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Ozone Disinfection of Dry-Weather Urban Runoff and Storm Drain Water

A dissertation submitted in partial satisfaction of the requirements
for the degree Doctor of Environmental Science and Engineering

by

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DEDICATION

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ABSTRACT OF THE DISSERTATION

Ozone Disinfection of Dry-Weather Urban Runoff and Storm Drain Water

by

Gerald Edwin Greene

Doctor of Environmental Science and Engineering

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The Clean Water Act requires large municipalities to obtain National Pollutant Discharge Elimination System Storm Water Permits and mandates "controls to reduce the discharge of pollutants to the maximum extent practicable..." During dry-weather, storm drains discharge urban runoff from a myriad of sources including groundwater and landscape drainage, illegal drain connections, air conditioner and boiler bleed-off and wash waters. This highly variable flow contains physical, chemical and biologic pollutants including trash, industrial wastes, soot, fertilizers, pesticides, plant and animal wastes, and human pathogens. In the absence of chemical spills and trash, the major public health threat from these flows is associated with the exposure of bathers to pathogens.

Traditionally, microbially contaminated water has been treated by chlorination. However, growing apprehension regrading chlorine storage and mutagenic by-product formation, has encouraged the evaluation of other disinfectants. Ozone is an efficient oxidant that is formed from air or oxygen just prior to use, creates few mutagens, and rapidly dissipates. Ozonation assists other processes, including floatation, coagulation, filtration and biodegradation. This pilot plant study evaluated ozone disinfection of dry-weather urban storm drain runoff and characterized the contaminant variability.

The 12 mg/L mean ozone dose reduced total and fecal coliforms, enterococcus and virus counts an average of 3.4 log and higher dosages achieved 6 log disinfection. Although the mean concentration of most priority pollutants was below drinking water maximum contaminant levels, chlordane, o-xylene, phthalates and some heavy metals, appeared episodically at higher values. Polycyclic aromatic hydrocarbons, copper and zinc exceeded California Ocean Plan objectives, but met potable water standards. Effluent total coliform counts were correlated with dissolved ozone residuals, while ozone dose was dependent on total organic carbon concentrations. These functions are critical to the description, operation and control of a proposed dry-weather urban runoff, or storm drain, disinfection treatment facility, which includes modifications for accommodating highly variable flow, contaminant and discharge conditions. Institutional barriers that facilitate, or hinder, the construction and operation of the facility, are summarized.

INTRODUCTION

storm water
1 or 2 words

Background and National Issues

Although storm water runoff has long carried silts, salts, soot, organic wastes, and parasites from the land to various receiving waters, the negative impacts from these contaminants were normally palliated by nutrients that gave rise to rich wetlands and estuaries. Modern humans have accelerated this erosion process through chemical agriculture, mining, and the construction of crowded urban centers that must dispose of enormous quantities of physical, chemical and biologic wastes faster than natural processes can assimilate it. A recent effort to control water pollution and remediate past transgressions is the Federal Water Pollution Control Act of 1972, and its 1977 and 1987 Water Quality Act amendments, or the Clean Water Act. This mandate has greatly reduced wastewater emissions from publicly owned treatment works (POTWs), refineries, manufacturing, paper mills, power stations, and other high volume sources.

These point sources have identifiable discharge points, which are amenable to monitoring, and pollutant emissions, which can be reduced by process modifications or additional treatment technologies. When these discharges enter "navigable" waters of the United States, the source must obtain, and comply with, a National Pollutant Discharge Elimination System (NPDES) permit. This program has consolidated the regulatory impetus on the most serious pollution problems and significantly decreased contaminant emissions. This dramatic success is in sharp contrast to the more modest achievements in restricting the emission of nonpoint source pollution.

