the registration, sale, transportation, or use of economic poisons, and any of these ordinances, laws, or regulations are void and of no force or effect." Only county agricultural commissioners are authorized to regulate pesticides locally under the supervision and control of DPR. City councils and county boards of supervisors are not permitted to adopt regulations (Food and Agricultural Code, § 11501.1). DPR took the position that both ordinances passed by Palo Alto and San Jose were invalid based on section 11501.1.

Despite good intentions to comply with effluent limitations, POTWs will increasingly face the same dilemma: compliance by imposing local ordinances to reduce loading of toxics, or support of legislation that will prohibit the use of offending toxics in their service area. With the implementation of a successful copper and tributyltin program, local governmental agencies will be able to rely on DPR to provide thorough research on the issue, perform an alternatives analysis, and offer a workable administrative solution to the problem.

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PART TWO — THE FATE OF COPPER IN THE ENVIRONMENT

Pamela C. Wales

Introduction

Copper is a natural constituent of seawater at concentrations from 0.001 to 0.02 parts per million (ppm), and in unpolluted surface waters in the United States at concentrations between 0.001 and 0.010 ppm (Merck, 1989; US EPA, 1984). In natural waters, copper occurs primarily as the Cu^{2+} ion, in both free and complexed forms.

Copper is used in the formulation of a number of pesticidal products. Copper-containing active ingredients are registered for a variety of agricultural and non-agricultural uses in California (Table 1).

Table 1. Representative copper-containing active ingredients and examples of their non-agricultural use.

Active ingredient	Examples of use
Copper sulfate, pentahydrate	Root control in sewer systems. Algal control in lakes, ponds, drainage canals, potable-water reservoirs, swimming pools, spas, hot tubs. Wood preservative.
Copper ethanol-amine complexes	Algal control in swimming pools, hot tubs, spas.
Copper triethanol-amine complexes	Algal control in swimming pools, hot tubs, spas.
Copper napthenate	Wood preservatives and finishes for decks, wood siding and shakes, fences and outdoor wood furniture.
Copper sulfate, basic	Root control in sewer systems.
Copper hydroxide	Anti-fouling paints for ship and boat hulls, and other marine surfaces.
Copper oxide	Anti-fouling paints for ship and boat hulls, and other marine surfaces.
Copper sulfate, anhydrous	Algal control in lakes, ponds, drainage canals, potable-water reservoirs.

Copper sulfate is an inorganic compound, often used as an aquatic algicide and foliar fungicide. The blue crystals are used to control most algal species in surface water, potable water, and rice fields. The chemical is also used to kill tree roots in sewer lines. Copper sulfate is toxic to most plants; however, it can be used as a foliar fungicide when mixed with lime to form Bordeaux mixtures (Royal Society, 1991).

The pentahydrate form of copper sulfate ($CuSO_4 \cdot 5H_2O$) is the type most commonly used (Table 2). Also available in basic and anhydrous formulations, copper sulfate is commonly referred to by a variety of other names, including blue stone, blue vitriol, and blue copperas.

Table 2. Physical and chemical properties of copper sulfate, pentahydrate.

CAS number	7758–98–7
Molecular formula	$CuH_{10}O_9S$
Molecular weight	249.7
Vapor pressure	non-volatile

Environmental fate of copper

Fate in water and sediments

In natural waters, trace metals such as copper can exist in a variety of forms, or species, including those that are dissolved, colloidally dispersed or particulate. Dissolved species consist of several well-characterized inorganic forms (including Cu^{2+} and inorganic complexes such as $CuCO_3$, $Cu(OH)_2$, and $CuCl_2$), and less well-defined complexes with naturally present organic ligands such as phytoplankton metabolites and humic substances (Bruland et al., 1992; Donat et al., 1994; and Kuwabara et al., 1989).

Particulate species include copper associated with colloids, or adsorbed onto or incorporated into particles resuspended from sediments by tidal or storm activity. Particles may be classified as large (> 5 μm) or small (0.4 to 5 μm). Large particles are influenced by storm and tidal activity, turbulence and currents. The particles are typically resuspended from bottom sediments and are rapidly removed by resettling following the disturbance. Some of these organic forms are very stable and once deposited can exist unchanged in sediment for thousands of years (Brügmann, 1984). Large particles can also include living phytoplankton and zooplankton. Small particles typically stay suspended for extended periods of time, and can include free bacteria, small phytoplankton, inorganic and organic detritus, and silt (Bruland et al., 1992; Donat et al., 1994 ; and Kuwabara et al., 1989). Determinations of total copper can include all of these various chemical and physical forms, some of which are not biologically available.

The partitioning, speciation, and complexation of copper by dissolved organic ligands have been studied by several groups (van den Berg, 1982; Sunda and Ferguson, 1983; Brügmann, 1984; van den Berg et al., 1987; Moffett and Zika, 1987; Gardner and Gunn, 1989; Coale and Bruland, 1988; Kuwabara et al., 1989; Nimmo et al., 1989; van den Berg et al., 1990; Coale and Bruland, 1990; Donat and van den Berg, 1992; Bruland et al., 1992; and Donat et al., 1994). They report that the predominant chemical form of copper in seawater is that of an organic complex, and copper speciation is dominated by association with dissolved organic matter. Kuwabara et al. (1989) observed that dissolved copper concentrations vary indirectly with salinity and directly with dissolved organic carbon, and suggest that the trend is a result of organic complexation.

Copper has been demonstrated to have a strong affinity for organic molecules; in fact, in estuarine waters the predominant form of copper is that of an organic species (Nimmo et al., 1989; Gardener and Gunn, 1989). Several authors reported that more than 80% and usually more than 99% of the dissolved copper in estuaries is complexed with organic ligands (Bruland et al., 1992).

Nimmo et al. (1989) reported that 98–99% of all of the copper in Liverpool Bay occurred in organic complexes. Bruland et al. (1992) studied ambient copper speciation during October 1991 and April 1992 in South San Francisco Bay. They reported that of the 3.11 ppb total dissolved copper detected in October, 27% (0.84 ppb) was chelated by a strongly complexing organic ligand, while 65% (2.02 ppb) was associated with a weaker complexing organic ligand, resulting in a total of 92% of the dissolved copper existing as organic complexes. They found 8% (0.25 ppb) of the dissolved copper in inorganic forms, with 0.4% of the total dissolved copper as free Cu^{2+}, and $CuCO_3$ as the dominant inorganic species. Their results from the following April were similar, with over 95% of the total dissolved copper associated with organic complexes, and nearly 5% as inorganic species. They also observed in laboratory studies that the free or inorganic copper was buffered at ambient concentrations; however, when the total dissolved copper exceeded 5 ppb, the copper-complexing organic ligands became fully complexed and any additional copper added beyond that point existed as inorganic species.

Blutstein and Exton (1983) studied the binding capacity of filtered and unfiltered sewage effluent when mixed with seawater of varying salinity. They argue that the high levels of complexing capacity they observed in the vicinity of the sewage outfall is atypical of unpolluted seawater values due to the large amounts of dissolved organic material supplied by the outfall itself.

Fate in aquatic organisms

Bioavailability and bioaccumulation

The impact of copper on the aquatic environment is dependent on the form in which it is present, and may be influenced by a number of other environmental and biological processes that affect bioavailability. Exposure occurs in both solution and particulate phases; from sediments to food supply, organisms are exposed to a variety of physical and chemical forms of copper. In his extensive review of literature concerning the bioavailability of trace metals to aquatic organisms, Luoma (1983) outlined four processes that occur at the organism–environment interface and determine the bioaccumulation of metals:

- The characteristics of the interface itself.
- Reactivity of the metal species with the interface.
- The presence of other molecules that may play either an antagonistic or facilitative role in metal uptake.
- Physical factors such as temperature that may affect the rate of biochemical reactions.

The same mechanisms that control the uptake and transport of substances into tissues also apply to metal transport. The principle mechanisms are diffusion across cellular membranes, active transport across membranes via carrier molecules, endocytosis, and intracellular digestion. Endocytosis (pinocytosis) has been documented in molluscs. Intracellular digestion involves the engulfing of substances (including metals) by vesicles outside of the cell membrane, but within the lumen of the stomach, and the movement of these substance-laden vesicles across the membrane and into the organism. This is the major form of digestion used by molluscs. Of these four mechanisms, most trace metals are transported across the cell membrane via carrier molecules (Luoma, 1983).

According to Luoma (1983), two aspects of metal uptake in aquatic organisms are unique. In some circumstances metal concentration may never reach steady-state. Uptake may occur over the course of a lifetime. Secondly, the ultimate level of bioaccumulation is not solely a function of transportation rates.

The form of the metal present in the food source determines assimilation efficiency (Reinfelder and Fisher, 1991). Several studies have shown that the toxicity and bioavailability of copper are controlled by its free metal ion concentrations instead of by total metal concentrations. Metal species with the highest free energy such as the free copper ion exhibit the greatest bioavailability because they react most readily with the carrier molecules that facilitate the diffusion of essential substances across the cell membrane (Luoma, 1983).

When copper is complexed by organic ligands its toxicity is decreased, presumably by decreasing its free ion concentration (Donat et al., 1994; Daly et al., 1990; and Luoma, 1983). An exception to this involves metals associated with plant cell fluids within living phytoplankton. In one study, metals bound to living phytoplankton cellular fluids were bioavailable and readily assimilated by copepod herbivores, but when associated with plant cell walls and membranes, were defecated by the copepods (Reinfelder and Fisher, 1991).

The dissolved fraction also includes trace metals associated with colloids. The bioavailability of colloidally bound toxic metals is essentially unknown for marine organisms, however, one study carried out with colloidally associated iron suggests that colloidally bound iron is biologically unavailable for direct assimilation and must first be remineralized to a truly dissolved form before assimilation (Rich and Morel, 1990).

Organisms living in eutrophic estuarine waters or environments subject to anthropogenic discharges are less susceptible to trace metal stress than those living in oligotrophic, open-ocean waters. Organic materials, capable of complexing with copper ions, are more abundant in estuarine waters and discharges than in the open ocean, and lead to a reduction in the free ion concentration and, subsequently, the bioavailability (Luoma, 1983). In the open ocean, concentrations of free copper are nearly the same concentrations that will inhibit the growth of some species of phytoplankton and fish embryos, despite the low concentration of total copper. In estuarine waters, total copper concentrations are usually higher than those in the ocean, but free copper ion concentrations may be much lower if organic ligands are present.

Although sediments represent the most concentrated reservoir of metals in aquatic systems, metal concentrations in sediments do not necessarily reflect concentrations that are biologically available (Thomson et al., 1984). As in water, the chemical form of the metal present determines bioavailability. In sediments, particulate size plays an important role; as large metal-laden particles settle rapidly to the estuarine bottom and become buried under subsequent layers of sediment, they become essentially unavailable, and if undisturbed can exist unchanged in the sediments for thousands of years (Brügmann, 1984).

Deaver and Rodgers, Jr. (1994) examined the bioavailability of copper in amended wetland systems. Employing successive ten-day experiments with *Hyalella azteca* and *Chironomus tentans*, they evaluated the bioavailability and toxicity of aqueous and sediment-associated copper from copper sulfate-treated, untreated, and control wetlands. They reported that although in some cases copper remained acutely toxic over the six-month study period, total copper concentrations

in sediment had no relation to bioavailable copper. Thomson et al. (1984) studied the biological availability of sediment copper and reported that neither sediment–metal concentrations nor discharge concentrations were reliable indicators of the bioavailable fraction.

In his review of literature concerning the bioavailability of trace metals to aquatic organisms, Luoma (1983) summarized an extensive survey conducted by Luoma and Bryan in the late 1970s comparing the concentrations of several metals in the sediments of 17 estuaries with concentrations of the same metals in two deposit feeders, the burrowing clam, *Scrobulicaria plana*, and the polychaete worm, *Nephthys diversicolor*. They observed statistically significant but weak correlations between total metals in the tissues of *S. plana* for all metals surveyed, with the exception of copper, while stronger correlations were observed between sediment concentrations of copper and *N. diversicolor*. Similar results have been observed in estuarine snails; however, Luoma notes that studies of such magnitude in other bottom-feeding species have been limited by the poor understanding of their feeding habits.

Johansson et al. (1986) studied the variability in the uptake and partitioning of copper and other metals among the cytosolic proteins in *M. balthica*. They found that uptake of copper (as well as that of other trace metals) into the cytosolic metallothionein-like proteins (MLPs) was dependent on exposure, both in laboratory and natural settings. MLPs are a class of low-molecular-weight, cysteine-rich proteins that strongly bind to trace metals and are thought to play an important role in the metabolism and tolerance of metals in bivalves. They concluded that even though *M. balthica* showed many symptoms of a metal-stressed population, the population as a whole is as much as 50-fold more tolerant to copper than other populations living in other portions of San Francisco Bay. They also stated that despite indications of stress, they had not proven conclusively that Palo Alto populations of *M. balthica* were adversely affected by trace metals, and noted that further studies are needed to understand the relationships between cause and effect when benthic communities undergo changes in their population profiles.

Acute and chronic toxicity

The toxicity of copper to aquatic life is directly related to the activity of the free copper ion (Cu^{2+}) and possibly to some of the associated hydroxy substances. Most organic and inorganic copper complexes tend to be much less toxic than the free copper ion, and also have the ability to reduce the toxicity from total copper. Daly et al. (1990) studied the influence of dissolved organic matter on the toxicity of copper to the Australian freshwater shrimp, *Paratya australiensis*, in laboratory studies. They found the presence of dissolved organic material dramatically reduced the toxicity of copper, presumably through the formation of nontoxic copper organic complexes.

Most toxicity data are reported as either total or dissolved copper, and do not take free copper or complexed copper into account. This complicates the interpretation of the available toxicity data. Furthermore, increasing calcium hardness and associated carbonate alkalinity have been shown to reduce the acute toxicity of copper (U.S. EPA, 1984). A summary of some of the available toxicity data for aquatic species in California are presented in Table 3.

Copper is less toxic to mammals than to aquatic life. There is no evidence that humans have ever been poisoned from consumption of copper in water, or from consuming aquatic organisms with elevated tissue copper concentrations. However, copper is considered to be relatively toxic to

aquatic life and has been found to be chronically toxic in concentrations as low as 10 ppb (SWRCB, 1990).

Presence in the environment

Sources

Trace metals, including copper, enter coastal seawater from a variety of sources (Brügmann, 1984; Thomson et al., 1984; and Lacy, 1993). Examples of sources include:

- Surface runoff
- Atmospheric fallout
- Industrial, commercial, or residential wastewater discharge
- Leachates from landfills
- Leachates from mines
- Recreational, naval, and commercial shipping activities

Concentrations and distribution in marine, fresh, and estuarine waters

San Francisco Bay Region

San Francisco Bay is the largest estuary along the western coast of the United States, with a surface area of 1,240 km^2 (Flegal et al., 1991). It has been described as a three-component system with distinctly different hydrographic and geographic features (Conomus, 1979). These three components are 1) the northern reach, that includes San Pablo and Suisun bays, and the confluence of the Sacramento and San Joaquin rivers, 2) the southern reach, often referred to as the South Bay, and 3) the Central Bay, which connects the other two to the Pacific Ocean at the Golden Gate. The Bay serves as a home for a number of wildlife and waterfowl species, provides a passageway to spawning grounds in inland rivers for salmon and striped bass, and supports a wide variety of sport and commercial fishing. It also provides passageways and harbors for commercial and naval shipping, and has served as a receptacle for wastewater.

Flegal et al. (1991) studied the dissolved trace element cycles in San Francisco Bay. They reported that concentrations of many trace elements including copper in the South Bay were high with respect to concentrations at comparable salinities in the northern part of the system. In part, they attributed this effect to the bifurcated structure of the system. The deep northern reach receives large amounts of freshwater input from the Sacramento and San Joaquin rivers, resulting in a stratification of the water column in the bays and channels, with low-salinity surface currents flowing toward the ocean and comparatively high-salinity bottom currents flowing toward inland regions. In comparison, the predominantly shallow water column of the South Bay is vertically mixed, with wind-driven circulation accounting for the currents that exist in this area.

Table 3. Toxicity of copper to some aquatic species in California.

Species	Life stage	Exposure time	Type of study	Concentration	Comments	Reference
Capitala capitata	Adult	96 hr	LC_{50}	200 mg/L		Reish et al., 1976[a]
Capitala capitata	Adult	28 d	LC_{50}	200 mg/L		Reish et al., 1976[a]
Capitala capitata	Juvenile	96 hr	LC_{50}	200 mg/L		Reish et al., 1976[a]
Nereis diversicolor		96 hr	LC_{50}	500 mg/L		Bryan, 1974[a]
Nereis diversicolor		96 hr	LC_{50}	410–480 mg/L	Acute	Jones et al., 1976[a]
Nereis diversicolor		96 hr	LC_{50}	300 mg/L		Bryan and Hummerstone, 1971[a]
Abalone		48 hr	LC_{50}	85 mg/L		Harrison et al., 1977[a]
Mytilus edulis	Larva	2 hr	LC_{50}	>20,000 mg/L		Wisely and Buck, 1967[a]
Mytilus edulis	Adult	96 hr	LC_{50}	300 mg/L		Davenport, 1977[a]
Mytilus edulis	Adult	96 hr	LC_{50}	>300 mg/L		Abel, 1976[a]
Mytilus edulis	Adult	6 d	LC_{50}	20,000 mg/L		Delhaye and Cornett, 1975[a]
Crassostrea gigas	Embryo		LC_{50}	5.3 mg/L	Acute	Martin et al., 1981[b]
Crassostrea gigas	Embryo		LC_{50}	11.5 mg/L	Acute	Coglianese and Martin, 1981[b]
Mytilus edulis	Embryo		LC_{50}	5.8 mg/L	Acute	Martin et al., 1981[b]
Salmo gairdneri	Adult		LC_{50}	42.5 mg/L	Average acute	U.S. EPA, 1984.
Salmo gairdneri	Adult		LC_{50}	19.01 mg/L	Chronic	McKim et al., 1978[b]
Crassostrea gigas			EC_{50}	9.3-20.4 mg/L	MCV	S.R. Hansen & Associates, 1992
Thalassiosira pseudonana			EC_{50}	4.2–14.1 mg/L	MCV, dissolved	S.R. Hansen & Associates, 1992
Thalassiosira pseudonana			EC_{50}	7.3–28.3 mg/L	MCV, total Cu	S.R. Hansen & Associates, 1992
Thalassiosira pseudonana		~2–4 d	Growth	0.32 mg/L	Growth rate ceased	Sunda and Guillard, 1976
Nannochloris atomus		~2–5 d	Growth	0.003–0.13 mg/L	Growth rate inhibition	Sunda and Guillard, 1976
Lyngbya spp.			Population density	2.5 mg/L (total) or 12 ng/L (free Cu^{2+})	Population density markedly reduced	Leland and Carter, 1984
Spirogyra spp.			Population density	5 mg/L (total) or 25 ng/L (free Cu^{2+})	Population density markedly reduced	

[a] Taylor, D. and L. Carter. 1988.

[b] U.S. EPA, 1984.

There are corresponding differences in hydraulic residence times within the San Francisco Bay system. The estimated mean hydraulic residence time in the northern reach is 1.2 days during high-flow and 60 days during low-flow conditions. In the southern reach, residence times range from 120 days during high-flow and 160 days during low-flow conditions. While nearly all of the freshwater input to the system originates in the northern part of the Bay, it causes a seasonal flushing of the South Bay during winter high-runoff periods (Flegal et al., 1991).

Flegal et al. (1991) collected water samples from 27 locations throughout the Bay (eight from the southern reach, six from the Central Bay, and 13 from San Pablo and Suisun Bay in the northern reach) during April, August, and December 1989 (Table 4). The samples were collected from one meter below the water surface. During the study period, Flegal et al. (1991) reported that the normal seasonal flushing was absent as a result of drought conditions that had existed for three years. They recognized that the protracted low-flow conditions may have resulted in atypical trace element concentrations and distributions during their study period, but stated that these unusual low-flow conditions may become the norm considering the systematic increase in freshwater diversions and increased demands on the water supply from a growing population within the area. The authors attributed the difference in the distribution of copper (and the other trace elements they studied) to the relatively large inputs of anthropogenic wastes to the South Bay. Davis et al. (1990) reported that wastewater discharges of copper to the South Bay ranged from 28–46 kg/day, significantly higher than those from the northern reaches or the Sacramento–San Joaquin River Delta, at 7.4–13 kg/day). Flegal et al. (1991) concluded that inputs from wastewater discharges alone can account for all of the excess dissolved copper in the South Bay

Kuwabara et al. (1989) studied the trace metal associations in the water column of the South Bay during the months of March, April, July, and September of 1985. They reported dissolved copper distributions ranging from 24 to 66 nM and particulate copper distributions ranging from 22 to 65 μg/g. They found dissolved copper concentrations varied directly with the dissolved organic carbon concentration and indirectly with salinity. They also monitored municipal treatment plant effluent to the South Bay during the dry season when they conducted their study. They reported effluent total copper concentration ranges from 30 to 280 nM, and concluded that treatment plant effluent represented a significant source of trace copper input into the South Bay.