Nonpoint source pollution takes many forms, but can generally be categorized as mine, agricultural, or urban runoff. It is characterized by having a diffuse source, including tailing piles, large fields, and urban watersheds, with no serviceable means of assessing flow volumes and contaminant content. The flow of water and pollutants is strongly influenced by environmental factors such as soil type, slope, plant cover, and the type and rate of precipitation. The drainage from unconsolidated mine tailings and spoils can contain heavy metal bearing ores, sediments, and extraction fluids which can be washed into surface waters, causing locally devastating environmental effects. However, dilution and neutralization generally limit the extent of the impact and potable water treatments are available to limit the public health threat.

Agricultural, silvicultural, and feedlot runoff is contaminated with sediments, biological wastes, fertilizers, pesticides, and zoonotic microbes; resulting in siltation, oxygen depletion, eutrophication, fisheries decline, and reduced resource utilization. Agricultural pesticides have had a particularly dubious impact, and their residues are found worldwide. While restrictions and integrated pest management have reduced the consequences of pesticide use, many areas remain impacted by agricultural runoff.

The discharge of urban runoff occurs through two different mechanisms. In areas with combined sewer systems, dry-weather or nuisance runoff is collected and treated with the normal sanitary sewage flows. During precipitation events, the ratio of urban storm runoff to sewage increases and can exceed the system treatment and detention capacity, resulting in the discharge of combined sewer overflow (CSO) to the receiving water. In these areas, the urban runoff problem is negligible during dry-weather, but can cause a sewage discharge during significant precipitation events. Other cities have separate municipal sewer and storm drain systems resulting in urban runoff being continuously discharged without active treatment. In wet weather, after an initial flush of accumulated debris, large storm water flows carry low concentrations of pollutants into the receiving water, but the total mass emission of contaminants can be significant. During dry-weather, the runoff volume is orders of magnitude less, but contaminants may be at higher concentrations and the risk of human exposure is greater due to recreational activities adjacent to the outfall.

X The sources of dry-weather urban runoff are ubiquitous in cities and suburban areas, especially where impervious surface predominate. Groundwater sources include hillside drainage, basement sumps, utility vaults, construction site de-watering, and well flushing. In residential areas, excess landscape watering and drainage, property and automobile washdown, and swimming pool maintenance flush contaminants over the curb and into the gutter where they can eventually enter the storm drain system. The walls of catch basins and storm drains are often cracked allowing ground, fugitive, potable, or sanitary system water to infiltrate. During the pilot study, potable water, flowing from ruptured water mains and failed check valves at thousands of gallons per minute, flooded the storm drain on four occasions. The study was also suspended due to a ruptured sewer that collapsed into the storm drain, but could not be located until a sink hole formed. Industrial releases include air conditioner condensate, equipment cooling water, cooling tower and boiler bleed-off, fire sprinkler testing, fire fighting, steam cleaner wastewater, pipe maintenance and hydrotesting and restaurant cleanup. The floor drains in many areas where loading docks, motor vehicles, and dumpsters are washed down are illegally connected to the system, and even sanitary connections are carelessly or surreptitiously linked to storm drains.

While each of these individual discharge sources carries its own characteristic contaminants, the agglomeration also carries soot, dust, sediments, trash, animal and botanical wastes, and vehicular fluids that settle in drains, gutters and catchbasins. In addition, since most storm drains are subterranean, locating sources of pollution is challenging and often complicated by a lack of drainage information, privacy issues, property rights, and access that is safe from traffic. Even expensive sanitary surveys will only locate permanent connections and active discharges, while rarely identifying mobil sources and deliberate subterfuge. Beyond the challenge of ferreting sources, the most difficult aspect of controlling urban runoff pollution, is in safely anticipating the varying combination of hazardous materials and flow conditions.