Table 4. The distribution of dissolved copper in San Francisco Bay during April, August, and December 1989 (Flegal et al., 1991).

Sample	Dissolved copper concentrations (nmol/kg)		
Location	*April*	*August*	*December*
Extreme South Bay	68	73	43
Dumbarton Bridge	50	63	43
Redwood Creek	47	52	36
San Bruno Shoals	35	40	40
Hayward Flats	33	46	43
San Francisco Airport	31	36	37
San Leandro Channel	29	36	36
Hunter's Point Channel	22	32	23
Berkeley Flats	20	20	21
Golden Gate	17	16	8.5
Alcatraz Island	18	19	8.7
Angel/Treasure Islands	18	22	14
San Rafael Bridge Shore	22	23	17
San Rafael Bridge Channel	25	27	13
San Pedro Point	27	30	17
Petaluma River	31	35	—
Pinole Shoal Channel	32	38	20
Pinole Shoal Shore	29	33	22
Benicia Bridge	38	42	34
Pacheco Creek	38	39	34
Grizzly Bay	40	37	36
Port Chicago	39	—	36
Honkers Bay	37	35	36
Stake Point	—	26	—
Chips Island	36	34	34
New York Slough	36	28	35
Sacramento River	36	29	36

The Water Resources and Geological Division of the U.S. Geological Survey has conducted several studies on, and issued summaries of, the impact of wastewater discharges on the aquatic organisms living in San Francisco Bay (Kuwabara et al., 1989; Johansson et al., 1986; Cain and Luoma, 1985; Luoma et al., 1985; Thomson et al., 1984; Luoma, 1983; and Luoma and Cloern, 1982). In a summary of work concerning the use and protection of San Francisco Bay, Luoma and Cloern (1982) categorized wastewater discharge into continuous and intermittent sources and

identified several specific sources of copper contamination. Point sources, such as municipal discharge or industrial wastes, make up the continuous sources. An example of a continuous point source in San Francisco Bay is the Palo Alto sewage outfall in the South Bay. Two sources of intermittent discharge include seasonally varying storm runoff and fresh water inflows from rivers and streams, and accidental spills, sewage treatment plant breakdowns, and periodic dredging. An example of an intermittent discharge source includes San Francisquito Creek, a source of urban storm runoff.

The concentrations of toxic materials in organisms are often used as indicators of the presence of biologically important contaminants. Luoma and Cloern (1982) summarized and compared the results of several studies conducted in the Bay with those conducted in other California coastal bays. They report that concentrations of copper in the estuarine bivalve, *Macoma balthica*, in the South Bay exceed any previously reported from 37 European estuaries.

Luoma et al. (1985) discussed the concentrations of copper that were measured by Thomson-Becker and Luoma (1985) in the soft tissues of *M. balthica* living in South San Francisco Bay over a period of two to three years, and over a period of eight years at a metal-enriched site. These near-monthly monitoring data showed that the fluctuations of copper were greatest in the clams living at stations with the most metal enrichment and the least dilution and flushing of waste. The metal-enriched site was located 1 km south of a sewage treatment plant that contributed a substantial amount of copper to the area. Native *M. balthica* were collected from the intertidal zone at low tide, dissected, and their tissues and shells were analyzed for copper and other trace metals. Sediments were also collected from the surface oxidized layer at the sediment–water interface and analyzed for the same trace metals. Data were presented in graphs; therefore, exact values were not available. However, a consistent seasonal pattern of copper fluctuations was evident, with copper concentrations varying from approximately 50 to 500 μg/g body weight. The concentrations were reported to increase rapidly between September and November, reaching a maximum between December and March, and returning to a minimum each summer. They noted that this consistent seasonal fluctuation was not evident in the monthly samples of plant effluent, leading them to conclude that inputs from the waste treatment plant were not solely responsible for the changes observed in the clams. Although they reported that the spring decline in copper concentrations often occurred in concert with the decline in salinity associated with the influx of fresh water from the Sacramento and San Joaquin rivers, a direct influence of salinity on copper bioavailability was not established. A relationship between the amplitude of the fluctuations and the monitoring location was established. Fluctuations in the copper concentrations were greatest where both the sediment and animal copper concentrations were highest and the residence time of the water was longest. These conditions occurred at the extreme southern end of the South Bay.

Luoma et al. (1985) also concluded that the seasonal copper concentration fluctuations in *M. balthica* partially resulted from variations in tissue mass, and from hydrodynamic changes that occur annually. They also noted that the use of indicator organisms is the only method available to assess biological availability of metals in an estuary, and therefore, year-to-year variations in the concentrations of metals in estuaries will not be detected from just a few organism samples per year. The determination of seasonal fluctuations and an understanding of the mechanisms in effect require long-term studies.

Cain and Luoma (1985) compared the accumulation of copper in transplanted clams (*M. balthica*) to resident clams in the South Bay near Palo Alto, populations with very different exposure histories. They reported that copper accumulation in the transplants that previously had been exposed to very low levels of copper did not occur during times when increased concentrations of copper in the resident population indicated that exposure to copper was high. Furthermore, the accumulation of copper by the transplanted clams, compared to the resident clams, was not consistent between the summer and winter. The authors noted that summer accumulations were similar between the two groups; however, during the winter period, when environmental exposure was increased, net accumulation by the transplanted clams was much less than the resident population (Figure 1). The authors stated that if uptake and loss rates were the same in both populations, the net quantity of copper accumulated by the transplants should have been greater because they had a lower existing body burden. After eliminating the possibility of the transplantation and caging effects as a reason for the differences, they speculated that the difference in metal accumulation between the two groups might be the result of past environmental exposure. They suggested that the differences may be related to high concentrations of MLPs in resident clams that were routinely exposed to high levels of copper, due to chronic metal exposure. The authors observed that the results of their observations illustrate some of the limitations of using transplants as indicators of pollution impact upon resident populations.

Other locations in California

Young et al. (1979) used the bay mussel *Mytilus edulis* as a bioindicator to determine the contamination of copper and other trace metals in several Southern California harbors and coastal regions, comparing mussel distribution with corresponding bottom sediment values reported from other studies. They measured the concentrations of copper in digestive gland, gonad, and muscle tissues of *M. edulis* from the various locations. They also studied the degree to which aquatic biota can be contaminated by vessel-related activities in coastal and harbor waters, as compared to copper from run-off and aerial fall-out. They reported that 180,000 kg of copper were applied annually to vessels in Southern California, approximately 40,000 kg entered the coastal ecosystem because of storm run-off from surrounding populated areas, about 30,000 kg was contributed from aerial fall-out, and approximately 510,000 kg of copper were discharged via coastal submarine municipal outfalls (Table 5). They concluded that both vessel-related activities and coastal wastewater discharges can contribute to distinct elevations of trace metal pollutants in nearshore marine organisms.

Figure 1. Copper concentrations (μg/g) of resident and transplanted *Macoma balthica* from a copper-contaminated South San Francisco Bay site. Bars indicate ± one standard error of the mean (Cain and Luoma, 1985).

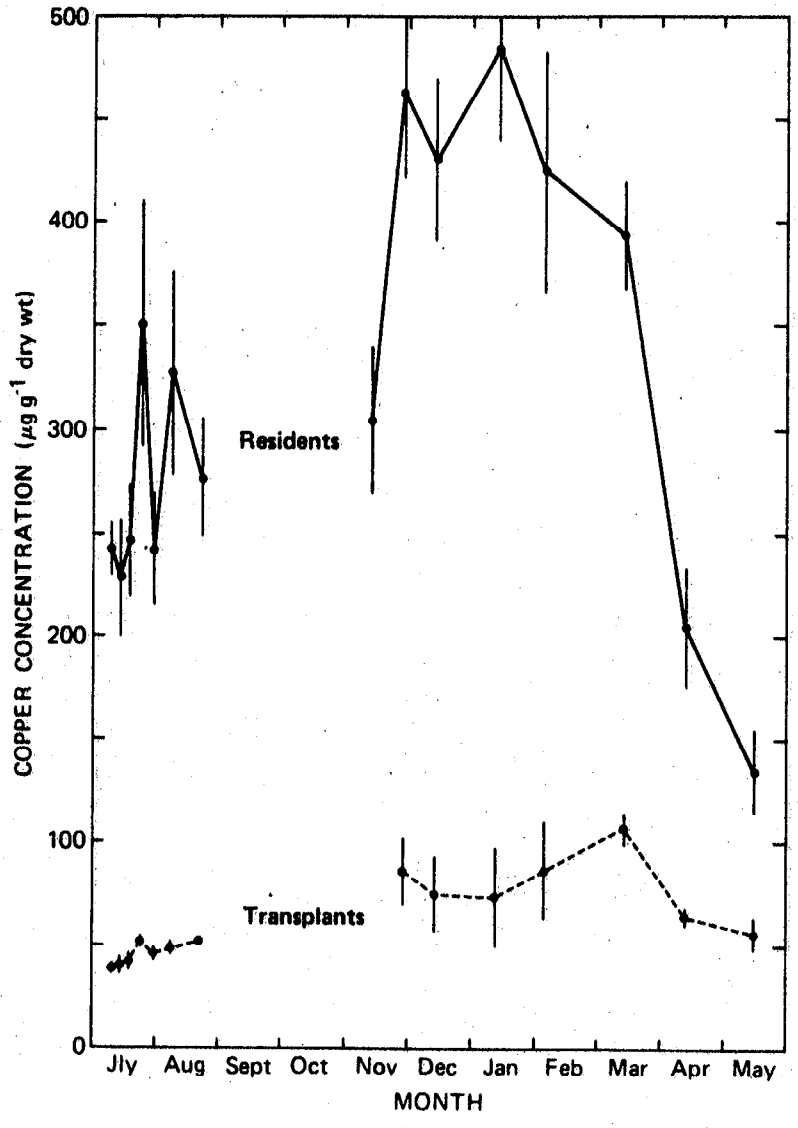


Table 5. The concentration of copper in *Mytilus edulis* tissues Southern California) (Young et al., 1979).

Site	Digestive gland (mg/kg dry wt)	Gonad (mg/kg dry wt)	Muscle tissue (mg/kg dry wt)	All other tissues (mg/kg dry wt)	Primary source of copper
Newport Harbor (Sta. I.) San Diego Bay	127 ±18	93±15	52±10	100±14	Large recreational vessel painting and repair facilities.
Coastal location (Sta. H.) San Diego Bay	16±1.0	9.6±0.2	5.7±0.3	11±0.6	
Royal Palms Beach, San Pedro Harbor	47±2.8	42±0.5	14±1.0	44±7.0	Submarine discharge of municipal wastewater from Los Angeles County Sanitation District
Coastal Stations, San Pedro Harbor	20±2.4	10±0.8	11±2.9	13±1.5	

McCain et al. (1992) studied the relationship between chemical pollution and associated fish diseases in San Diego Bay between 1984 and 1988. They reported that although the sediment concentrations of copper were significantly higher at sites within San Diego Bay (nearly 180 µg/g) compared to a nonurban Dana Point site (< 10 µg/g) located outside of the Bay, concentrations of copper from livers of white croakers and barred sand bass from San Diego and Dana Point did not differ significantly. The researchers observed this lack of a relationship between sediment and fish tissue concentrations consistent with the results of studies conducted along coastal waters in other parts of the United States.

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PART THREE — THE FATE OF TRIBUTYLTIN IN THE ENVIRONMENT

Pamela C. Wales

Introduction

Tributyltin (TBT) compounds are organic derivatives of tetravalent tin (Sn^{4+}) and have the general formula $(CH_3–CH_2–CH_2)_3$ Sn — R where R is a covalently linked anion or group. The nature of the covalently–linked anion or group influences the physical and chemical properties of the resulting TBT derivative, in particular its solubility in water and vapor pressure (IPCS, 1990). The commercially important tributyltin derivatives include TBT oxide, TBT benzoate, TBT methacrylate, TBT neodecanoate, and TBT fluoride (Table 6).

Table 6. Physical and chemical properties of some TBT derivatives .

	TBT oxide	TBT benzoate	TBT methacrylate	TBT neodecanoate	TBT fluoride
CAS number	56–35–9	4342–36–3	2155–70–6	28801–69–6	1983–10–4
Molecular formula:	$C_{24}H_{54}OSn_2$	$C_{19}H_{32}O_2Sn$	$C_{16}H_{32}O_2Sn$	$C_{22}H_{46}O_2Sn$	$C_{12}H_{27}FSn$
Molecular weight	596.2	411.2	375.2	461.4	309.1
Vapor pressure (Pa at 20°C)	1×10^{-3}	2×10^{-4}	3×10^{-2}	—	—
Density (20°C)	1.17–1.18	≈1.2	1.14	—	1.25
Solubility	750 mg/L @ pH 6.6 31,000 mg/L @ pH 8.1	—	—	—	—

Sources: IPCS, 1990; Lewis, Jr., 1992; U.S. EPA, 1987.

Environmental fate of tributyltin

Since the late 1970s, when the ecological and economic effects of TBT on an important commercial stock of oysters in Arcachon Bay, France became evident, several groups have studied the environmental persistence and fate of TBT in aquatic ecosystems. It soon became evident that this long-acting, effective antifouling biocide had a detrimental affect on non-target organisms. The threshold concentration for biological effects was determined to be low, at about 20 ng TBT per liter of seawater. Based on this information, in 1982 France became the first country to take regulatory action by banning the use of TBT paints on all pleasure craft of less than 25 m in length, in an attempt to protect French oyster culture farms. French oyster farms have estimated losses at around $147 million during the period from 1977 until 1983, one year following the ban of TBT hull paints by that government. Following further research, both the United States and the United Kingdom enacted similar control measures. Evidence that only a few nanograms of TBT per liter

of seawater elicited a morphological change in a marine snail resulted in a lowering of the environmental quality target levels to 2 ng TBT per liter in the United Kingdom (Alzieu, 1991; Mee and Fowler, 1991; Waite et al., 1991). Reports from several regions in the United States showing TBT concentrations that exceeded the toxic limits for several sensitive marine species led to regulatory and legislative action to restrict the use of TBT antifouling paints on craft less than 25 meters in length, to require the use of low-release–rate paints in authorized applications, and to remove TBT paints from retail sale (IPCS, 1990). California followed suit, adopting regulations in January 1988 that restricted the use of TBT paints to large vessels (> 25 m in length). California's Department of Fish and Game and Department of Pesticide Regulation have monitored TBT and dibutyltin levels in Lake Tahoe and San Diego Bay since 1987 to assess the effectiveness of use restrictions. Residues in the sediments and organisms in these areas have declined sharply, demonstrating that restrictions on use have reduced TBT levels in these aquatic environments (Menconi, 1994).

Although there is some disagreement between the results of the different studies, it is generally agreed that:

- Because of its low solubility in water, TBT preferentially leaves the aqueous phase and adsorbs onto suspended particles and the sediment, in the aquatic environment.
- Significant amounts of TBT are associated with sediments in estuaries.
- TBT is more persistent in sediments than in the water column.
- The main factors limiting the persistence of TBT in aquatic ecosystems are the photolysis of TBT in water and biological degradation in water and sediment.
- TBT degrades through a series of debutylation steps to dibutyltin (DBT) and monobutyltin (MBT).
- The highest levels of TBT in the aquatic environment are primarily associated with ship or boat maintenance areas, and secondarily effluent outfall areas.
- The fate of TBT varies in the aquatic environment: physical and chemical properties operating in one region may not be applicable to others.

Fate in water

Estuarine water

Estuarine environments are dynamic systems, characterized by high biological productivity, and fluctuations in salinity, amounts of suspended particulates, and ionic concentrations. These areas also tend to receive input from the development of harbors and marinas, the encroachment of urban areas, and run-off from urban and agricultural activities.

Several studies address the fate of tributyltin in an estuarine environment (Lee et al., 1989; Seligman et al., 1989; Stang and Seligman, 1987; Donard and Weber, 1985). The World Health Organization has summarized many other studies (IPCS, 1990). Generally, the fate of the tributyltin derivatives in the estuarine environment is closely associated with their low solubility in water and their lipophilic characteristics. When TBT is introduced into natural waters, partitioning occurs and TBT leaves the aqueous phase and preferentially adsorbs onto suspended particles. The degree of adsorption depends on the characteristics and amount of the suspended particles, the salinity and temperature of the water, and the presence of dissolved organic material.

The reported amount of TBT that is adsorbed onto suspended particles ranges from 10 to 95% and varies with the conditions present (IPCS, 1990). Data suggest that in salinities approaching that of seawater, TBT is more strongly adsorbed, while in less saline water, TBT adsorption is reduced.

Once adsorbed, degradation of TBT occurs by biological action. Lee et al. (1989) reported that microalgae (dinoflagellates and diatoms) play an important role in degradation of TBT in sunlit estuarine waters. They monitored the degradation of TBT in sunlight and in darkness, in natural estuarine water and estuarine water from which they had removed the biological components by filtration and/or poisoning with a 3% formalin solution. The authors reported that TBT degradation in unaltered estuarine water occurred faster in sunlight than in darkness, with half-lives ranging from 3–13 days. This is consistent with another report of half-lives in the marine environment ranging from 4–14 days (Seligman et al., 1989). However, Evans and Huggett (1991) reported a degradation half-life of two to three years, based on statistical modeling of data collected during an intensive monitoring program they conducted from 1986 to 1989 in two tidal creeks of the Chesapeake Bay. Lee et al. (1989) noted that TBT degradation did not occur in the water lacking biotic components. When unaltered estuarine water was supplemented with nitrates, the degradation half-life was reduced to one to two days, and was associated with the stimulation of algal growths.

Non-estuarine water

Stang and Goldberg (1989) reported the average rate of degradation of TBT in fresh water is about the same as that in marine water; however, Stallard et al. (1987) reported that fresh and brackish waters generally had a much lower DBT/TBT ratio (an indication of the degree of degradation) than did comparable seawater samples. They concluded from their studies that TBT degradation may occur at a slower rate in fresh water than in seawater. Other studies have suggested that the degradation processes that occur in fresh water are not so much affected by the differences between salt and fresh water, but by the various physical characteristics such as turbidity, circulation, tidal flushing, and nature of source of contaminants present in a given body of water (Stang and Goldberg, 1989; Huggett et al., 1986).

Fate in sediments and sludge

Fate in sediments

Many studies address the fate of TBT in marine and estuarine sediments (Dowson et al., 1993a; Dowson et al., 1993b; Stang et al., 1992; Kram et al., 1989; Krone et al., 1989; Seligman et al., 1989; Unger et al., 1988; Maguire et al., 1985; Maguire and Tkacz, 1985; Maguire, 1984; and Maguire et al., 1983). Most of these studies concern the degradation of TBT in sediments; some also address the bioavailability of sediment-bound TBT (Table 7).

Table 7. A summary of tributyltin degradation studies in aquatic sediments.

Half-life of degradation	Location of sediment	Additional comments	Reference
10 months	Toronto Harbor, Canada	Desorption half-life, sterile sediment	Maguire and Tkacz, 1985a
4 months	Toronto Harbor, Canada	Water-sediment mixture	Maguire and Tkacz, 1985b
23 weeks	San Diego Bay, CA		Stang and Seligman, 1986
0.9–5.2 years	Essex and Suffolk, U.K.	Estuarine and freshwater sediment cores	Dowson et al. 1993a
1–2.1 years	Essex and Suffolk, U.K.	Controlled lab conditions, surface sediments	Dowson et al. 1993b

TBT degradation is slower in sediment than in water, with half-lives in months instead of days.