Storm drain and urban runoff contaminants can be split into physical, chemical and biological pollutants. The former subset includes primarily sediments and trash, such as papers, plastics, food containers, balloons, balls, styrofoam, condoms, wheel weights and other automobile parts, cigarettes, coins, keys, cans, glass, construction materials, rocks, bricks and other similar items. Although biological and chemical contaminants can adsorb onto trash, the impact is primarily aesthetic. The collection and removal of floatable trash is a costly beach maintenance issue and it is estimated that over 4,000 tons are removed annually from Santa Monica Bay beaches (SMBRP 1994). The problem becomes especially acute after winter storms flush accumulated trash through the storm drain system and onto adjacent beach areas, where it can kill wildlife through ingestion, entanglement, or suffocation. Fortunately, trash is among the most easily eliminated pollutants and it is likely that best management practices, such as augmented street sweeping and public education, can be moderately effective.

Chemical contaminants in urban runoff have a variety of origins and toxicities. They include salt from de-icing operations and water softeners, oils and grease from vehicles and food processors (Stenstrom, Silverman, and Bursztynsky 1982), acids and metals from sources that include motor vehicles, metal finishers, and paints (SMBRP 1994), solvents, phthalate plasticizers, antifreezes, fertilizers, pesticides, herbicides, polychlorinated biphenyls (Suffet et al. 1993), and combustion by-products such as, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dioxins and furans (Fisher et al. in press). Most of the more toxic components were present in the water phase at low or trace (μg or ng/L) concentrations (Greene 1992, Fisher et al. in press, Suffet et al. 1993), but some were at mg/Kg levels in sediments (Greene 1992). The latter study also detected high concentrations of the pesticide chlordane and the solvent o-xylene during separate "spill" events. While dilution with receiving water generally reduced contaminant concentrations to levels that do not present a public health threat, the sediment bound fraction is significant and may warrant retention and treatment.

The primary human health threat in urban runoff is probably from biological contaminants, which include both botanical and animal wastes and opportunistic and pathogenic microorganisms. Plant wastes, including both living and dried tissues, are often washed or blown from street surface into catch basins and storm drains, but can also be dumped there by careless gardeners. Detritivores decompose this matter and may exert a significant oxygen demand, especially where low spots in the system allow stagnant conditions to predominate. Although these infections are rarely life threatening, some of these organisms are opportunistic and can invade living tissues.

Animal wastes have many of the same characteristics as botanical matter, but can also contain human pathogens, especially if the runoff is contaminated by sewage. Among the disease-causing microorganisms detected in urban and storm drain runoff are enterovirus like polio, coxsackie B, and echo, and bacteria including *Pseudomonas aeruginosa, Staphylococcus aureus, Enterococcus* sp., and *Salmonella* sp. (O'Shea and Field 1992). Furthermore, zoonotic diseases that normally afflict animal populations, such as plague, giardiasis, and cryptosporidiosis, may also cause infections in humans. Storm drains often discharge into recreational waters, which may be adjacent to public beaches, and the risk of human exposure appears to be significant. This exposure risk varies with climate and, while surfers expose themselves to storm runoff, dry-weather flows impact surfers and bathers that include children and other sensitive individuals.

Pathogen surveys found enteric virus in each of three Santa Monica Bay storm drains and the Pico-Kenter drain contained virus during three consecutive years (Gold et al. 1992). Although illegal wastewater connections, or ruptured sewage lines, were the most likely cause origin of these pathogens, other potential sources include failing septic systems, the local homeless population, recreational vehicles, and sanitary waste dumping. Zoonotic organisms are also liberated with the feces of wild and domestic animals and can be carried to the drain system by coprophagous insects such as flies and roaches. In summary, many sources and transmission routes exist for transporting human pathogens into the storm drain system and recreational receiving waters.