Municipal wastewater and sewage sludge

One group has investigated the concentration and fate of TBT during sewage sludge treatment in Zurich, Switzerland (Fent et al., 1991). The authors found that municipal wastewater and sewage were contaminated by organotin compounds; raw sewage sludge contained TBT, DBT, and MBT residues ranging from 0.28–0.83 mg/kg. Like the situation in sediment, TBT in wastewater and sewage sludge is primarily adsorbed onto particulate matter. They monitored the fate of the organotin compounds at various conditions (aerobic, anaerobic, mesophilic, thermophilic) and found the degradation rate of TBT during sludge treatment to be low, regardless of the conditions. They concluded that the abundance of nutrient materials present in sewage sludge may interfere in the degradation of TBT.

Fate in aquatic organisms

Tributyltin has been called the most toxic substance ever intentionally introduced into the marine environment (Mee and Fowler, 1991; IPCS, 1990). It first entered the marine environment in the mid-1960s as an active ingredient in marine antifouling paints. TBT is one hundred to one thousand times more toxic to laboratory animals than the zinc and copper compounds it replaced (Lenihan et al., 1990; Stallard et al., 1987). During the decade following its introduction, sales of TBT increased as manufacturers and users recognized the cost effectiveness of its use. The environmental and economic impact of TBT did not become evident until the deformative and reproductive failures of *Crassostrea gigas* (an important commercial stock of oyster) were noted in Arcachon Bay, France during the late 1970s (Alzieu, 1991; Mee and Fowler, 1991).

Once in the marine environment, TBT can be taken up by marine organisms through exposure to TBT-contaminated water and sediments, or ingestion of TBT-contaminated food sources.

The mechanisms of the storage and the elimination of TBT by the organism depends upon that organism's ability to metabolize the compound (Lee, 1991). The World Health Organization (IPCS, 1990) and U.S. EPA (1987) have provided excellent summaries of the earlier efforts to understand the environmental fate of this compound.

Bioavailability and bioaccumulation

Several groups have studied the bioavailability and bioaccumulation of tributyltin in a variety of marine life. In general, they have found that:

- the behavior of TBT resembles that of other hydrophobic, nonpolar organic compounds in that it tends to accumulate differentially in the lipid-containing portions of tissues and cells with the highest concentrations in the viscera and gills (Lee, 1991; Laughlin, Jr. et al., 1986).
- even when exposed to low ambient concentrations of dissolved TBT, marine mussels will quickly and effectively accumulate TBT.
- although dibutyltin and tributyltin compounds are functionally similar, TBT is much more toxic in both acute and sublethal responses than DBT (Laughlin, Jr. and French, 1989).
- estuarine sediments represent a significant source of TBT contamination, particularly to bottom-feeding organisms in these environments.

Laughlin, Jr. et al. (1989) studied the accumulation of tributyltin by the blue mussel *(Mytilus edulis)* in the San Francisco Bay. They found that in the laboratory, marine mussels rapidly and efficiently accumulated TBT when exposed to ambient concentrations as low as 0.5 µg/L seawater. They reported that uptake also occurred, and at a much higher rate, when TBT was associated with the phytoplankton *Isochrysis galbana*, the major food source of the blue mussel. They found the highest concentrations of TBT in the gill tissue and viscera (4.5 µg TBT/g tissue after 47 days of exposure to TBT-contaminated water, and ≈5 µg TBT/g tissue following 30 days of exposure to contaminated *I. galbana*). Once TBT-exposed mussels were returned to the field, the half-life for depuration was reported to be 14 days.

Mytilus edulis was also the subject of research conducted by Short and Sharp (1989). They measured tissue concentrations of TBT in bay mussels collected from California, Washington and Alaska in 1986 and 1987 in an attempt to estimate the decline of environmental TBT that should have resulted from enacted legislation limiting the use of TBT-containing antifouling paints in those areas. They reported concentrations of TBT ranging from < 0.005 to 1.08 µg TBT/g tissue. The highest concentrations of TBT were associated with marinas or areas of high boat traffic, however, TBT was detected in mussels living in areas with little to no boat traffic. They concluded that sources of TBT pollution are not limited solely to marinas or areas of boat traffic, and significant decreases in the concentration of TBT in mussel tissues should result in less than one year following an appreciable reduction of the amount of TBT released into coastal waters.

Batley et al. (1989) measured the accumulation of tributyltin (as inorganic tin, Sn) by the Sydney rock oyster (*Saccostrea commercialis*) and the Pacific oyster (*C. gigas*) sampled from estuaries in New South Wales, Australia. They found tissue concentrations ranging from < 2 ng Sn/g in rock oysters from areas with no TBT exposure to 130 ng Sn/g in rock oysters exposed to high densities of boat traffic or poor tidal flushing. Shell deformities and reduced tissue weights were

associated with all samples exposed to water concentrations of TBT in excess of 10 ng Sn/L. Specimens of the Pacific oyster, growing alongside Sydney rock oysters, contained 2–3 times greater concentrations of TBT.

The impact of TBT and inorganic tin on species living in the estuaries and coastal regions of the United Kingdom (UK) was assessed by Langston et al. (1990). They noted that sediment-bound TBT exhibited a higher degree of bioavailability than dissolved TBT, especially among estuarine bottom-dwelling species, such as the clam, *Scobicularia plana*. They also reported that the presence of aqueous concentrations of inorganic tin (mostly as the relatively insoluble $SnO[OH_3]^-$) seemed to offset some of the deleterious effects of the organotin, and suggested that the bioavailability and environmental impact of tin, as for many other metals, are related to chemical speciation.

Lenihan et al. (1990) studied the changes in community patterns induced by tributyltin in the hard-bottom, or fouling, communities of San Diego Bay. They found a large difference in the characteristic species that comprised the communities dwelling in areas of few boats, as opposed to those dwelling in areas relatively free of boat and marina activities. Areas with much vessel activity were reportedly characterized by sepulid polychaete worms, filamentous algae, and a tunicate, *Ciona intestinalis*. In areas with little or no boat or marina activity, these groups were replaced by mussels, sponges, bryozoans, and other tunicates, reportedly those hard-bottom communities characteristic of natural reefs. The authors concluded that community patterns in back-bays with many boats could be caused by the contamination with TBT (from anti-fouling paints) coupled with poor flushing or water circulation.

Deposit-feeding bivalves from 25 estuaries in England and Wales consistently contained higher concentrations of organotin than did other coexisting benthic organisms, indicating that preferential uptake of organotins from sediments may be an important route for bioaccumulation in *S. plana* (Langston and Burt, 1991). The authors measured the concentrations of TBT, DBT, inorganic tin and total tin in water, sediments and deposit-feeding clams to compare the bioavailability of different forms of tin, and studied the kinetics of TBT accumulation and elimination in the clams. They found that TBT and DBT are rapidly bioaccumulated from sediments. The authors reported that within a few days, clams held in sediments containing 10 µg TBT/g accumulated tissue levels of 25–30 µg TBT/g, a level sufficiently toxic to result in the death of these clams within two weeks, while clams held just above the sediment surface in the same tanks without direct contact with sediment, had only accumulated < 5 µg TBT/g after 50 days. They concluded that the sediments rather than desorbed TBT were the major vector for bioaccumulation.

In studying the subsequent elimination of TBT from *S. plana*, Langston and Burt (1991) found initially that elimination was rapid in those clams previously exposed to 1.0 µg TBT/g, and somewhat slower for those clams exposed to lower concentrations. From laboratory studies, they calculated half-lives of 14.5 and 27.5 days for clams previously treated with 1.0 and 0.3 µg TBT/g, respectively. They reported a half-life of about 50 days for clams that were collected from contaminated estuaries and placed in tanks of TBT-water in the laboratory.

Acute and chronic toxicity

There are several studies that address the toxicity of tributyltin to marine life. In general, these studies show that:

- organotins lead to an altered biology/ecology of numerous species. Extreme gross morphological and physiological sexual anomalies have been documented in many estuarine and marine species.
- the NOEL for TBT in oysters may be as low as 2 ng/L of seawater;
- all of the characteristic effects associated with TBT poisoning are hormonally regulated: TBT and hormones share common metabolic pathways.

Laughlin, Jr. and French (1989) examined the toxicity responses by zoeae of the mud crab *Rhithropanopeus harrisii* to TBT and DBT in the laboratory. They found TBT to be 54 and 65 times more toxic than DBT for crabs collected from Sykes Creek, Florida and Petaluma River, California, respectively. They reported LC_{50} values for both TBT and DBT. These values varied depending on the species origin. LC_{50} values reported for California crab zoeae were 13.0 µg TBT/L and 0.807 mg DBT/L, and for the Florida crabs were 33.0 µg TBT/L and 1.66 mg DBT/L.

Langston et al. (1990) assessed the deleterious effects of TBT-contaminated water on the dogwhelk, *Nucella lapillus*, a marine gastropod, by correlating a sequence of TBT-induced reproductive abnormalities, termed imposex, with the concentration of TBT in the aqueous environment. These phenomena, first identified in the estuarine snail *Ilyanassa obsoleta*, involve the development of a penis, vas deferens, and nonfunctional oviduct by female gastropods (Smith, 1980). The degree to which development of these anomalous characteristics affects the organism varies with the individual species, and may eventually lead to sterilization and death for the individual and ultimately to the loss of whole populations. In the case of *N. lapillus*, treatment with TBT has been demonstrated to convert ovaries into sperm-producing testes (Gibbs et al., 1988). Langston et al. (1990) reported that the initiation of imposex occurred at seawater concentrations below 1 ng/L (measured às inorganic Sn) and complete sterilization occurred after prolonged exposure to 3 ng/L. They warned that population recovery would not be possible until seawater TBT concentrations fall below the level that does not sterilize all developing females (about 2 ng/L), a level that was adopted as an environmental quality target (EQT) by the UK.

Curtis and Barse (1990), while studying the imposex phenomenon in the estuarine snail *I. obsoleta* living in the estuarine habitats of southern Delaware, reported that the same conditions that generate imposex in the female also affect male sexuality in this species. Two observations led the authors to this conclusion: 1) healthy *I. obsoleta* males normally lose the penis following reproduction, however they tend to retain it where female imposex-inducing conditions (the presence of organotin molecules in the water) were strong; and 2) males parasitized by trematodes normally lose the penis, but do not under the conditions that cause imposex.

The effects of tributyltin contamination in oysters have been summarized by Alzieu (1991). Documented abnormalities in *C. gigas*, an oyster of commercial importance, include the formation of wafer-like chambers of the shell following the abnormal secretion of an interlamellar jelly, reproductive failures, and mortality. The no-effect level (NOEL) was determined to be 20 ng/L,

while exposure to TBT levels as low as 50 ng/L caused mortality after two days, although Alzieu et al. (1991) reported that levels as low as 2 ng/L can cause deformities. In comparison, the NOEL for copper chloride is nearly five hundred times higher, at 10 µg/L.

Stephenson (1991) assayed the affects of TBT toxicity on *C. gigas* oysters in 26 bays, estuaries, and near-shore locations in California, including marinas, sewage, and refinery discharge areas, abandoned harbors and off-shore areas, following observations in Coos Bay, Oregon and Morro Bay, California, where oyster-growing areas had either been abandoned or oysters living there manifested the chambering deformities characteristic of TBT toxicity. He reported that at TBT levels of 40 ng/L no oysters developed normally or were commercially viable. Even at 10 ng/L, deformities were noted in developing oysters. Stephenson did not evaluate development at TBT levels below 10 ng/L.

Salazar and Salazar (1991) conducted field transplant tests from 1987 to 1990 in San Diego Bay to assess effects of TBT contamination on mussel growth rates. They measured mean concentrations of TBT in seawater ranging from 2 to 530 ng/L with corresponding tissue concentrations between 0.1 to 3.2 µg/g. They reported that normal growth was dependent on seawater and tissue TBT concentrations, with the lowest growth rates occurring at the most contaminated sites. The NOEL concentration has been estimated at 0.5 µg/g, which corresponds to those oysters exposed to TBT concentrations of about 25 ng/L or less (Page and Widdows, 1990).

Lee (1991) summarized recent work on the metabolism of TBT by marine animals and described possible metabolic linkages to the observed effects of TBT toxicity. He relates that tributyltin, like many other toxic compounds, is hydrophobic and tends to accumulate in the lipid-rich portions of tissues and cells. Marine organisms eliminate hydrophobic compounds by metabolizing and transforming them to water-soluble polar molecules. Generally, the metabolic breakdown of toxic compounds reduces their persistence and toxicity by accelerating their elimination. In some cases, the metabolites are more toxic than their parent compounds.

Lee (1991) reports that the research concerning tributyltin has demonstrated that this polar hydrophobic substance enters animals via lipid membranes and is metabolized in two phases. The first phase involves the hydroxylation of TBT to four hydroxydibutyltin derivatives through the cytochrome P-450–dependent mono-oxygenase system. The second phase involves conjugation of the hydroxydibutyltin derivatives to sugar or sulfate molecules, and the subsequent rapid elimination of these highly polar conjugates from the body. According to Lee, vertebrates and a number of the decapod crustaceans have well-developed cytochrome P-450 systems. In these organisms, the P-450 system is usually involved in vitamin D synthesis and/or calcium metabolism. Molluscs, however, typically exhibit very low cytochrome P-450 and mono-oxygenase activity, and therefore, substantially reduced rates of TBT degradation, which results in the accumulation rather than the elimination of TBT. The evidence suggests that the accumulation of TBT results in a hormonal imbalance in molluscs (as hormones and toxic substances are known to share common metabolic pathways) and leads to the structural and functional abnormalities commonly associated with TBT toxicity in these animals.

Presence in the environment

Sources

Tributyltin compounds are contained in pesticides registered in California for use in antifoulant paints on boats, ships, and marine structures such as piers and docks; as wood preservatives, molluscicides, and disinfectants; and as biocides for use in cooling towers, pulp and paper mills, and textile mills. The oxide and neodecanoate derivatives of TBT are contained in pesticides registered as active ingredients for use as biocides in cooling towers (DPR, 1995).

Concentrations and distribution in marine, fresh, and estuarine waters

The highest levels of TBT in the marine environment are located near marinas, boat yards and drydocks, and points where effluent from cooling tower blowdown is released. Concentrations of TBT are affected by the degree of tidal flushing and turbidity present (Uhler et al., 1993; IPCS, 1990; Lenihan et al., 1990). In areas of shallow water, with little or poor circulation of tidal waters, TBT may accumulate in the water and ultimately the sediments (Valkirs et al., 1986).

San Francisco Bay Region

In 1986, Stallard et al. (1987) monitored the concentrations of butyltin compounds at over eighty sites along the California coast, including San Francisco Bay. They found concentrations of TBT in the San Francisco Bay area waters ranged from 4 ng/L (ppt) in Vallejo to 570 ng/L at the Antioch Yacht Club. Sediment-bound TBT concentrations ranged from none detected (in several locations) to 7.7 ng/g (ppb) in the Oakland Estuary at Jack London Marina. They measured the concentrations of DBT and MBT at each site, and reported that, in general, DBT and MBT were found in lesser concentrations than TBT, although exceptions were noted. They also surveyed the aquatic biota at each sampling site, recording the identity and relative number of each species present. They reported that there was a conspicuous absence of native organisms, especially molluscs, in areas where TBT concentrations (in either the sediment or water column) exceeded about 100 ppt.

Stallard et al. (1987) reported that higher concentrations of butyltins were found in marina waters than in either harbor or coastal waters, and that fresh and brackish waters generally had a much lower DBT/TBT ratio (an indication of the degree of degradation) that comparable seawater samples. They speculated that TBT degradation may occur at a slower rate in fresh water than in seawater.

Other locations in California

From 1983 to 1985, Valkirs et al. (1986) monitored the concentrations of several butyltin compounds (TBT, DBT, and MBT) and inorganic tin in water samples taken from ten sites within San Diego Bay. They found that concentrations of all organotin compounds increased over time, ranging from the MDL (< 0.01 µg/L) to 0.93 µg/L, and attributed their observations to increased boating activity and topography. The relatively narrow entrance channels to many portions of the San Diego Bay limit water circulation in these areas, and therefore affect the levels of contaminants released into these areas.

San Diego Bay was also the location for TBT stratification and variability studies conducted by Stang et al. (1989). They monitored concentrations of TBT in near-surface and near-bottom water over a 25-hour period at the entrance to Shelter Island yacht basin. They reported surface

water concentrations varying from 20–225 ng TBT/L and bottom water concentrations varying from < 1–77 ng TBT/L. The highest surface water concentrations were associated with ebbing tides, while the lowest were associated with flooding tides. The reported bottom water concentrations were nearly always lower than the surface water concentrations, and varied 180° out-of-phase with the surface water concentrations. The authors concluded that a vertical stratification of the water column occurred during ebbing tides and dissipated during the flooding tides. They indicated that TBT concentrations in natural waters are dynamic and are subject to the spatial and temporal changes characteristic of the particular site of interest.

Stang and Goldberg (1989) measured the butyltin concentrations at twenty-seven locations throughout California, primarily in river and lake marina waters. They reported measurable amounts of butyltin compounds in a majority of the freshwater samples collected. The highest concentrations were at the Discovery Bay Yacht Harbor (140 ng TBT/L) and at the San Joaquin Sailing Club (110 ng TBT/L), both of which berth vessels that travel downriver to marine areas. However, TBT was found in 19 other marinas in freshwater lakes with no boat access to marine waters, eleven of which contained environmentally significant levels of TBT (levels ≥ 10 ng TBT/L). The authors attributed the presence of TBT in freshwater to the unnecessary use of TBT-containing hull paints on boats harbored in these marinas. In studying the TBT/DBT ratio, they found them to be similar to those reported for marine water, and concluded that the factors that govern degradation in the marine environment also affect TBT degradation in the freshwater environment.

Valkirs et al. (1991) conducted prolonged monitoring of TBT concentrations in San Diego Bay from 1988 to 1990 to determine if legislative restrictions on the use of TBT-containing antifouling paints (effective January 1988) affected TBT concentrations in the Bay. They reported that surface water concentrations significantly decreased compared to previous studies they conducted (Valkirs et al., 1986). Tissue samples taken from *M. edulis* living in the monitored areas also showed a decrease in tissue concentrations of TBT; however, the authors report that sediment-bound concentrations of TBT did not reflect the decreases observed in the water column.

Other locations in the United States

Huggett et al. (1986) conducted a monitoring program for tributyltin concentration in the Southern Chesapeake Bay and Elizabeth River, both in Virginia. Chesapeake Bay was chosen for this study based on the increasingly large number of recreational, naval and commercial vessels moored within its waters. The Elizabeth River estuarine system was selected because of the high degree of industrialization along its banks. The authors reported that the data collected demonstrated that tributyltin concentrations vary to a large degree over time and space; concentrations an order of magnitude apart were found at the same location within the same week, while concentrations different by a magnitude of two were found in samples taken from different locations within the same marina at the same time. The authors warn that such variabilities must be considered when interpreting results from monitoring studies.

Evans and Huggett (1991) monitored the presence of tributyltin during a three-year program of weekly sampling at nine locations within two tidal creeks of the Chesapeake Bay. They statistically modeled the results of this intensive monitoring program, which began in July 1986 and

concluded in the summer of 1989. From their studies they calculated a degradation half-life for TBT of two to three years.

Contributions from urban effluent

Urban effluent has been identified as a potential source of TBT entering the estuarine and marine environment. The predominant source of TBT in urban effluent is discharge from cooling towers, or blow-down (Clean Bay Plan, 1994). Other sources of TBT in urban effluent may include exterior-grade wood preservatives for use on siding, decks, and outdoor furniture, or disinfectant and antimicrobial cleaners, toilet bowl cleaners, and antibacterial carpet and upholstery shampoos, all designed for hospital and institutional use (DPR, 1995).

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PART FOUR — ALTERNATIVES TO THE USE OF COPPER SULFATE FOR CONTROL OF ROOT INTRUSION IN SEWER LINES

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Introduction

Root intrusion in sewer lines can be a significant problem for municipalities (Ralph (Bus) Breese, pers. comm.; Farral Crawford, pers. comm.). However, surveys have shown that residential service laterals—the portion of the sewer line extending from houses and apartments to the main sewer lines that run along the street—are the source of most problems with sewer system root intrusion (Sullivan et al., 1977a; Sullivan et al., 1977b; Tobiason, 1990). Root intrusion into lateral service lines can be controlled by introducing copper sulfate purchased over the counter into residential drains (Brandenburg, 1994; Will, 1991). For this reason, this alternatives analysis will primarily focus on methods to control root intrusion in service laterals, although discussion of root control methods from the perspective of municipalities is included as well.

Control of root intrusion—copper sulfate and alternatives

Plant roots do not prefer waterlogged conditions. With few exceptions, roots generally seek and grow in environments high in humidity rather than in standing water where they die, deprived of oxygen (Sullivan et al., 1977a; Sullivan et al., 1977b). Sewer pipes are only partially filled with water at any given time and the air within them is warm and moist, an optimal environment for roots. Air, rather than water, is a limiting factor in root development. Roots do not break pipes to gain access to water, but rather flourish in moist soil near a seepage, penetrate the pipe at the seepage point, and then proliferate within the humid air in the pipe, ultimately causing a blockage (Brennan et al., 1989). Roots tend to enter points of sewer defects near the top or sides of the pipe, rather than at the bottom. Consequently, copper and other chemicals that are simply poured down toilets, cleanouts, or manholes in liquid form to control roots in sewer lines have a tendency to flow under the bulk of the root masses, doing little damage to roots unless the roots actually reach all the way down to the water line in the pipe (Sullivan et al., 1977a; Ralph (Bus) Breese, pers. comm.; Farral Crawford, pers. comm.). This method of chemical application for root control allows little control of actual concentration of the product or duration of exposure to roots in the pipe line. Adequate chemical concentration and contact time are critical to root control. Copper does not prevent regrowth of roots that it kills. Ahrens et al. (1970) demonstrated that even when using high concentrations of copper sulfate, root kill was incomplete and phytotoxicity to vegetation resulted. In addition, copper sulfate is toxic to microflora, including those that rot and decay killed roots as well as those that are necessary to the sewage treatment plant (Sullivan et al., 1977b; Mossar, 1991).

Alternatives to copper sulfate each have their own particular niche and value, as well as limitations in given situations (Table 8, page 56). Moreover, each site and situation has its own set of unique parameters. An attempt was made to identify the comparative costs of the various alternatives; however, meaningful comparisons of the feasibility of these alternatives should not be

based on cost. Soil type, sewer pipe material, line depth, line size, line condition, ease of access, tree species, tree age, root mass, proximity of roots to lines and availability of treatment options are just a few of the parameters that enter into the overall cost equation. Thus, one method is likely to be more suitable than another for that specific situation, notwithstanding cost. In addition, some alternatives are simply inappropriate and impractical for a given situation. The costs given are merely gross estimates and are in no way meant to reflect what the actual costs might be for a particular site. The costs described are merely intended to provide a relative comparison of alternatives, not an accurate cost estimate that will be applicable in all cases. The costs given, therefore, should not be construed as an objective basis for comparison of alternatives. On the contrary, durability and longevity of repair, duration of repair process, labor and equipment necessary as well as disruption of service and above-ground activity are probably far more realistic criteria by which to compare the feasibility of alternatives for a given situation. In addition, mention of trade names in this report in no way implies endorsement by DPR.

Short-Term Control Measures

Chemical alternatives

Toby's Foaming Root Killer D—Manufactured by Toby's Chemical Co. and marketed by General Chemical Company, Toby's Foaming Root Killer D contains 0.5% dichlobenil, and is a non-systemic herbicide specifically designed for the control of tree roots. The product foams on contact with water and fills the line with foam solution, including the air space above the water line, insuring good contact of the herbicide with roots growing into the pipeline from the top and sides of the pipe. To apply to 4-inch residential laterals, two pounds are added to the toilet bowl or cleanout, followed by quickly flushing with about five gallons of water.

Advantages: Dichlobenil is an effective root growth inhibitor and root killer. The foam formulation fills the line and makes good contact with roots that hang down from the top and sides of the pipe. The foaming feature makes the product especially useful for lines with low flows since it does not require blocking of a line and filling it up with liquid to ensure adequate contact with roots. Unlike copper sulfate, dichlobenil does not destroy root-decomposing microflora or microflora important to treatment plants. Dichlobenil is an effective root inhibitor even at sublethal concentrations (Sullivan et al., 1977b). It has good residual activity, repressing root growth for 13 years. It is readily available in bulk quantities and can be applied without need of a contractor, special license, or special application equipment. The foam product distributes well through pipes even in hilly topography. It provides longer term control than cutting the roots. There is no service disruption, excavation, or flow diversion necessary. In some parts of the country, it can also be dusted into sewers by licensed contractors to insure higher concentrations of herbicide come into contact with the exposed roots.

Disadvantages: The foam eventually drips and drains away, taking a good deal of chemical with it. Much of the chemical is wasted on filling empty line without contacting any roots, although this is not the case with the sewer-dusting type of application. Dichlobenil provides only temporary control of root intrusion. Roots will eventually grow back and require subsequent action if the pipe condition and environment are left unchanged.

Costs: Depending on the quantity ordered, 2-pound containers range from $16 to $18 per pound. Larger quantities can be as little as $8 to $9 per pound. There are no other costs. No contractor, license, or any specialized equipment is required. Based on label-recommended dosages, the cost for one residential lateral treatment would be about that of a 2-pound container for the entire lateral. Thus, if the lateral line is around 20 feet long, the cost would be approximately $1 per foot. For larger lines of municipalities, based on label-recommended dosages, the cost would be slightly more than $1.20 per foot for an 8-inch line.

Sanafoam™ Vaporooter® II and Foamcoat™ Vaporooter®—Manufactured by Airrigation Engineering, Sanafoam Vaporooter II is 24.25% metam-sodium and 1.95% dichlobenil. Foamcoat Vaporooter is 28.4% metam-sodium and 1.73% dichlobenil. Both products are applied as a foam produced by a piece of equipment called a Foamaker available from the chemical manufacturer. The purpose of the foam is to ensure good contact of the herbicide with roots growing into the pipeline from the top and the sides of the pipe. Sanafoam Vaporooter II is used to fill the line with foam, whereas Foamcoat Vaporooter is designed to coat the inside of the line with approximately a 2-inch layer of foam rather than fill all the airspace. Foamcoat Vaporooter is designed to be more economical for use in large diameter pipelines so that good contact with intruding roots is achieved without having to fill up a relatively large diameter pipeline with foam. For homeowners, Sanafoam Vaporooter II is applied by a contractor.

Advantages: The chemicals are efficacious, provide residual activity for one to three years, and are well distributed within the pipe, providing good contact with roots penetrating from the tops and sides of the pipe. Use of these products provides longer term control than cutting. There is no service disruption, excavation, or flow diversion necessary. The foam product distributes well through pipes even in hilly topography. After repeated treatments to kill regrowing roots, residual control may last for up to five years (Farral Crawford, pers. comm.; Michael Parks, pers. comm.). Because the Sanafoam application equipment comes in a range of size and prices, contractors and municipalities can purchase equipment that fits their particular budget and needs. The price of the equipment includes training and certification of the operating personnel by the manufacturer.

Disadvantages: This method requires either contractor application, or purchase of application equipment (Foamaker®). City of Sacramento personnel believe that for long-term effectiveness it should be used in conjunction with root cutting to clean out killed roots. Using this method of control, the municipality of Rockville, Illinois chemically killed roots without cutting or cleaning and experienced problems with dead roots falling off, accumulating at connections of laterals and mains, and collecting debris (Sutton, 1984). Although this material inhibits root regrowth much longer than cutting, it provides only temporary control of root intrusion. Roots will eventually grow back and require subsequent action as long as the pipeline environment remains unchanged. One municipality interviewed had used this material in the past but stopped because they experienced problems with phytotoxicity to trees, turf, and shrubs. Others said they do not prefer this method because they want to avoid the liability of handling or using metam-sodium (Dan McKenna, pers. comm.). Metam-sodium is toxic to microflora necessary to treatment plants. The product does not work as well during the drier months in California when pipeline flows are lower (Farral Crawford, pers. comm.). If a municipality goes to the expense to invest in the application

equipment, it still may not be able to afford the personnel costs associated with application. The equipment and crew must be able to work quickly and efficiently to make this method cost-effective (Farral Crawford, pers. comm.).

Costs: Typically, herbicide foam treatments costs range from about $1.00 per foot (Claudia Norton, pers. comm.) to $2.50 per foot (Tobiason, 1990). Contractors frequently perform a root cutting/line cleaning before treatment. If the equipment is already owned, then the material cost for Sanafoam Vaporooter II is about 33¢ per foot for an 8-inch line (one gallon costs $52 and makes 400 gallons of foam that will fill 160 linear feet of 8-inch diameter pipe). The cost of the chemical varies with the quantity purchased. The initial investment in the Foamaker can range from $9,000 to $29,000 depending on the size and versatility of the machine chosen. The cost of the equipment includes the cost of training and certification of the operating personnel by the manufacturer. According to Airrigation Engineering Co. representatives, such equipment should last for ten years with good maintenance (Barbara Tiernan, pers. comm.). Personnel from the City of Chico (Chris Boza, pers. comm.; Michael Parks, pers. comm.) feel that Sanafoam Vaporooter II gives them three to five year control in lines of up to 14 inches. They estimate their cost of treatment is somewhere around $9–$12 per linear foot, taking into consideration the expense of the equipment and labor.

There are a number of other chemical root-control products on the market that are currently registered in California containing little or no copper. However, no users of these products could be located, nor was cost per foot information available. The following products are included in this category.

- ***Angus Hot Rod with 2,6-D***® is a compound that contains 56% sodium hydroxide and 0.5% dichlobenil. The label allows municipal users.
- ***Rooto***® is a product that contains 85.69% sodium hydroxide and 0.3% copper sulfate.
- ***Root Out***™ is a product that contains 2.1% dichlobenil.

Physical and Mechanical Alternatives

Root cutting—One of the most widely used methods of protecting sewers from root intrusion is by cutting or clearing by using a rotating blade or other device inserted in the line. Root cutting and line clearing provides the quickest, most immediate relief for root-clogged systems. Clear lines usually last for a few months without any further action. There are a number of devices designed to cut, mulch, or blast roots out of a line. For homeowners, private contractors such as Roto-rooter® can do the job, or they can rent a cutting device and do the work themselves. Municipalities have several devices to clear lines of roots. Listed below are three such devices that are specifically designed to cut roots in sewers.

- ***Ohio Root Cutter***®—This is essentially a circular, double-edged, coarse-toothed saw blade that saws the roots off while spinning at about 1,000 rpm. It is necessary when roots are more than one half centimeter in diameter. According to those in the industry, few municipalities are still using the Ohio Cutter because it tends to be somewhat labor intensive and dangerous, frequently causing back injury. The cutting blades need to be replaced relatively often (sometimes several times per week, or even per day), at a cost of about $20 each.

• ***Chain Flailer***—The chain flailer is lighter, easier to use, and safer than the Ohio Cutter, and tends to mulch the entire mass of exposed roots rather than just cutting them off and leaving stubs in the pipe. Sacramento and San Luis Obispo counties have used the chain flailer satisfactorily. They use special hardened chain from Sweden of a critical size. The flailer chains may need to be replaced frequently. New replacement chains run about $20 (Ralph (Bus) Breese, pers. comm.). In general, the chains have about 1,000 hours of usefulness.

• ***Hydro Jetcut***—The Hydrojet Cutter is a remote controlled pipe-cleaning system that uses a high pressure water jet system and closed circuit-television. It features a body and head that can rotate 360 degrees. It is more appropriate for small jobs, such as a single root-intruded joint or treatment of service laterals, rather than entire sewer lines. It can take out small rootlets, but isn't very effective against larger roots. It cuts relatively slowly, and requires a long time to set up (James Ovady, pers. comm.).

Advantages: Root cutting and line clearing provide the quickest, most immediate relief for root- clogged systems, and are chemical-free.

Disadvantages: Cutting is only a short-term, temporary solution, as the roots immediately begin to grow back, becoming larger and more vigorous than before (Rolf and Stål, 1994; Sullivan et al., 1977b; Sutton, 1984). Root cutting equipment can not always be used effectively if lines are badly misaligned, in lines in which laterals protrude into mains, or if lines run very deep. The logistical and space requirements of the equipment can be a problem if access is not convenient. Occasionally crews have problems getting cutting equipment to the sewer entrance site when manhole access is not located in or near a street (for example in backyards). Removal and disposal of root material from the line after cutting can sometimes be a problem as well. A sewer in poor condition can actually be damaged by cutting or flailing equipment (Sullivan and Ewing, 1985; James Ovady, pers. comm.). Some pipe materials are inappropriate for certain pieces of equipment. For example, the chain flailer can be used without problems in concrete pipes but can damage other types of pipes such as those made from clay (James Ovady, pers. comm.). The Ohio cutter and similar heavy equipment can sometimes be a safety problem, particularly for back injuries, resulting in workers' compensation claims (Ralph (Bus) Breese, pers. comm.). In addition, root cutting equipment requires a significant capital investment. The initial cost to purchase a chain flailer, for example, is about $16,500 (James Ovady, pers. comm.). But in addition to the initial purchase, there are costs associated with maintenance, replacement parts, and the well-trained labor needed to operate it.

Relative Costs: For the homeowner, Roto-rooter-type companies do the job at a cost of about $50–$70 per hour (Will, 1991). The homeowner can rent a cutting device for about $50 to $60 per day (e.g., $55 at River City Rentals, Sacramento). For municipalities, it costs roughly $500 (including labor, maintenance, and new parts) to do a typical root cutting/clearing with an Ohio cutter for a block-long sewer line, a job requiring about three hours' work. The same job using other equipment may cost more or less, depending on numerous factors such as the crew size, accessibility to the entrance, the line size and depth, removal and disposal of material from manholes and distance to disposal site, the need and degree of traffic control necessary, the availability of water, the structural condition and material of the sewer, the degree of root

intrusion, and weather conditions. For comparison, the chain flailer takes about one-half hour to do the same job at about one-fourth the cost as the Ohio Root Cutter (Ralph (Bus) Breese, pers. comm.). Rodding or jetting lines clear of small roots costs roughly $1.00 per foot (Tobiason, 1990).

Installation of Y-Cleanouts—Some municipalities that require homeowners to assume responsibility for the condition of their own lateral service lines have encouraged homeowners to install Y-shaped cleanouts near the street easement to ensure ready access for future root intrusion control by cutting or other action. To encourage this, homeowners in some areas have been offered future root-cutting maintenance of their laterals by the municipality at no charge (Ron Morrow, pers. comm.). In some municipalities street-access cleanouts are required for all new construction (Sutton, 1984).

Advantages: The main advantage of Y-cleanouts is ease of access for mitigation of root intrusion with cutting equipment or other means. This provides for immediate relief of future root problems by cutting, if nothing else.

Disadvantages: Y-cleanout installation involves high up-front costs to the homeowner. It provides for only temporary relief, and potentially sets up a municipality for a substantial amount of future, labor-intensive cutting work. Root problems will get worse if cutting is the only approach, regardless of the convenience of access.

Costs: A typical cost for installation of a Y-cleanout by a local contractor was estimated by one city expert at about $800 per lateral (Ron Morrow, pers. comm.). However, amortized over time, such costs might be considered relatively reasonable by the homeowner.

Long-term Control Measures

Excavation and Replacement of Line—Excavation of a defective line and replacement with a new one is the most long-term solution, and in some cases the only certain remedy to a faulty sewer line (Brennan et al., 1989). This is particularly true for replacement with ABS or PVC (solvent-welded) type pipe that has fewer, and more water-tight joints than the commonly used clay pipe. Excavation and replacement of old deteriorated lines usually involves heavy equipment and is fairly labor intensive, as well as disruptive to traffic and other above-ground activities. Several options exist for replacement materials. For example, among other materials, municipalities can opt for more jointed, vitrified clay pipe (VCP), cast iron pipe, or plastic solvent-welded pipe such as PVC or ABS pipe. The City of Chico is replacing more and more defective sewer lines with ABS and PVC solvent welded pipe in particularly troublesome root intrusion areas since this repair lasts much longer (Chris Boza, pers. comm.). After a line has been cut, cleaned, and Vaporooter-treated several times and the pipe line continues to be a trouble spot, the City of Sacramento frequently replaces or relines the troublesome line (Farral Crawford, pers. comm.).

Advantages: Replacement provides the most long-lasting repair. Correctly installed solvent-welded pipe, in particular, features few joints and is not vulnerable to root intrusion since root- attracting leaks are unlikely (Uni-Bell PVC Pipe Assoc., 1991; Randy Becker, pers. comm.). The life expectancy of a new plastic pipe line is likely to be greater than a repaired VCP line. Ten to thirty years (or better) of relief from root intrusion is possible, depending on the pipe material used and

the quality of installation (Tobiason, 1990; Randy Becker, pers. comm.; Claudia Norton, pers. comm.).

Disadvantages: Potentially high up-front costs, the inconveniences associated with excavation (disruption of service, traffic diversion), and longer time for repair than trenchless repair methods are major tradeoffs for the long-term benefit of excavation and replacement with a new line.

Costs: The greatest portion of the cost of line replacement is for excavation. Chris Boza (pers. comm.) estimates that in Chico it costs roughly $30 per foot just to open a trench without doing any work to the line itself. The Sacramento County Water Quality District (SCWQD) estimates a cost of about $120 per foot for excavation and replacement of a 10-inch-diameter line with lateral connections (Hassey et al., 1991). It should be noted that costs for excavation and replacement can vary greatly from site to site. For example, to replace typical residential laterals in Orange County it can cost from $2,000 and higher (Ron Morrow, pers. comm.). In the San Francisco Bay Area the same repair can range from $1,500 to $3,500 for 4-inch laterals, that tend to be shallower than main sewer lines (Will, 1991). However, when amortized over the expected ten to 30 years of relatively maintenance-free lines, such costs become much more affordable, in the range of $50 to $120 per year.

Trenchless Replacement of Lines—Some systems can provide for replacement pipe of the same diameter or even a larger diameter in the same space without excavation. One such system is the Miller Xpandit® trenchless system that uses a splitting head that breaks and displaces the old pipe, and pulls a new high density polyethylene thermoplastic pipe (HDPE) into place behind it.

Advantages: There is no reduction in pipe diameter as is the case with pipe liners. With this pipe replacement system, it is possible not only to replace a pipe line with one of the same size, it is actually possible to replace a pipe with a new line that has up to 50% greater cross-sectional area. The Miller Xpandit trenchless system can be used to replace pipes from about four to 20 inches in diameter (Collins Orton, pers. comm.).

Disadvantages: The system is relatively expensive, and requires an excavation pit at one or both ends of the pipeline being replaced to accommodate the winching equipment and the new sections of pipe being pulled into place. Reconnection of laterals may also be labor intensive and expensive.

Costs: The Xpandit system of pipe replacement runs about $60 to $100 per foot, depending upon several factors, including the number and length of lines being replaced, and whether lateral connections are involved. A recent job in Washington involving the replacement of about 10,000 feet of various sized lines cost about $75 per foot (Collins Orton, pers. comm.).

Cured In-Place Pipe (CIPP)—Inversion lining or Cured In-place Pipe behaves as a flexible conduit in a rigid pipe. Currently, the best known CIPP product is Insituform®. A 1993 Amoco Chemical Company advertisement in the industry periodical Trenchless Technology made the statement that over 10 million feet of Insituform pipe has been installed in the United States.

Felt tubes that are impregnated with a resin are manufactured to precisely fit a specific size of pipe. One end of the Insituform sleeve is attached to the end of an inversion tube at the entrance to the existing pipe. Pressurized cold water forces the sleeve into the old pipe, turning it inside out as it goes. The new Insitutube walls that are resin-impregnated, are pressed firmly into continuous

contact with the walls of the old pipe. The smooth side of the Insitutube sleeve becomes the interior of the new pipe. After the insitutube is inverted all the way through the old pipe, the water is heated and the hot water cures the resin, changing the pliable insitutube into a hardened, seamless, jointless, pipe-within-a-pipe (referred to at that point as Insitupipe™). When Insituform is used for sewer mains, reconnecting service laterals can be accomplished by a remote-controlled, television-monitored cutter that cuts out the lateral connections where the CIPP liner is distinctly dimpled. It can cut as many as 65 lateral connections in a day (Anonymous, 1994a). Insituform requires about 12 hours to cure. Because it is a trenchless repair procedure, many businesses choose Insituform for sewers that run under buildings and structures (Olson, 1986).

Advantages: There is little disturbance to people and property, and there is relatively little down-time for the sewer system. There is little or no excavation involved, making this method of sewer repair much faster than excavation and replacement. It can be done in hours to days instead of days to weeks. This is especially true for deeply placed lines that would require considerably more excavation. The new pipe has good strength, durability, and longevity. Insituform liners are flexible and can repeatedly go around corners and 90-degree bends. Insituform provides a seamless and jointless pipe line which means there are no joints to open or leak, thus preventing the attraction of tree roots. The smooth walls on the new pipe provide low-flow resistance and increased flow volume, compared to unlined clay pipe (Utz, 1983). Insituform is resistant to a wide variety of chemicals, so it does not quickly degrade or deteriorate from chemicals. Even Insituform-lined sewers that carry high-strength industrial/chemical waste hold up well (Olson, 1986). In fact, different kinds of resins can be used depending on the type of sewage effluent, e.g., in industrial vs. suburban areas. The flexibility of Insituform eliminates the need for large pits through which to load inflexible pipe liners. Insituform comes in a wide range of sizes. It can reline 4-inch service laterals up to 120-inch pipelines (Anonymous, 1994b). Because Insituform is a trenchless repair method it avoids a significant amount of injury to the root systems of valuable trees by avoiding excavation (Utz, 1983). Where legal or physical access to a site is a problem, Insituform is of great benefit (Olson, 1986). The new pipe material can also be patched, welded, or bored making any future repairs much easier (Farral Crawford, pers. comm.).

Disadvantages: Before relining, the old pipe must first be thoroughly cleaned. Safety may be a concern during installation, since hot water or steam under pressure used for curing can be hazardous, particularly considering the height at which the hot water must be drawn and discharged into the inversion tube. The resulting pipe is smaller in diameter than the original pipe. Sometimes it is difficult to get trucks and the necessary equipment near the entrance site to pipelines when the entrance is not conveniently located in the street.

Costs: Costs may be relatively high, compared to some other repair methods. Costs may also vary from job to job depending on a number of variables. For example, the EPA Certification 91-24 Handbook (July 1991 edition) lists the cost for Insituform-lining of a 10-inch line at $80 per foot, but SCWQD reported that the actual cost for a 10-inch line on a project without any laterals was $140 per foot (Hassey et al., 1991). On the other hand, on a Nashville project, 4,400 linear feet of 8-inch clay pipe was relined for $44.50 per foot (Bible and Hinte, 1993). In Northern California, a typical four-inch residential lateral relining could run about $2,500, or about $60 per

foot (Claudia Norton, pers. comm.). As another example, Insituform Midsouth Co. completed a repair using this method, that included cleaning, television monitoring, and relining of 63 service laterals, each about 20 feet long, for $1,475 per service line, or roughly $74 per foot (Bible and Hinte, 1993). Although the method is currently somewhat expensive, it is the opinion of some in the industry that if the patent for this technology expires, more companies might offer this technology, that could result in a reduction of the cost of this method of repair.

Fold and Form PVC Pipe—Fold and Form PVC is a polyvinyl chloride pipe material that is soft and flexible at ambient temperature, but is cured to a hard state with hot water or steam after being pulled or pushed through an existing pipeline. The PVC lines the walls of the existing damaged pipeline. One of the best known fold and form PVC pipe products is Nupipe®. It is transported in a softened condition, then pulled into the old pipeline through a heat containment chamber. A rounding device then conforms the softened material to the walls of the old pipeline, and pushes any water out ahead of the pipe-rounding device. The pipe is then allowed to cool and harden. Recently the service laterals of residents of the City of Willits, California, as well as a number of larger city sewer lines, were lined with Nupipe (Claudia Norton, pers. comm.).

Advantages: Installation of Nupipe is a quick, trenchless operation that can reline a 100- to 200-foot line in two to four hours. A lack of joints and seams halts seepage and attraction of roots. Flow is maintained or improved as a result of the lack of joints, the smooth inner PVC surface, and the smooth transition at existing offsets and deflections. The new pipe is flush against the old deteriorated pipe, maintaining structural strength.

Disadvantages: Unlike Insituform, Nupipe will not work in 90° bends because it is pulled by a winch through a heat containment tube. A good pre-cleaning of the pipe is necessary. Some spot repair may be necessary first before lining, depending on the degree of damage to and general condition of pipe line (misaligned, crushed pipe will not accommodate the liner very well). There may be additional costs associated with preliminary evaluation of the line for straightness and defects. The resulting pipe is smaller in diameter than the original pipe. Nupipe is only available in four to 12 inch size pipe, as opposed to four to 120 inch for Insituform.

Costs: The cost to reline a typical service lateral with Nupipe is about $2,000, or about $30 to $60 per foot (Claudia Norton, pers. comm.). The cost for larger diameter pipes is about $20 to $40 per foot, depending upon how much line is being done (Claudia Norton, pers. comm.). Other economic factors to consider include the size and weight of liners (the thicker and heavier the liner needed, the more expensive to make, ship, and handle), the type and amount of pre-cleaning procedures necessary (effort and equipment required), the degree of damage and general condition of pipe line (misaligned or crushed), the costs associated with proving the line for straightness and defects, the number of service laterals that will need to be cut and reconnected, the amount and type of spot repairs necessary before lining, and any traffic control or diversion.

Chemical Grouting—Chemical grouting and sealing is done to stop the seepage of water from sewer lines that attracts tree roots. There are a number of different grouting systems and a number of different grouts available on the market with different curing or hardening times, strengths, and textures to suit different situations. Chemical grouting involves the use of a television camera

and robotic device that can locate problem areas, prepare surfaces, and apply grout to seal defects one at a time by remote control. Grout packing devices generally have two inflatable ends that, when inflated, seal off the defect from the rest of the line, permitting the gel packer to fill the void with the gel-grout material. The grout is forced into the joint and/or the cavity that may also exist to some degree outside the line. The newly grouted repair is air pressure-tested on the spot. The herbicide dichlobenil is sometimes added to grout to inhibit future root intrusion. The Gelco Company, for example, frequently adds the dichlobenil product Casoron herbicide to its grout (Claudia Norton, pers. comm.). For maximum effectiveness, a thorough precleaning of the line to be grouted is necessary. Grouts have typically been acrylamide gels mixed with diatomaceous earth, although now acrylics and urethane grouts are being used as well, depending on the soil type and other site variables. However, due to environmental and health concerns acrylamide gels may be on the way out (Berry and Magill, 1992; Claudia Norton, pers. comm.). According to Claudia Norton, formerly of the Gelco Company, a common practice is to grout all of the joints in a line if one is bad, rather than to grout only the joints with obvious, visible defects.

Advantages: Grouting can be done using a television camera and grout packer to seal pipe joints and pipe defects in pipes 4 inches and larger. The equipment inspects and seals in one operation. Dichlobenil can be added to the grout giving added effectiveness and residual protection against future root intrusion.

Disadvantages: Lines must be thoroughly cleaned before television camera inspection and grouting. Although basically cost-effective in the short term, grouting thus far has been somewhat inconsistent in long-term dependability. Grouting is impractical for use with lines that are badly deteriorated, badly misaligned, or have large voids. It works well for repairing leaky joints, providing the line is reasonably straight and in good structural condition, but is not particularly effective for repairing structural breaks in the lines. If structural damage is present it may be necessary to do some excavation and spot repairs first. Adequate curing and bonding has sometimes been a problem, particularly in wet environments, that may result in the need for return visits to the site for additional follow-up repairs (Berry and Magill, 1992; Hassey et al., 1991). It is very difficult to adequately grout repair defects and joints near lateral connections with mains since there isn't an effective way to seal off one end of the defect area so that pumping pressure can be applied. It is also ineffective for cracks or defects that extend longer than the grout packing device. Grouting does not work well for joints with more than just a slight amount of displacement due to the inability to apply pressure to the grout. Since grout repair jobs are frequently put out to bid, it is always possible that low-bid contractors may do an inadequate packing job, necessitating follow-up visits and repairs (Claudia Norton, pers. comm.). In a 1986 EPA report, a multifaceted approach to repairing the sewer lines of Hagerstown, Maryland is described in which four methods of repair were used, including grouting. Although all four methods successfully reduced the amount of mainline seepage to ground water in the short run, a number of sections that received grouting treatments began to deteriorate shortly thereafter (within two to three years), so plans were made to reline them with Insituform (Olson, 1986). Sacramento County also experienced mixed results from a grouting and sealing procedure done by a contractor as part of an on-site demonstration project (Hassey et al., 1991). In addition, robot breakdowns do occur, causing down-time and

delays due to repairs and parts replacement during the job (Hassey et al., 1991). In some cases the weight of the umbilical cord to the robotic device can be a limitation, and the robot's motor drive may be inadequate to pull the device very far into a line, in which case it must be winched manually (Hassey et al., 1991). The future availability of acrylamide gels is questionable, and none of the newer urethane and acrylic grouts and other substitutes for the acrylamide grouts have been completely satisfactory (Berry and Magill, 1992). Residuals in empty grout containers have been classified as hazardous, creating storage and disposal problems. Consequently, grouting costs have risen (Berry and Magill, 1992). Without herbicide additives, grout alone may not adequately stop root intrusion (Tobiason, 1990).

Costs: Grouting can be done for about $8 to $10 per foot (done over a 5,000 line foot stretch of 8″ pipeline) by a contractor. A grout-repaired pipe line could conceivably then last from five to 40 years, depending on the quality of installation (Claudia Norton, pers. comm.). The actual cost of a Sika robotic system repair of a 10-inch line on a job in Sacramento County was $70 per foot (Hassey et al., 1991). The cost to purchase the equipment is approximately $600,000 with a life expectancy of five years. Thus, it would require roughly a $120,000 per year investment over the useful life of the robotic system equipment. Estimated operating cost is another $208,280 per year, or about $105 per hour (based on 2,000 hours of use per year) (Hassey et al., 1991). Other economic factors to consider in grouting include the type and expense of grout (type determined by soil type); the type and amount of pre-cleaning procedures necessary (manpower and equipment required); the degree of prior damage to or general condition of the pipe line (misaligned or shifted pipe will take more effort and time if it can be grout repaired); the size of voids and flaws (length of cracks); and the amount and type of spot repair necessary before grouting (excavation included).

Sealing—Sealants are applied to imperfections in the pipe via gravity and hydrostatic pressure (by maintaining a high column of liquid) in a two-solution, two-phase process. A well-documented sealing product/system that can be used for both 4-inch service laterals and larger municipal lines is the Sanipor System. When the two solutions mix, the stabilizers within each react and a strongly polymerized polysilicic acid gel results. Soil particles and sand grains are bonded to form a cohesive concrete-like mass that solidly encapsulates the defective area and is impermeable to water.

Advantages: There is no need for television inspection, since the sealant temporarily fills the line and is forced into any cracks or defects that may be present. Using this method the entire line is sealed rather than just one defect at a time (Claudia Norton, pers. comm.).

Disadvantages: Since there is no way to see the actual size of the defects and voids outside the lines without excavation, there may be large undetected cavities surrounding the pipes such as might occur from leaking water washing away soil. Such defects or holes can result in a rather large and unexpected volume of material being used, resulting in an unanticipated increased cost for materials (Claudia Norton, pers. comm.).

Costs: Approximately $25-30 per foot (Claudia Norton, pers. comm.).

Point Repair—Sections of pipe are point repaired when they are too damaged for repair by less complete rehabilitation procedures. The process usually involves the trenchless repair of a

damaged section of pipe that generally doesn't exceed 15 feet in length. It frequently involves repair of a leaking joint or faulty service connection, but differs from other pipe-repair operations that involve entire manhole-to-manhole lengths. Most systems available involve the application of either some type of grouting system, a cured in-place pipe sleeve, or an epoxy-based spray. The systems differ the most from one another in the method of application. Some use robotic devices, others use a winched-into place sleeve piece, and others may use a combination of methods. Some repair methods are only designed to repair larger pipe lines, but some repair methods are appropriate for 4-inch residential service laterals as well (and are identified as such below). There's a number of point repair methods currently available, and technology is rapidly changing. Following is a partial list of some examples of such systems (Thomas, 1994):

- ***Performance Liner***® (LMK Enterprises) is a seamless tube of custom length and thickness of cured in-place liner pipe (CIPP). It is appropriate for the repair of 4-inch pipe. It is installed by the inversion liner method, with the exception that it is cured at ambient temperatures rather than with hot water or steam, as Insituform. It is available in lengths from five to 100 feet for repairing 4-inch lines. It is a quick, clean, trenchless repair that places a seamless new pipe section in a damaged one, and is done by licensed contractors.
- ***Amkrete***® (Amkrete Company) is a cured-in-place process involving the injection of epoxy resin into faulty areas and defects from 12 to 44 inches long in pipelines with diameters from 4 to 24 inches.
- ***Eco-liner Pipe Repair***® (American Pipeline Supply Co.) is a replacement system to repair 2- to 12-foot long sections of 6- to 15-inch diameter pipes by installation of a new epoxy-reinforced fiberglass pipe within the existing line.
- ***Econoliner***® (Avanti International) is a CIPP repair for sections of 6- to 30-inch diameter pipes of any material as short as three feet long.
- ***Form-A-Pipe***® (American Logiball) is a CIPP repair that involves the installation of a fiberglass-impregnated mat inside broken sections of pipe.
- ***Link Pipe Grouting Sleeve***® (Link Pipe Co.) is a stainless steel sleeve that is grouted into place.
- ***Magnaliner***® (I.S. Inspection Services) is a composite resin liner for rerounding collapsed pipe sections six inches in diameter and larger. This system can repair sections one to 80 feet long. The literature indicates the installation cost is less than 50% of a repair involving excavation.
- ***Sika Robotics***® (Sika Robotics, Inc.) is a self-contained repair system involving a color television camera, computer software-controlled robot, and a two-part epoxy resin. It is designed to repair pipes from 6 inches to 33 inches in diameter.
- ***Ka-Te System***® (Ka-Te USA) is a robotic point repair system that epoxy-seals/repairs defects such as faulty protruding lateral connections (it grinds them down flush before sealing), offset joints, holes, or cracks.

Advantages: A quick, clean, trenchless spot repair offers considerable savings over excavation and replacement of an entire line. Usually such point repair systems provide good durability of repair. An EPA study showed that lack of deterioration was a plus for point repair (Olson, 1986).

Disadvantages: Some systems may be labor intensive. Some excavation of a line may be necessary for certain point repairs. Point repair methods are strictly for spot repairs. If a line has numerous leaks, it may be more cost effective to simply renovate the entire pipeline with CIPP, fold-and-form PVC pipe, or a sealant system. Licensing may be required for use of patented materials or equipment, requiring the use of a contractor, potentially increasing costs. With some systems the diameter of the pipe may be reduced. That may be a disadvantage, particularly with smaller diameter pipe.

Costs: Cost comparisons for the various point repair systems were given by Thomas (1994). Robotics cost in the range of $500 to $2,000. Stainless steel sleeves cost from $2,000 to $3,000. Sectional patch repairs range from $2,500 to $4,500. Excavation repairs are highly variable, from $2,500 to $15,000. In the City of Sacramento, one particular spot repair of a 30-inch main line with an 18-inch long repair piece cost $3,000 ($2,000 per foot), but that was considered relatively inexpensive by city staff, considering the major excavation and replacement work that did not have to be done, together with the labor and time savings as well as the reduced disruption of service and traffic (Farral Crawford, pers. comm.). As an example of a residential 4-inch pipe line point repair, the cost for a contractor to repair a 4-inch pipe line with the Performance Liner might run roughly from $50 to $100 per foot, depending upon the site variables (LMK Enterprises 1995).

Slip Lining—Slip lining is the insertion of smaller diameter rigid liner pipe into an existing pipe. A slip liner is pushed or pulled into an old pipe from an excavated pit that is large enough to maneuver the rigid liners into the existing pipe. A slip liner is usually made of plastic or fiberglass. Two systems are approved for slip lining in the United States. One method is the Spirolite System (made by Chevron Chemical Co.) that is a high-density polyethylene (HDPE) thermoplastic pipe. This type of liner has a bell and spigot joint design. HDPE is suitable for lining pipe lines up to 48 inches in diameter. The second method is referred to as Centrifugally Cast Fiberglass Reinforced Polyester Pipe (FRP) (manufactured by Hobas USA, Inc.) that also features a bell and spigot joint design. Pipe diameters larger than 48 inches necessitate liner walls that are thickened for strength. However, this thickening of the HDPE liner restricts flow. For those larger diameter lines, the FRP pipe is preferable because it provides the necessary strength without excessively thick walls (Anonymous, 1994b). Generally some type of grout or other hardening agent must be placed between the liner and the existing pipe to maintain structural strength (Claudia Norton, pers. comm.).

Advantages: Slightly flexible PVC type pipe allows long lengths of sewer to be relined in a no-dig, trenchless repair. The resultant line has fewer, water-tight solvent-welded joints.

Disadvantages: Slip lining doesn't work well where the line isn't relatively straight. It is also not advantageous where a lot of service connections are present along the lines since they all have to be precisely located, excavated, cut, and reconnected. Workers in the city of Vancouver found that locating the connection points was a major problem on a slip lining repair project (Baker, 1980). Service laterals must be treated as spot repairs requiring excavation. Unlike CIPP inversion liners where lateral connections are more easily recognized because they are somewhat dimpled at connection points, lateral connection points must be very precisely located and cut when slip lining.

This may involve excavation at each lateral connection point. Residential 4-inch lines are too narrow for slip lining (Will, 1991). Slip lining requires much more time than Insituform installation (Olson, 1986). Because of the lack of flexibility of the pipe liners, slip lining requires a large pit at the end of at least one end of the pipe to be lined. Slip liner pipes are typically available in 20-foot lengths, regardless of diameter, so these entrance pits are always required. There is also a limit to the length of the line being slip lined due to friction from the new pipe being pulled through. Slip lining doesn't surmount major changes in sewer line alignment, nor does it work well for sewer lines with projecting service laterals. The sealing of liners at manholes is a specialty job requiring special expertise and sealant (Sullivan et al., 1977a). Flow capacity and geometric requirements may preclude a reduced diameter pipe, and changes in pipe size are not easily adjusted for. According to Los Angeles City sewer designer Calvin Jin, large diameter slip line pipes (e.g., 48 inches) do not bend well enough to accommodate horizontal bends in lines. For this and for 90 degree turns, large pits must be excavated to accommodate custom-fitted pieces to navigate the turns (Anonymous, 1994b). HDPE is also buoyant, adding to its difficulty to install (Anonymous, 1994b). The space between the slip line and the original pipe must be addressed as well, since the liner is not as structurally rigid as the original pipe. Some type of grout or rigid filler must be applied around the liner for strength and stability.

Costs: There are a large number of economic factors that affect the cost of slip lining, such as the size and weight of the rigid liners. Thicker, heavier pipe is more expensive to make, ship, and handle. Some of the factors that must be taken into consideration include (1) the type and amount of pre-cleaning procedures (manpower and equipment required) necessary; (2) the degree of damage to and general condition of pipe line (misaligned or shifted pipe will take more effort and time, if possible to do at all); (3) the cost of proving the line for straightness and proper alignment to determine the practicality of using slip liners at all; (4) the depth of the main line, that determines the size of pit necessary, including restoration and repair of the pit area, and indirectly, the size of equipment and crew needed; (5) the number of service laterals and their depth that affect job cost since they may all have to be excavated and cut; (6) the amount and type of spot repair necessary before slip lining; (7) the amount of time of traffic control or diversion; (8) and the amount of grout or filler material needed to fill annular space between the new slip line and the old sewer pipe including in and around lateral service lines (to prevent movement, increase strength and stability, and prevent infiltration or leakage). Because of the large number of variable cost factors, it is very difficult to standardize the cost of slip lining (Claudia Norton, pers. comm.). Sullivan and Ewing (1985) provide a list of 48 separate and variable economic factors to consider in estimating a slip lining job. In general, the relative costs for slip lining are somewhat less than fold-and-form PVC and somewhat more than grouting, which might place it very roughly at about $20 to $40 per foot (Claudia Norton, pers. comm.), however these costs could vary substantially depending on a number of factors.

Preventive Control Measures

Tree Removal—Homeowners who are plagued with sewer root problems frequently want to resort to tree removal, particularly at a municipality's expense, because it is perceived that this will

finally put an end to the problem. Sacramento's City Arborist performs over 300 root damage evaluations each year, usually related to hardscape damage, that is, damage to walkways, driveways, streets, and curbs made of concrete, asphalt, or other hard materials. All city arborists interviewed stated that tree removal is a last resort and generally not done merely because of root intrusion into service laterals. On the contrary, municipalities go to great lengths to preserve trees. In addition, tree and shrub root systems are tremendously large and fibrous and extend for distances well beyond their above-ground parts. Just removing one plant does not guarantee that the same niche will not be exploited by the root system of another tree or shrub in the area, and immediately or eventually cause more root intrusion.

Advantages: In rare cases, tree removal may be the most appropriate long-term resolution of a chronically severe root intrusion problem.

Disadvantages: Tree removal is an expensive and, unfortunately, temporary procedure since the roots of other plants can move in to occupy the same niche if the leaky line is not repaired or replaced (Brennan et al., 1989). According to several municipality-employed professional arborists, rarely, if ever, is tree removal justified on the basis of root intrusion. The high cost of removal, the loss of economic value to municipal or private property, the loss of shade and energy conservation (Ken DeYoung, pers. comm.), and the unlikelihood of the problem being permanently resolved despite the removal, are all reasons against tree removal to solve the root intrusion problem. In addition, unless the stump of the removed tree is thoroughly killed, the roots of some species will continue to grow even after the tree is removed (Tobiason, 1990).

Costs: According to professional arborists, the cost of the actual tree removal itself can easily exceed $1,000 depending upon the complexity of the removal, the proximity of vulnerable targets (such as structures, other trees, and utility lines) to falling limbs, and the amount of time and caution necessary to do the job safely. For example, tree removal with replacement of the root-damaged portion of the sewer line in the City of San Francisco can run $5,000, according to city personnel. In addition, the economic, energy, aesthetic, and other losses to a property may outweigh the perceived economic benefits of tree removal. The dollar value reduction to the property value alone could place the loss of a typical front yard tree with an 18-inch diameter trunk at several thousand dollars (Fitzpatrick and Verkade, 1990).

Tree Species Selection and Site Planing with Utilities in Mind—Selection of trees for specific criteria such as non-invasive roots or correctly proportioned tree to lot size, can go a long way to prevention of future root intrusion problems. Certain species are recognized by arborists as having notoriously invasive roots in landscapes including willow, poplar, eucalyptus, mulberry, liquidambar, elm, ash, magnolia, black acacia, carob, both species of pepper trees, and *Ficus*, and should naturally be avoided in areas of close proximity to sewer lines, particularly service laterals. Instead, species that are known for less invasive root systems should be considered to prevent potential root intrusion problems in the future. Some agencies and municipalities whose services are at risk to tree root intrusion have professional arborists on staff to help with preventive site planning decisions as well as to trouble shoot existing problems involving tree root intrusion. Pacific Gas and Electric, for example, uses a copyrighted software product of its own called TreeFinder

that helps in the selection of tree species based on specific criteria, including root invasiveness (Steve Cieslewicz, pers. comm.).

Advantages: Prevention and avoidance of a problem altogether is usually cost-effective.

Disadvantages: There are no disadvantages to avoiding a problem in the first place via careful planning. However, not all homeowners or landscape architects are knowledgeable about the various horticultural characteristics of tree species, including root behavior. Probably few are aware of resources for tree selection information or have ready access to good information on species selection criteria. In addition, the out-of-sight- out-of-mind aspect probably factors in also, as homeowners and municipal site planners may not be cognizant of the precise location of utility and other lines, and consequently are not aware when they plant trees or shrubs with invasive roots in close proximity to their service laterals (Steve Cieslewicz, pers. comm.).

Costs: Potentially hundreds to thousands of dollars in corrective efforts may be saved by avoiding the use of a known troublesome species, and by avoiding planting in a location that is in close proximity to service lines. Most communities have information sources such as libraries, nurseries, and cooperative extension offices that can provide information and advice pertaining to tree selection. Some communities have enacted ordinances barring certain tree species in future planting and on rare occasions have even ordered removal of existing stands, thus potentially avoiding the costs of repairs or replacement (Tobiason, 1990).

Root Barriers—Root barriers are principally used to protect hardscapes such as sidewalks and curbs from the destructive forces of growing, enlarging tree roots. Experiments by University of California Cooperative Extension personnel indicate that root barriers have the ability to significantly reduce the damage potential of tree roots (Steinmaus, 1994). Although a DPR survey located few persons who have actually had experience using root barriers specifically to protect sewer lines, most reported success in protecting hardscapes. Theoretically, root barriers should protect sewer lines as effectively as they protect hardscapes, either by blocking roots in a linear manner (e.g., along a trench) or with the flexible barriers via wrapping the pipes. Root barriers work best as a preventive measure when trees are first planted. When working with the root systems of well-established, mature trees, some selective, directional root pruning is recommended to assure best results with the barriers (Joe Borden, pers. comm.; Mark Beaudoin, pers. comm.). There are a number of different materials used as root barriers. Three examples of root barriers that have relatively wide industry use are the ***Deep Root Barrier®***, the ***Biobarrier Root Control System®***, and ***copper wire cloth*** (manufactured by the Howard Copper Wire Cloth Company).

Deep Root Barrier is a ribbed, solid plastic barrier that is intended to physically block and redirect roots. These barriers come in three different forms. With one form, flexible 2-foot interlocking panels can be used to surround a root system or to isolate it via a linear wall from areas to be protected from invasive roots. A second type is also used in linear applications, and consists of rigid, interlocking 2-foot wide panels. A third type is a pre-formed round planter designed for trees that will be relatively small at maturity (12-inch trunk caliper or smaller). Linear barriers come in heights of 12 inches up to 48 inches, and the round pre-formed barrier is 18 inches in height. The Biobarrier Root Control System consists of a spun-bound polypropylene cloth mesh in which beads of the nonsystemic herbicide, trifluralin, are incorporated. This is designed to

inhibit root growth near the surface of the mesh barrier by establishing an in-soil vapor zone of trifluralin approximately two inches wide on each side of the fabric. Root growth is inhibited in this region because the trifluralin stops cell division of the root tips (Tracy Whittaker, pers. comm.). The herbicide used in the Biobarrier is not systemic, thus it is not phytotoxic to above ground parts (Tracy Whittaker, 1994). "Surround installation" of Biobarrier for the protection of sewer lines and septic systems is described by the promotional literature and the Technical Application Manual for Biobarrier (Remay, Inc., 1994). Unfortunately, no one who had used Biobarrier in this manner could be located. However, the Carmichael Recreation and Park District used Biobarrier in a surround application by wrapping it around flood-control drainage pipes that were installed as replacements for previous drainage lines that had been crushed and severely displaced by roots of some *Liquidambar* trees. The trees were considered too important to remove since they serve in the summer shading of non-air conditioned buildings. After three years, they have had no signs of any problems with the tree roots damaging the Biobarrier-wrapped, replacement pipeline (Ken DeYoung, pers. comm.).

Copper wire cloth (manufactured by the Howard Copper Wire Cloth Company) controls roots by permitting initial penetration by rootlets through the copper mesh, but it eventually prunes them off by constriction and girdling as they enlarge.

Another root barrier method involves the use of machine-compacted soil as a root barrier. The purpose of this type of barrier is to withhold the aeration requirements of roots, and thus prevent their entry into the compacted area of soil.

Advantages: Avoiding root intrusion by effectively blocking off invasive roots from sewer lines may be an effective measure with potentially hundreds to thousands of dollars in savings by making corrective efforts and repairs unnecessary. Particularly in the case of newly planted trees, root barriers may be effective in redirecting or restricting directional root growth, and prevent them from becoming a threat to the sewer lines.

Disadvantages: Not all root barriers work equally well in all soils, on all sites, or for all tree species. Careful attention must be given to installation, as roots can go over, under, around, or through improperly installed barriers. Some root barriers permit free movement of air, water, and nutrients. Others, such as those made of solid plastic do not, and if installed improperly, can stress a tree and lead to tree health problems. Likewise, soil compaction is likely to stress all plant life in the compacted zone. This is a better approach for hardscape protection, where nothing is intended to grow. If a tree already has exposed surface roots, Biobarrier cannot be used since it cannot be effective if exposed to air. Nobody can say for sure at this point how long the effect of any of the root barriers last after installation, since they haven't been widely used for very long. Some municipalities do not like the potential liability of using barriers with an herbicide, and prefer not to use those types (Dan McKenna, pers. comm.). Root pruning, while being beneficial and making root barriers more effective, can be labor intensive and may involve a significant amount of excavation (Mark Beaudoin, pers. comm.; Joe Borden, pers. comm.). In addition, to correctly prune the roots of mature trees requires considerable arboricultural training, and would probably necessitate the expense of the contracted services of a professional arborist. In some cases the confines of

hardscapes and the presence of utility lines or underground cables in and around roots can make installation and use of barriers impractical (Dan McKenna, pers. comm.).

Costs: In San Jose, using soil compaction as a barrier costs a minimum of $12 per square foot due to the specialized equipment involved. The labor for mechanical trenching to retrofit-install a barrier to an established tree's root zone may be expensive, depending on the site conditions, the difficulty in trenching through the soil, the amount of root pruning necessary, the depth of the soil and roots, and the size and type of the barrier to install, among other factors. Trenching and installation of copper wire cloth to protect a vulnerable section of sewer line San Francisco, for example, can run as high as $700–$1,000 (Dan McKenna, pers. comm.). Biobarrier costs approximately $1.00 per square foot. Deep Root plastic barriers cost approximately $3.58 per linear foot for an 18-inch deep barrier (it comes in two-foot long connecting panels). Copper wire cloth is about $3.00 per linear foot, or about $1.00 per square foot (it comes in rolls measuring three by 100 feet). In addition, the services of a highly skilled certified professional arborist may run $50 to $75 per hour for consultation alone, without any labor for root pruning, or other work (Roger Poulsen, pers. comm.).

Table 8. A summary of copper sulfate alternatives. Cost estimates are not comparative, as each site and method has its own set of restrictions and variables that affect overall costs.

Municipal Alternatives

Category	*Product or practice*	*Duration*	*Major limitations*	*Approximate cost*
Chemical	Toby's Foaming Root Killer D®	Short term	Temporary measure	$1.00–$1.20 per foot
Chemical	Sanafoam® Vaporooter® II	Short term	Temporary; need equipment	$.35 per foot + equipment cost
Mechanical cutting	Root cutters, flailers, rodders	Short term	Temporary; need equipment	$0.25–$1.00 per foot + equipment cost
Construction	Y-cleanout installation	Short term	Expensive, temporary measure	up to $800 per site
Replacement	Excavation and replacement	Long term	Expensive, disruptive	$120–$500 per foot
Trenchless replacement	Pipe bursting and replacement	Long term	Expensive; excavation pits	$60–$100 per foot
Trenchless replacement	Slip lining	Long term	Diameter reduction, excavation pits	$20–$40 per foot
Liners	Cured in-place liners	Long term	Diameter reduction	$80–$140 per foot
Liners	Fold and form PVC	Long term	Straight lines only	$20–$40 per foot
Grouting and sealing	Chemical grout	Long term	Variable results	$8–$70 per foot
Grouting and sealing	Sealant	Long term	Large voids a problem	$25–$30 per foot
Point repair	Liners, grouts, and combinations	Long term	Few repairs per line only	$500–$15,000 per site
Tree removal	Tree removal	Short to long term	Expensive, temporary, tree loss	$1,000–$5,000 per site
Prevention	Species and site planing	Long term	Limited information distribution	$0–undetermined (for consultant)
Prevention	Root barriers	Long term	Installation quality critical	Up to $1,000 per site

Residential Alternatives

Category	*Product or practice*	*Duration*	*Major limitations*	*Approximate cost*
Chemical	Toby's Foaming Root Killer D®	Short term	Temporary measure	$1.00–$1.20 per foot
Chemical	Sanafoam® Vaporooter® II	Short term	Temporary; need contractor	$1.00 per foot + cutting costs
Mechanical cutting	Root cutting	Short term	Temporary; contractor or rental	$50–$140 per site
Construction	Y-cleanout installation	Short term	Temporary; expensive	up to $800 per site
Replacement	Excavation and replacement	Long term	Expensive and disruptive	$2,000– $100,000 per site
Liners	Cured in-place liners	Long term	Diameter reduction	$60–$80 per foot
Liners	Fold and form PVC	Long term	Straight lines only	$30–$60 per foot
Grouting and sealing	Chemical grout	Long term	Variable results	$8–$10 per foot
Grouting and sealing	Sealant	Long term	Large voids a problem	$25–$30 per foot
Point repair	Liners, grouts, and combinations	Long term	Few repairs per line only	$50–$100 per foot
Tree removal	Tree removal	Short to long term	Expensive, temporary, tree loss	$1,000–$5,000 per site
Prevention	Species and site planing	Long term	Limited information distribution	$0–undetermined (for consultant)
Prevention	Root barriers	Long term	Installation quality critical	Up to $1,000 per site

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PART FIVE — ALTERNATIVES TO THE USE OF TRIBUTYLTIN FOR THE CONTROL OF MICROORGANISMS IN COOLING WATER SYSTEMS

Adolf L. Braun and R. Patrick Akers

Introduction

In 1992, the California Regional Water Quality Control Board, San Francisco Bay Region adopted a shallow-water effluent limitation for tributyltin of 5 parts per trillion (ppt) (= 0.005 µg/L) for the San Francisco Bay. During 1992 and 1993, samples from discharges of the Palo Alto Regional Water Quality Control Plant (RWQCP) exceeded the effluent limit of tributyltin. RWQCP staff searched for various tributyltin sources, and found that tributyltin in the discharge of some cooling water systems was the most obvious source in their service area (RWQCP, 1993; RWQCP, 1994). (Tributyltin is one of several active ingredients used to kill microorganisms in cooling towers.) Staff calculated that only one gallon of 2 percent tributyltin solution discharged to the sewer and treated with other waste water at the RWQCP would contaminate more than 2.4 billion gallons of the effluent to a level exceeding the 5 ppt tributyltin effluent limitation. This means that even very small discharges (on the order of one hundred milliliters) of tributyltin-containing products could put the city of Palo Alto in violation of their discharge permit, which would force the San Francisco Bay Area Regional Water Quality Control Board to impose fines of up to $25,000 per day for non-compliance.

Cooling water systems

There are three types of cooling water systems: once-through, closed loop/chill, and open recirculating. The once-through system wastes water; because of water conservation efforts new installations are prohibited and existing systems are being phased out (RWQCP, 1994). In a once-through system, constantly replenished water is discharged as waste after it cool heated ventilation water. The closed loop/chill water system does not discharge the water except for maintenance, which may occur yearly. Water circulates continuously as in a car radiator, absorbing heat and transfering it elsewhere. The recirculating water is not exposed to sunlight, so algal growth is not a problem. The open-recirculating system or evaporative cooling system is the most commonly used for commercial air conditioning and industrial cooling systems. This system consists of pumps, a heat exchanger, and a cooling tower. Water absorbs heat and releases it through evaporation occurring in the cooling tower. Because it is an open system, the recirculating water is more prone to collect silt, dirt, and microbiological contamination than the closed loop/chill water system. Algae grow in the water in response to exposure to sunlight. In addition, water is lost due to evaporation which changes the basic chemistry of the water. Salts, minerals and metals in the cooling tower water become concentrated as the water evaporates during use. A portion of this water (blowdown) is frequently drained and replaced with fresh water.

The quality of water circulating through the cooling system (particularly open-recirculating systems) can influence the efficiency of the system, the degree of maintenance required, and the useful life of the system components. Heat exchangers and cooling towers are susceptible to

microbiological contamination and fouling from suspended solids other than mineral salt (scale) deposits. The water flow in these sites is very low, providing an ideal environment for microorganisms to grow (Lutey, 1991). Bacteria, algae, and other microorganisms grow readily in cooling towers. They can form an insulating coating on heat transfer surfaces, restrict fluid flow, promote corrosion, and attack organic structural components such as wood (ASHRAE, 1992). Eighty to 90 percent of open-recirculating cooling water system failures are directly or indirectly related to problems caused by microorganisms. A general rule of thumb is that a 0.01 inch layer of biological slime, often referred to as biofilm or biomass, will cause a 10 percent decrease in the efficiency of the cooling system (Glen Heikkinen, pers. comm.). Biological slime can build up within four to eight hours on heat transfer surfaces (Lutey, 1991). If the causal organisms are not controlled with microorganism-killing biocides, the cooling system may have to be shut down for cleaning. If the system is essential to a sensitive environment such as a hospital, shutting it down may be extremely costly.

Proper maintenance of cooling water systems by monitoring of biocide levels and microbial populations is more practical and economical than allowing the system to get out of control (Glen Heikkinen, pers. comm.). Biocides containing tributyltin or other active ingredients are used to control microorganisms in cooling water systems. The use of an oxidation-reduction probe (ORP) allows for the convenient measurement of biocide levels, some of which kill through oxidation reactions.

Tributyltin compounds do not degrade easily and can persist in the environment (see Part Three). In addition, tin, especially in its organic form, is toxic to aquatic organisms, accumulates in fish, and, if consumed, transfers to humans (Berman et al., 1991).

The purpose of this section is to identify and assess potential alternative to tributyltin for the control of microorganisms in cooling water systems. Part of this assessment includes their cost (Table 10).

Biocides Used for Cooling Water Systems

Methods for obtaining information on biocides

The Department of Pesticide Regulation maintains information on active and inert ingredients of each pesticidal product registered in California. A computer program was used to identify all currently registered products that active ingredients used as biocides in cooling water systems (Tables 9 and 10).

Information on these biocides was also gathered from face-to-face interviews with employees of various companies providing water treatment services to cooling water installations and from published literature.

Use and methods of feeding biocides in cooling water systems

Both broad- and narrow-spectrum biocides are used in cooling water systems. The use of broad-spectrum biocides ensures adequate contact time for target microorganisms, necessary because they are not always killed by immediate contact with most organic non-metallic microbiocides (Lutey, 1991). Alternating treatments with different biocides—the broad-spectrum oxidizing biocides and the (primarily) more specific non-oxidizing compounds—and blends of

biocides generally give the most effective results and prevent resistant microorganisms from becoming dominant (Glen Heikkinen, pers. comm.; Lutey, 1991). However, due to the limitations of oxidizing biocides, such as their corrosive characteristics, non-oxidizing biocides are more widely used to control microorganisms in cooling water systems (Lutey, 1991). Other chemicals such as copper are routinely added in small amounts to protect metal components.

The manner in which these biocides are fed to a system is important. For instance, overfeeding may increase treatment costs, corrosion of metals, and foaming. There are three methods to feed biocides regularly for the control of microorganisms in water cooling systems:

1) **Continuous feed method.** Currently this application method is becoming more common, as automated biocidal feeders, chemical feed pumps, and test kits to monitor the level of the biocides become more available. A low but effective concentration of the biocides is fed continuously to keep bacterial populations from entering into a rapid (logarithmic) growth phase (Lutey, 1991; Buckman Laboratories, 1982). This method ensures uniform treatment and makes service of the cooling water system easy. Another benefit of this method is that it saves water and biocides (Louis Ruiz, pers. comm.), and warns operators when problems develop (Glen Heikkinen, pers. comm.).

2) **Intermittent feed method.** With this method, biocides are also fed into cooling towers by chemical metering pumps, but these are generally timer-controlled so that they activate at given intervals and operate for a predetermined period of time to deliver the amount of biocide required. This feed system accurately meters the desired treatment dose on a consistently controlled basis, so that the bacterial population never achieves a logarithmic reproductive rate (Lutey, 1991; Buckman Laboratories, 1982). Good control of the microorganisms can be maintained at low biocide concentrations, thereby reducing the potential for corrosion due to overdosing. Both the intermittent and continuous feed methods are used to maintain clean recirculating cooling water systems. Because of its accuracy, the intermittent feed method is preferred over continuous feed for large recirculating cooling water systems (Buckman Laboratories, 1982). This feed method also introduces a higher concentration of biocide into the system, so a more effective concentration is likely to enter the system.

3) **Slug feed method.** When the cooling water system is fouled with an overgrowth of microorganisms, high concentrations (shock dosages) of biocides are added manually at regular intervals. Depending on microbiological growth, degree of external contamination of the cooling water system, and the amount of suspended solids in the circulating water, shock doses are made once or twice per week until control is achieved and the cooling system can return to routine maintenance (Lutey, 1991; Buckman Laboratories, 1982). This method is considered the most effective feed method to clean a fouled system (Buckman Laboratories, 1982). Limitations include the possibility of overfeeding (Lutey, 1991) and worker exposure from feeding the biocide manually (Louis Ruiz, pers. comm.).

Organotin compounds in cooling water systems

Bis-tributyltin is the most common organotin biocide (Buckman Laboratories, 1982). There are currently 12 tributyltin-containing products registered for recirculating cooling water systems (Table 9).

Tributyltin compounds are non-oxidizing biocides that are most effective against fungi, specifically the wood-rotting fungi (Buckman Laboratories, 1982; Glen Heikkinen, Jim Lagunich, Bob Cunningham, pers. comms.). They are moderately effective against bacteria and algae (Richard Cannon, pers. comm.). Tributyltin compounds inhibit the growth of microorganisms by permeating their cell walls and disrupting enzymatic activities (John Davies, pers. comm.). They are very effective when the water has a pH range of 6.5 and 9.0, but have a slow biocidal activity. They require a contact time of 6–8 hours (Lutey, 1991; Jim Rauh, pers. comm.). Their long residence time makes them attractive biocides for use in open- and closed-recirculating cooling water systems. Tributyltin compounds are considered biostats, inhibiting the growth or reproduction of microorganisms, and are only used to prevent plugging and fouling problems in towers made of wood. They have no odor and are not difficult or particularly dangerous to handle (Richard Cannon, pers. comm.). High silt levels and cellulose fibers can inactivate these compounds (Lutey, 1991; John Davies, pers. comm.). Tributyltin compounds are not easily degradable and thus have long-lasting residual effects (Bob Cunningham, pers. comm.). They can persist in the environment for a long time (Lutey, 1991).

Tributyltin compounds are often mixed with quaternary ammonium compounds to enhance their dispersibility and to provide some synergistic effects (Lutey, 1991; Buckman Laboratories, 1982; Bob Cunningham, William Dignin, and Jim Lagunich, pers. comms.). In addition, tributyltin compounds reduce foaming of the quaternary ammonium compounds (William Dignin, pers. comm.). These mixtures are commonly used in open- and closed-recirculating cooling water systems.

Table 9. Tributyltin-containing products registered in California for use in recirculating cooling water systems.

Product name	Manufacturer	Percent active ingredient
Dearcide 717	W. R. Grace & Co.	2.25
Formulation HS-69D	H & S Chemicals Division	2.25
Formulation HS-138D	H & S Chemicals Division	4.50
Garratt-Callahan Formula 34-A	Garratt-Callahan Co.	2.50
Nalco 2532 Microorganism Control Chemical	Nalco Chemical Company	2.50
Nalco 7328 Microorganism Control Chemical	Nalco Chemical Company	2.50
Nalco Visco 3951	Nalco Chemical Company	2.50
Sanatox 2219	San Joaquin Chemicals, Inc.	5.00
Skasol Microbiocide No. 8	Skasol Incorporated	0.51
TEI-4	CH2O, Inc.	2.25
West C-106	Water & Energy Systems Technology, Inc.	5.00
West C-113 Algicide	Water & Energy Systems Technology, Inc.	5.00

Alternative Control Methods

Synthetic chemical options or practices which, like tributyltin, are used as biocides in cooling water systems are identified in this section. These alternatives are classified as either oxidizers and non-oxidizers.

Oxidizers

Halogen donors

Chlorine and chlorine-generating compounds require the cooling tower water to have a pH between 6.0 to 7.5 (Lutey, 1991). The following chemicals can be classified under this group of compounds:

• ***Chlorine*** (e.g., Olin Chlorine®) added to cooling water as a gas hydrolyzes to hypochlorous acid, the biocidal agent. Maximum formation of hypochlorous acid occurs when the water being treated has a pH of 6.0 (Lutey, 1991). At a pH of 8.5, only 8 percent of the chlorine gas is converted to hypochlorous acid, thus requiring higher dosages of chlorine to control microorganisms effectively (Bob Cunningham, pers. comm.). Many present-day cooling water treatment programs operate with the cooling water pH in the range of 8.0 to 8.5 or higher. Thus, chlorine is less effective than other biocides that are less affected by these higher pH values. Chlorine is an inexpensive, reliable broad-spectrum compound, requiring a one-hour contact time. This compound is inactivated by water with a pH higher than 9.0, sunlight, aeration, hydrogen sulfide, and ammonia (Lutey, 1991; John Davies, pers. comm.). Chlorine is potentially corrosive when the water has a pH lower than 6.0, and it can adversely affect wood. Chlorine application equipment is expensive and requires extensive maintenance. Chlorine gas is dangerous to handle (Lutey, 1991; Buckman Laboratories, 1982). Its use is limited due to environmental regulatory restrictions on the discharge of chloramines and halomethanes (Lutey, 1991).

• ***Calcium and sodium hypochlorite*** (e.g., Sanatox 2243® and Nalco 7345®, respectively) are salts of hypochlorous acid, the biocidal agent. They are broad-spectrum biocides and are effective against all bacteria, fungi, and algae (Lutey, 1991). They act by oxidizing proteins, interfering with respiration and metabolism, and destroying cell walls. They are most effective when the pH of the water is between 6.5 and 7.5, requiring a short (one hour) contact time at this pH range. Hypochlorite salts are easier to handle than chlorine gas, but have the same limitations. They are also more expensive than chlorine gas (Lutey, 1991; Buckman Laboratories, 1982; John Davies, pers. comm.). They are often alternated with polymeric quaternary ammonium compounds (Richard Cannon, pers. comm.).

• ***Solid organo-chlorinated-hydantoins*** are effective against all types of bacteria, fungi, and algae. They oxidize proteins, interfere with respiration and metabolism of microorganisms, and destroy cell walls. They are most effective when the pH of the water is in the range of 8.0 and 9.0, which is a common pH range in cooling towers with present maintenance practices. A one-hour contact time is required for effectiveness (John Davis and Jim Rauh, pers. comms.). In many instances these compounds do not have the limitations that are encountered with gaseous and liquid biocides. Generally, they are not strong oxidizing compounds. Chlorine is slowly released. Consequently, contaminating organic material and high pH affect their efficacy less than chlorine gas or the hypochlorites. They are inactivated when the pH of the water is 10.0, or in the presence

of hydrogen sulfide and ammonia (John Davis, pers. comm.). Their widespread use is mainly limited by cost and the difficulty of controlling the rate they dissolve in water. Examples of active ingredients for this group of compounds are 1,3-dichloro-5-ethyl-5-methyl hydantoin (e.g., Dearcide 735®) and 1,3-dichloro-5,5-dimethyl hydantoin (e.g., Nalco 7346®).

• The ***triazinetriones*** are similar in their characteristics to the chlorinated-hydantoins, except they are more soluble in water and can provide higher concentrations of chlorine more quickly (Bob Cunningham, pers. comm.). Examples of active ingredients for this group of compounds are sodium dichloro-S-triazinetrione (e.g., A-109 Microbiocide®), sodium dichloro-S-triazinetrione dihydrate (e.g., Betz Entec 362®), and trichloro-S-triazinetrione (e.g., Sanatox 2247®).

Bromine-generating compounds

• The ***bromine-substituted hydantoins*** or solid organo-bromine compounds have many of the same characteristics, advantages, and limitations as the chlorinated hydantoins. The most commonly used active ingredient within this group of compounds is 1-bromo-3-chloro-5,5-dimethyl-hydantoin (BCDMH) (e.g., Sanatox 2080®). This compound is very effective against bacteria, but less effective against algae and fungi. It is formulated as tablets that dissolve slowly in water. This biocide is not as pH sensitive as chlorine. It is most effective when the pH of the treated water is in the range of 6.0 to 9.0, which is a typical range found in cooling towers. In open-recirculating cooling water systems, BCDMH is alternately used with polymeric quaternary ammonium compounds. Because BCDMH is an oxidizer, it can contribute to corrosion and diminish the effectiveness of some corrosion inhibitors (Richard Cannon and William Dignin, pers. comms.). (Corrosion destroys the metal components of the cooling system; inhibition of corrosion is an important part of water system management, along with microbial and scale control.) BCDMH is considered one of many viable alternatives to tributyltin compounds (Richard Cannon, and Ellis Atwater, pers. comms.).

• ***Sodium bromide*** (e.g., Skasol MB-B) is formulated as a liquid or solid product and must be activated with sodium hypochlorite, which releases hypobromous acid, the actual biocidal agent. This product is an effective biocide for bacterial and algal control and is efficacious over a wider pH range than chlorine and the chlorine-generating compounds. For instance, at pH 8.3, which is characteristic for many cooling towers, less than 13 percent of active hypochlorous acid is available as a biocide. On the other hand, over 70 percent of hypobromous acid remains at this pH (Midland Research Laboratories). Sodium bromide is becoming more accepted as an alternative to chlorination, despite its higher oxidation potential (Lutey, 1991; Bob Cunningham, pers. comm.).

Non-halogen donors

• ***Chlorine dioxide*** (e.g., Dura Klor®) is a gas that does not convert to hypochlorous acid in water as chlorine does. It remains as dissolved chlorine dioxide in solution (Buckman Laboratories, 1982). This microbiocide is an excellent bactericide and algicide. It is more effective at higher water pH ranges than chlorine. Consequently, chlorine dioxide is more effective than chlorine gas and sodium hypochlorite in present-day cooling water treatment programs. Sodium dichloride does not react with ammonia, so it does not lose its effectiveness, unlike the halogenated hydantoins (Jim Rauh, pers. comm.). Chlorine dioxide is unstable and explosive and thus is

produced on-site and fed directly into the system (Chambers, 1962). Sodium chlorite, one of the precursors commonly used to generate chlorine dioxide, can also be explosive. Although techniques for safely handling the precursors have been developed, these techniques add to the cost and complexity of the system. This makes chlorine dioxide more expensive than most of the chlorine generators (Lutey, 1991; Ken Swanson, pers. comm.). Chlorine dioxide is a strong oxidizer and can be potentially very corrosive (Chambers, 1962; Bob Cunningham, pers. comm.).

• ***Ozone***, a gas, is a strong but unstable biocide. It is usually fed continuously or intermittently to the water added to the cooling tower to prevent contamination of a clean system (Buckman Laboratories, 1982). When used at concentrations of 20 to 40 ppb, this gas is an excellent bactericide, but a poor algicide. Ozone is also very effective against fungi at concentrations of 40 to 50 ppb, but at these levels, ozone begins to leave solution (outgas). Dissolved in water, it does not pollute the environment and is harmless to aquatic organisms after decomposition to oxygen. Ozone in air is extremely corrosive to nearly everything, including wood and metals (Ken Swanson and Ellis Atwater, pers. comms.). Ozone dissolved in water does not seem to cause corrosion as other oxidizers do (Ken Swanson, pers. comm.). Like chlorine, ozone is affected by the pH of the water (Lutey, 1991), but does not increase inorganic salt content and is a more powerful biocide. Water temperatures of 110°F or higher will inactivate ozone (Puckorius, 1993). Ozone has to be generated on-site with ozone generators, using high voltage. This requires a large initial investment in generation equipment needed for an ozone application system (Lutey, 1991). The ozone generation system should run efficiently to keep electrical costs down. Although ozone is a very effective microbiocide, its use in cooling water systems is limited to small units or to specific areas within a larger system because of the high cost to generate the needed ozone (Ken Swanson, pers. comm.). Also, its residence time in water is short, so it is difficult to generate enough ozone at a single point to provide effective concentrations to every part of a large system.

Non-oxidizers

Examples of the most commonly used compounds in this group are:

Organo-bromine compounds are most effective against bacteria and fungi, but are weak algicides (Lutey, 1991; Friend et al., 1980). They act extremely rapidly—used under situations when the bacterial population is out of control—requiring a contact time of only half an hour. These compounds interfere with cell respiration. Organo-bromines are effective when the pH of the water is in the range of 6.0 and 9.0. High temperature, sunlight and sulfide ions will inactivate them (Lutey, 1991; John Davis, pers. comm.). They are less hazardous to handle than the isothiazoline compounds. An example of this group of compounds is 2,2-dibromo-3-nitrilopropionamide (DBNPA), the active ingredient of Antimicrobial 7413®. DBNPA is considered another viable alternative to tributyltin compounds for use in recirculating cooling water treatment programs (Larry Grab, pers. comm.).

Triazines are another group of biocides. Effective against algae, they are used only when algae cannot be controlled by other biocides, most often where cooling towers are exposed to sunlight (Glen Heikkinen, pers. comm.). These compounds are reasonably safe and easy to handle. Examples of active ingredients for this group of compounds are hexahydro-1,3,5-tris(2-hydroxyethyl)-S-triazine (e.g., Duracool 6451®) and terbuthylazine (e.g., Nalco 2834®).

Isothiazoline compounds are generally a mixture of two isothiazoline chemicals. For instance, 2-methyl-4-isothiazoline-3-one and 5-chloro-2-methyl-4-isothiazolin-3-one are the active ingredients of Dearcide 702®. Isothiazoline compounds are used as broad-spectrum biocides in open- and closed-recirculating cooling water systems. These biocides are most effective when the pH of the water is in the range of 6.5 and 9.0 (John Davies and Ron Derbyshire, pers. comms.). They are most effective against bacteria and moderately effective against algae and fungi. They inhibit respiration and food transport through their cell walls. They can be used as slug treatments or continuously fed (Ken Swanson and William Dignin, pers. comms.). At recommended label rates, these compounds act relatively slowly, requiring a contact time of six hours, and do not affect components of the cooling water system (John Davies, Ken Swanson, and Bob Cunningham, pers. comms.). Fouled systems can be more economically treated by combining isothiazolines with a penetrant/biodispersant, which reduces the amount of biocide needed (Lutey, 1991). Isothiazolines are inactivated in the presence of sulfite and sulfide compounds (John Davies and Bob Cunningham, pers. comms.). They should be carefully handled because they can cause severe dermal effects. For this reason, automated feeding systems are recommended (Lutey, 1991; Ron Derbyshire, pers. comm.). They are considered viable options to tributyltin (Ellis Atwater, William Dignin, and Larry Grab, pers. comms.), but do contain traces of copper as a stabilizer. Copper, like tributyltin, is also problematic for some POTWs trying to meet their effluent limitation. Less of these products are currently used as biocides in cooling water systems and some manufacturers are preparing to replace the copper with iron to stabilize the compounds. Viable options to the isothiazoline and tributyltin compounds are DBNPA and glutaraldehyde (Glen Heikkinen, Richard Cannon, Larry Grab, and William Dignin, pers. comms.).

Quaternary ammonium salts are commonly known as quats. They are the largest class of non-oxidizing biocides (Lutey, 1991; Ward, n.d.). The quats are most effective against bacteria and algae when the pH of the water is in the range of 7.5 and 9.0. They are not effective biocides against fungi regardless of the pH of the water. Like organotin compounds and glutaraldehyde, they act very slowly, requiring a contact time of six to eight hours. Their mode is attack of phospholipids in the cell membrane and blocking of normal cell wall activity. The quats are classified as biostats and considered another viable option to tributyltin compounds. Like organotin compounds, the quats are inactivated by high silt levels and cellulose fibers (Lutey, 1991; John Davies, pers. comm.). Their efficacy is generally affected by high chloride concentrations (Lutey, 1991), dirt, and calcium salts (William Dignin, pers. comm.). The quats may create foaming problems even when used at recommended rates, and this is a major limitation of their use (Lutey, 1991).

There are at least eleven different quat compounds, most of them variants of alkyl ammonium chlorides, for example alkyl (58% C14, 28% C16, 14% C12) dimethylbenzyl ammonium chloride (e.g., Sanatox 2201®). Dodecylguanidine hydrochloride (e.g., Betz Entec 349®) is another quat. Polymeric quaternary ammonium compounds or poly-quats are among the most widely used of the quat compounds. The poly-quats are effective broad-spectrum biocides when the pH of the treated water is in the range of 7.5 to 9.0 (Shair et al.,. 1978). They are effective against algae, bacteria, and have some fungicidal activity (Lutey, 1991; Jim Rauh, pers. comm.). The major poly-quat is poly[oxyethylene (dimethyliminio) ethylene-(dimethyliminio) ethylene

dichloride] (e.g., Midland 605®) (Buckman Laboratories, 1982). Sometimes also known as a water-soluble cationic polymer, this poly-quat is more of a biostat than a biocide, but it is effective at maintaining control in a cooling system once a desired level of cleanliness has been achieved. This compound must be alternated with another biocide, usually an oxidizer such as chlorine. The compound is safe to handle and is also used in pools and spas (Richard Cannon and Jack Walker, pers. comms.). Suspended solids in the water may inhibit its efficacy (Lutey, 1991).

Biocide formulations used in cooling water systems to control microorganisms often contain two or more different active ingredients. These blends not only provide broader and possibly synergistic activity against target microorganisms, but may also help prevent resistance. For example, quats are frequently combined with tributyltin because tributyltins help suppress the foaming problems of the quats, and the quats help increase the solubility of the tributyltins, which otherwise have a tendency to come out of solution (Lutey, 1991; Buckman Laboratories, 1982). Due to increasing costs for the development of new active ingredients, current research is focused on the development of these synergistic blends (Lutey, 1991).

Organo-sulfur compounds are commonly used in cooling water treatment programs. They include active ingredients, such as methylene bisthiocyanate (e.g., Dearcide 709®), potassium N-methyldithiocarbamate (e.g., Skasol MB-X®), and both sodium (e.g., Formula 37®) and potassium dimethyldithiocarbamate (e.g., Midland 638®) (Buckman Laboratories, 1982). The organo-sulfur compounds are formulated as a liquid or powder (William Dignin and Jim Lagunich, pers. comms.). They do not foam (William Dignin, pers. comm.) and are generally applied alone or in combination with other biocides (Lutey, 1991). These compounds are most effective against bacteria and less effective against fungi and algae. The pH of the treated water should be in the range of 7.5 and 9.5. Their mode of action is chelation of essential metallic ions, which interrupts the metabolic processes of microorganisms. Low pH of the treated water and the presence of heavy metals, such as iron, inactivate these compounds (Lutey, 1991; John Davies, pers. comm.). They act slowly, requiring a contact (exposure) time of 8 hours (John Davies and Jim Rauh, pers. comms.). An exception is methylene bisthiocyanate, which requires a contact time of about two hours (Lutey, 1991). Methylene bisthiocyanate hydrolyzes (degrades) rapidly at a water pH above 8.0, losing its efficacy (Lutey, 1991; Ward). Thus, cooling water systems operating in the alkaline range require higher concentrations or more frequent applications of this biocide (Ward, n.d.). Methylene bisthiocyanate is not easy to handle and feed. It does not dissolve in water readily as the carbamates (see *organo-sulfur compounds* above) (Lutey, 1991). Methylene bisthiocyanate mixed with 2-(thiocyanomethylthio)benzothiazole (discussed below) is considered a viable alternative to tributyltin because the two act synergistically, resulting in a very rapid kill of the microorganisms present in the cooling water system (Jim Lagunich and Jim Rauh, pers. comms.).

Glutaraldehyde (e.g, Nalco 8396®) is a broad-spectrum biocide and is effective against all bacteria, fungi, and algae. It is most effective when the pH of the water is higher than 6.0 (John Davies and William Dignin, pers. comms.). Its mode of action is reaction with and crosslinking amino groups of proteins in the cell nucleus. It acts relatively slowly, requiring a contact time of 6 to 8 hours (John Davies, pers. comm.). Glutaraldehyde does not foam (William Dignin, pers. comm.) and rapidly degrades to carbon dioxide and water (Richard Cannon, pers. comm.). Biocides based on liquid formulations of glutaraldehyde are widely used in situations where

bacteria are troublesome, including those associated with microbiologically influenced corrosion. They are one of several commonly used biocides in open- and closed-recirculation cooling water systems (Glen Heikkinen and Ellis Atwater, pers. comms.; Lutey, 1991) and are considered viable options to tributyltin compounds (William Dignin and Larry Grab, pers. comms.). Their disposal in cooling water treatments is not a problem, because they break down to carbon dioxide and water (Lutey, 1991). Glutaraldehyde is inactivated by ammonia or primary amines at concentrations higher than 200 ppm (John Davies and Larry Grab, pers. comms.). It has an unpleasant odor and can cause blindness if splashed in the eyes (Richard Cannon, pers. comm.).

Organic thiocyano-azole compounds are generally used to control severe microbiological problems, such as plugging, fouling and microbiologically influenced corrosion. An example is 2-(thiocyanomethylthio)benzothiazole (TCMTB) (e.g., West C-118®). It is an effective fungicide primarily used to protect wooden cooling tower structures from wood-rotting fungi (Lutey, 1991; Mayur et al., 1991; Buckman Laboratories, 1982). It also effectively controls bacteria that cause microbiologically influenced corrosion (Lutey, 1991). TCMTB does not cause foaming, but is hazardous to handle. Since it is formulated as a solvent-based liquid, care must be taken to choose handling and pumping equipment that can tolerate the solvent. High levels of sulfides, when present in the treated water, will inactivate this biocide (Jim Luganich, pers. comm.). When used in a routine microorganism control program, TCMTB is usually mixed with methylene bisthiocyanate (Lutey, 1991; Jim Luganich, pers. comm.).

Cost comparisons for tributyltin alternatives

Costs of products used for cooling towers were obtained through a series of steps.

1) The recommended range of treatment dosages and frequencies were determined from the label.

2) The type of use of the product was determined. In most cases, a product can be used two ways: a) to clean an especially dirty or fouled system, and b) to maintain a system once it is acceptably clean. Cleaning a fouled system generally employs a pulse of disinfectant at an elevated concentration for a relatively short time and is done only infrequently. Maintenance generally employs a lower concentration, released at regular, relatively frequent intervals. Usually the timing and dosages of the maintenance regime is explicitly stated on the label, while only the dosage of the cleaning regime is explicitly stated, and the timing is left to the discretion of the operator on an as-needed basis. In most well-managed, non-industrial cooling water systems, cleaning should be necessary only once or twice per year. We allowed for one cleaning dosage per month. In practice, a cleaning episode might require several doses, but our estimates should still allow for a relatively high rate of cleaning, perhaps two to four times per year. Labels usually provide a range for all dosages and frequencies.

3) Costs were standardized to a one-month period and 1,000 gallons of system capacity.

4) A range of costs per pound of the product was determined by contacting a dealer.

5) Monthly maintenance cost was taken as the product of dosage, frequency, and cost per pound of the product. The lower bound of the cost range was the product of the lower bound of each term, and the upper bound was similarly calculated using the upper bound of each term.

6) Since we allowed for one cleanup dosage per month, cleanup cost was the product of dosage and cost per pound. Again, lower and upper bounds were calculated.

7) Overall monthly costs were calculated by summing the maintenance and cleanup costs, again summing across lower bounds to obtain the overall lower bound, and summing across upper bounds to obtain the overall upper bound.

Table 10. Cost comparison of alternatives to tributyltin for cooling water systems.

Product name[1]	Active ingredient, percent	Cost of material[2]	Total cost per month
➥ *Chlorine-generating compounds*			
Nalco 2590	65.0% calcium hypochorite	$5.64–$5.85/lb	$6.35–$6.57
Nalco Acti-Plus 2818 (= Nalco 7345)	8.3% sodium hypochorite	$1.86–$3.32/lb	$11.80–$42.14
Skasol MB-H	12.5% sodium hypochorite	$1.05–$4.72/lb	$3.28–$39.27
• *Solid organo-chlorinated hydantoins*			
Nalco 7346	1-bromo-3-chloro-5,5-dimethyl hydantoin, 60.0%; 27.4%[a]; 10.6%[b]	$5.26–$5.53/lb	$5.79–$129.96
a) 1,3-dichloro-5,5-dimethyl hydantoin; b) 1,3-dichloro-5-ethyl-5-methyl hydantoin			
• *Triazinetriones*			
7419 Microbiocide (AWT)	34%[a]	$4.06–$4.35/lb	$7.11–$15.21
A-109 Microbiocide (ASE)	34%[b]	$4.07–$4.52/lb	$7.13–$15.82
A-809 Microbiocide (ATC)	34%[b]	$3.47/lb	$6.08–$12.15
Betz Entec 362	99.5%[b]	$7.91/lb	$4.75–$90.97
ChemTreat C-2185	98.8%[c]	$9.50/lb	$1.81–$3.33
Dearcide 716 (DD)	25%[c]	$3.72/lb	$8.14–$16.29
G-C Formula 36	25%[b]	$2.75–$3.80/lb	$4.82–$6.65

a) sodium dichloro-S-triazinetrione; b) sodium dichloro-S-triazinetrione dihydrate; c) trichloro-S-triazinetrione

➥ *Bromine-generating compounds*

Nalco 7346 (see *solid organo-chlorinated hydantoins* above)

7215 Microbiocide (AWT)	92.5%★	$8.25/lb	$5.78–$47.03
7215 Microbiocide (ATC)	92.5%★	$8.23/lb	$5.78–$46.91
7215 Microbiocide (ASE)	92.5%★	$10.53–$11.40/lb	$7.38–$64.98
Chemcide 935 (CWT)	92.5%★	$9.07/lb	$6.35–$251.65
ChemTreat C-2189 Tablets	92.5%★	$8.92/lb or $0.39/tablet	$6.24–$50.84
G-C Formula 314-T	92.5%★	$6.00–$9.35/lb or $0.26–$0.41/tablet	$4.20–$53.30
Sanatox 2060 (SJC)	93.5%★	$6.80–$7.30/lb	$44.76–$41.61
Sanatox 2080 (SJC)	92.5%★	$6.80–$7.30/lb	$44.76–$41.61

★ 1-bromo-3-chloro-5,5-dimethylhydantoin

G-C Formula 318	40.0% sodium bromide	$1.55/lb	$0.01–$7.98
Nalco Acti-Brom 1338	42.8% sodium bromide	$1.45/lb	$0.02–$6.89
Nalco Acti-Brom 7342	42.8% sodium bromide	$1.54–$3.34/lb	$0.02–$15.74

➥ *Organobromine compounds*

7413 Antimicrobial (ATC)	5.0%✣	$5.89/lb	$4.58–$634.18
7413 Antimicrobial (ASE)	5.0%✣	$6.91–$7.05/lb	$5.38–$759.07
Betz Entec 345 A	5.0%✣	$5.17/lb	$4.19–$584.99
Antimicrobial DB-5 (CPL)	5.0%✣	$3.05/lb	$2.37–$328.39
ChemTreat CL-207	5.0%✣	$5.45/lb	$4.20–$577.81
Dearcide 723 (DD)	20.0%✣	$7.36–$7.46/lb	$2.35–$204.55
Dearcide 734 (DD)	40.0%✣	$42.19/lb or $18.60/tablet	$55.80
Nalco 2510	20.0%✣	$11.88–$12.33/lb	$2.71–$9.94

✣ 2,2-dibromo-3-nitrilopropionamide

➥ *Triazines*

Nalco 2834	4.0%✲	$6.66–$7.56/lb	$15.59–$17.69
Nalco 7336	4.0%✲	$4.27/lb	$10.02

✲ terbuthylazine: 2-(tert-butylamino)-4-chloro-6-(ethylamino)-S-triazine

➥ ***Isothiazoline compounds***

Ancocide 4070 (ACC)	1.2%[a]; 3.5%[b]	$3.32/lb	$9.09–$55.31
7423 Microbiocide (ASE)	1.2%[a]; 0.4%[b]	$4.86–$5.16/lb	$13.41–$86.48
Betz Entec 368 (Betz Entec)	1.2%[a]; 0.4%[b]	$3.72/lb	$10.27–$62.35
ChemTreat C-2155	4.3%[a]; 1.3%[b]	$3.89/2-oz bag	$31.12–$155.60
ChemTreat CL-2150	1.2%[a]; 0.4%[b]	$3.40–$3.70/lb	$9.38–$62.01
Dearcide 702 (DD)	1.2%[a]; 0.4%[b]	$3.70–$3.80/lb	$32.41–$63.69
G-C Formula 313	4.3%[a]; 1.3%[b]	$1.78–$2.23/lb	$32.08–$200.40
G-C Formula 315	1.2%[a]; 0.4%[b]	$3.65–$5.15/lb	$10.08–$86.32
Nalco 2810	4.3%[a]; 1.3%[b]	$9.05–$11.60/packet	$72.40–$464.00
Nalco 7330	1.2%[a]; 0.4%[b]	$4.43–$4.94/lb	$38.81–$82.79

a) 5-chloro-2-methyl-4-isothiazolin-3-one; b) 2-methyl-4-isothiazolin-3-one

➥ ***Quaternary ammonium salts*** — **Quats**

Betz Entec 349	10.0%[a]; methylene bis (thiocyanate), 5.0%	$7.24–$7.50/lb	$8.69–$63.75
Dearcide 737 (see *glutaraldehydes* above)			
G-C Formula 30-A	7%[b]	$1.50–$2.20/lb	$7.98–$23.39
G-C Formula 35	25%[c]; isopropyl alcohol, 10%	$3.25–$4.55/lb	$6.77–$14.19
Nalco 8396 (see *glutaraldehydes* above)			
Sanatox 2201 (SJC)	10%[b]	$18.70/gal	$18.40–$70.86
Sanatox 2203 (SJC)	20%[b]	$21.00/gal	$10.01–$37.73

a) dodecylguanidine hydrochloride; b) alkyl dimethyl benzyl ammonium chloride; c) dodecyl dimethyl ammonium chloride

➥ ***Quaternary ammonium salts*** — **Polyquats**

7416 Microbiocide (AWT)	15%✣	$3.50–$3.59/lb	$2.32–$38.52
7618 (ATC)	5%✣	$3.05/lb	$6.24–$99.58
A-806 Algaecide (ATC)	15%✣	$3.46/lb	$2.32–$37.20
7618 Microbiocide (ASE)	5%✣	$3.20-$5.16/lb	$6.52–$168.53
A-106 Microbiocide (ASE)	15%✣	$3.64–$3.75/lb	$2.44–$40.30
Algae Control Ed Liquid (CPL)	15%✣	$2.10–$2.40/lb	$1.41–$25.73
Dearcide 722 (DD)	15%✣	$2.75–$2.89/lb	$1.84–$30.69
G-C Formula 32	18%✣	$3.30–$4.55/lb	$1.82–$40.31
Nalco 2594	20%✣	$4.36–$5.80/lb	$1.31–$45.84
Skasol MB-5	15%✣	$3.63–$14.53/lb	$2.46–$155.60
WC 620	10%✣	$2.98–$3.83/lb	$3.02–$62.28
WC 625	15%✣	$3.32–$3.89/lb	$2.23–$41.70
WC 630	30%✣	$4.25–$4.89/lb	$2.34–$25.82

✣ poly[oxyethylene (dimethyliminio) ethylene(dimethyliminio)ethylene dichloride]

➥ *Organo-sulfur compounds*

7212 Microbiocide (ATC)	25.0%[a]	$3.33/lb	$4.42–$26.17
7212 Microbiocide (ASE)	25.0%[a]	$3.22–$3.52/lb	$4.27–$27.67
Betz Entec 349 (see *quats* above)			
Chemcide 942 (see *organic thiocyano-azole compounds* below)			
Chemcide 946 (see *organic thiocyano-azole compounds* below)			
Chemicide 965 (CWT)	20.0%[a]	$2.60/lb	$4.24–$25.30
ChemTreat CL-216	15.0%[b]; 15.0%[f]	$2.45–$5.30/lb	$6.42–$34.76
Dearcide 709 (DD)	9.3%[d]	$6.47–$6.51/lb	$9.70–$19.53
Dearcide 714 (DD)	15.0%[b]; 15.0%[f]	$2.34–$2.48/lb	$6.13–$16.22
9927 Microbiocide (Eco)	3.7%[e]; 5.1%[c]	$1.52–$2.05/lb	$2.16–$60.80
G-C Formula 31-A	4.5%[b]; 4.5%[f]	$1.55–$2.25/lb	$12.25–$28.58
G-C Formula 37	15.0%[b]; 15. %[f]	$2.75–$3.80/lb	$7.56–$16.98
G-C Formula 38-A	7.4%[e]; 10.2%[c]	$3.45–$4.80/lb	$1.11–$23.04
G-C Formula 39	50.0%[a]	$3.60–$5.05/lb	$1.76–$36.92
G-C Formula 317	40.0%[b]; 40.0%[f]	$0.40–$0.54/lb ($0.10–$0.14/bag)	$0.60–$1.08
Skasol MB-X	7.4%[e]; 10.2%[c]	$3.47–$8.74/lb	$2.49–$129.23
Antifoulant C-101 (WTC)	3.7%[e]; 5.1%[c]	$13.05–$16.66/gal	$2.11–$56.13
WC 600	7.4%[e] 10.2%[c]	$3.64–$4.25/lb	$2.61–$62.85

a) potassium dimethyldithiocarbamate; b) sodium dimethyldithiocarbamate; c) potassium N-methyldithiocarbamate; d) methylene bisthiocyanate; e) disodium cyanodithiomidocarbonate; f) disodium ethylene-1,2-bisdithiocarbamate (nabam)

➥ *Gluteraldehyde*

7420 Microbiocide (AWT)	15.0% gluteraldehyde	$4.22–$4.54/lb	$36.08–$88.43
7420 Microbiocide (ATC)	15.0% gluteraldehyde	$4.39/lb	$37.53–$85.44
7420 Microbiocide (ASE.)	15.0% gluteraldehyde	$5.43–$5.73/lb	$46.43–$111.56
7421 Microbiocide (ASE)	45.0% gluteraldehyde	$10.83–$11.26/lb	$30.08–$72.96
Betz Entec 445	45.0% gluteraldehyde	$8.34–$10.23/lb	$23.44–$67.00
GA-15 Microbiocide (CPL)	15.0% gluteraldehyde	$2.51/lb	$21.46–$48.90
ChemTreat CL-2111	45.0% gluteraldehyde	$7.10/lb	$19.45–$45.15
Dearcide 733 (DD)	45.0% gluteraldehyde	$5.78–$5.96/lb	$16.01–$38.57
Dearcide 737 (DD)	42.5% gluteraldehyde; alkyl dimethyl benzyl ammonium chloride, 7.5%	$8.02–$8.12/lb	$19.89–$47.26
G-C Formula 312	45.0% gluteraldehyde	$5.45–$7.60/lb	$15.75–$51.38
Nalco 7338	45.0% gluteraldehyde	$5.16–$8.81/lb	$14.15–$56.29
Nalco 8396	14.0% gluteraldehyde; alkyl dimethyl benzyl ammonium chloride, 2.5%	$3.45–$4.71/lb	$2.62–$8.41
Microbiocide No. 4 (Ska)	15.0% gluteraldehyde	$5.01–$5.32/lb	$42.96–$103.89

➥ ***Organic thiocyano-azole compounds***			
Chemcide 942 (CWT)	methylene bis(thiocyanate), 2.5%; 2.5%✹	$7.50/lb	$3.38–$74.33
Chemicide 946 (CWT)	methylene bis(thiocyanate) 10%; 10.0%✹	$15.53/lb	$1.90–$42.40

✹ 2-(thiocyanomethylthio)benzothiazole (TCMTB)

[1] *Abbreviations for manufacturers of alternatives to tributyltin:* **ACC** = Anderson Chemical Company, Inc.; **ASE** = Aqua Serv Engineers, Inc.; **ATC** = AquaTreat Chemicals, Inc.; **AWT** = American Water Technology; **Betz** = Betz Entec; **ChemTreat** = ChemTreat, Inc.; **CPL** = Chem Pro Laboratory, Inc.; **CWT** = Chemco Water Technology; **DD** = Dearborn Division—W.R. Grace & Co.; **Eco** = Ecolab, Inc., Water Care Services; **G-C** = Garratt-Callahan Chemical Co.; **Nalco** = Nalco Chemical Co.; **SJC** = San Joaquin Chemicals, Inc.; **Ska** = Skasol, Inc.; **WC** = WC Chemical Engineering; **WTC** = Water-Tech Chemical Specialties, Inc.

[2] Total cost of material per month was calculated using estimates for monthly maintenance and a one-day cleanup pulse per month. To request a copy of cost descriptions of tributyltin alternatives, please write to:

Cost Comparison of Tributyltin Alternatives
Department of Pesticide Regulation
Environmental Monitoring and Pest Management
1020 N Street, Room 161
Sacramento, CA 95814–5624

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PART SIX — OPTIONS FOR CONTROLLING COPPER AND TRIBUTYLTIN-CONTAINING COMPOUNDS

A. W. Fabre

The Department of Pesticide Regulation (DPR) is committed to establishing a high-priority program to address the problem of excessive copper and tributyltin found in the effluent of Publicly Owned Treatment Works (POTWs) in the San Francisco Bay Area (Bay Area). A contributing source of these metals is associated with the use of pesticide products containing copper and tributyltin as active ingredients. DPR has identified administrative options that could be used to address this problem.

Voluntary Program

A cooperative outreach (voluntary) program has been used by several Bay Area POTWs in an effort to change pest control practices of residents, small businesses, and municipalities.

Advantage

- Educates users of copper and tributyltin pesticides and encourages them to switch to alternative compounds.

Disadvantages

- Involves added costs to local agencies.
- Requires coordination among users in municipalities in the Bay Area to obtain compliance.
- Requires coordination of municipalities within the boundaries of POTWs to obtain compliance.

Regulatory Program

DPR can use one of three regulatory options to address the problem of excessive copper and tributyltin discharges resulting from pesticide use in the Bay Area. These options include 1) cancellation of copper and tributyltin pesticide products, 2) designation of copper and tributyltin pesticides as restricted materials, and 3) prohibition of the sale and use of copper and tributyltin pesticides. Each option would reduce discharges to waterbodies in California attributable to copper and tributyltin. However, users would have to change their management practices for controlling roots in sewers and microorganisms in cooling water systems.

Option 1—Cancellation of copper- and tributyltin-containing products

A comprehensive prohibition of copper and tributyltin pesticides would result in their total elimination throughout California, including uses as fungicides and algicides.

Advantage

- Reduces the possibility of accidentally using canceled products.

Disadvantages

- Provides a solution that does not focus on the Bay Area. Inconveniences users outside of the Bay Area who do not contribute to discharges into the Bay.
- Fails to recognize that these materials are used throughout California for a wide range of agricultural and industrial uses and generally do not contribute to adverse aquatic effects.

Option 2—Restricted material status for copper- and tributyltin-containing products

Designation as a restricted material is the most complex option for addressing the problem of excessive copper and tributyltin discharges from POTWs in the Bay Area. The permitting procedure for restricted materials is intended to regulate pesticides that are used agriculturally. Many of the current uses of copper and tributyltin pesticides are not agricultural; therefore, the mechanisms appropriate for agricultural use pesticides may not apply to this situation.

Advantages

- Allows inspection of applications by county agricultural commissioners, facilitates notification of intent to apply restricted materials, and requires reporting of all pesticide applications of restricted materials, which would increase workload for users and county offices.
- Provides a way to monitor compliance with additional use requirements specified by regulations.

Disadvantages

- Allows sale of restricted materials only by licensed pesticide dealers, who are required to maintain sales records.
- Allows application of restricted materials only by certified applicators or by individuals under the direct supervision of certified applicators.
- Allows possession and application of restricted materials under permit issued by the county agricultural commissioner.
- Increases costs for retailers, pesticide dealers, pesticide applicators, local agencies, and users.

Option 3—Restrictions on sale and use

Statutory authority is provided by the Food and Agricultural Code for the prohibition and regulation of environmentally harmful materials (§ 14102). For example, DPR has adopted regulations governing the release rate of tributyltin from antifouling paints and coatings. Option 3 would prohibit the sale and use of copper- and tributyltin-containing products used for root control and cooling tower biocides in the counties of (1) San Francisco, (2) Santa Clara, (3) San Mateo, (4) Alameda, (5) Contra Costa, (6) Solano, (7) Napa, (8) Marin, and (9) Sonoma.

Advantages

- Tailors the prohibition of sale and use in the Bay Area for copper used to control roots in sewers and tributyltin used to control microorganisms in cooling water systems.
- Limits sale and use prohibition to copper- and tributyltin-containing products that have label instructions for use in sewers or cooling water systems.

Disadvantage

- Requires county agricultural commissioners of the nine affected Bay Area counties to redirect their efforts to monitor sales of copper- and tributyltin-containing products used in sewers or cooling water systems.