To begin controlling the emission of contaminants in urban runoff, the United States Environmental Protection Agency (USEPA) recently established the Municipal and Industrial Storm Water National Pollutant Discharge Elimination System Permit Program (USEPA 1990). This mandate requires pollution-prone industries and urban areas with populations over 100,000 to implement best management practices (BMPs) that reduce the potential for runoff contamination, monitor their runoff quality, and annually report their progress. Regulators expect that the monitoring program results will identify sources and practices that emit unacceptable levels of contamination, so that further preventive measures can be implemented. In some areas, like the Santa

Monica Bay, programs with goals beyond those of the federal regulations have been initiated (SMBRP 1994). One proposal includes storm drains in a basin-wide mass emissions program with source-specific discharge performance goals. Sources exceeding these discharge goals would be re-evaluated to assure that BMPs have been optimized to the maximum extent practicable. Others proposals advocate storm drain effluent limitations based on California Ocean Plan Objectives (SWRCB 1990), which are often far more restrictive than even potable water maximum contaminant levels.

Local Issues

In order to preserve the reputation of its famous beach, and in anticipation of these pending initiatives, the City of Santa Monica began investigating technologies to decontaminate the effluent from the Pico-Kenter storm drain. For over a decade, this discharge has been reported to contain biological and chemical pollution and, as the fourth largest drain in the Santa Monica Bay (Stenstrom and Strecker 1993), it has the potential to be a significant cause of environmental degradation. While the City environmental program includes many best management practices, it has been unable to achieve the desired level of pollution abatement, partially because less than half of the catchment is within the City border. Given these considerations, and the limited effectiveness of many best management practices, it was proposed that the dry-weather urban runoff be pumped to the City of Los Angeles Hyperion Wastewater Treatment Plant. This option was eventually rejected because of: 1) limited treatment capacity; 2) pending effluent water quality litigation; and 3) concerns that the City would exceed its wastewater discharge allotment, resulting in a significant monetary penalty.

A consulting firm was engaged to propose potential treatment technologies that could be used to disinfect the dry-weather effluent. The primary alternatives selected were chlorine gas injection, with dechlorination prior to discharge, and ultra-violet (UV) light irradiation (JMM 1987). Although these proposals were based on sound engineering principles and practices, chlorination was unacceptable to the community because of concerns regarding chlorine gas storage and the formation of halogenated disinfection by-products (DBPs). The disinfection by-products include halomethanes, haloacetic acids, haloketones, and aldehydes, that form during the oxidation of organic matter by chlorine and their formation potential is correlated with the total organic carbon concentration. Some are mutagenic or, in the case of the trihalomethanes carcinogenic. Although less hazardous, disinfection using UV irradiation requires that suspended solids be maintained below 20 mg/L, an unrealistically low value given that the design specifications required only screening. The rejection of these alternatives lead to the evaluation of ozone for disinfection the dry-weather storm drain effluents.

The Environmental Science and Engineering Internship

As described in the appendices, ozone has been used in water treatment for over a century and the decision to evaluate its use in disinfecting urban runoff was a natural extension of recent water and wastewater studies. After obtaining a sponsor to provide equipment, the Santa Monica City Engineer selected the author to conduct an evaluation on ozone disinfection efficacy, tentatively planned for April of 1989. When preparations began in February, a review of the project plan indicated that the desired objectives were unachievable with the available fiscal reserves. Fortunately, the Santa Monica Bay Restoration Project requested proposals for action demonstration projects aimed at improving the bay environment. A proposal for studying both ozone disinfection of storm drain effluents and characterizing the chemical contamination in the Pico-Kenter drain, was prepared by the author, and selected from among a dozen submissions to be offered funding. After further competition and agency negotiation, this proposal was selected to receive 70% of the available $140,000 in grant funding.

Based on this support, and the concurrence of the doctoral chair, the project was developed into an Environmental Science and Engineering Program Internship, with the study utilizing the facilities of the City of Santa Monica and the University of California at Los Angeles, Laboratory of Biomedical and Environmental Science. Following the finalization of formal interagency agreements in October 1989, project staff were procured, facility preparations completed, supplies ordered, and sampling initiated in late November of 1989. During the study, the project objectives were modified based on the recommendations of a seven member Technical Review Board composed of: Mr. Desi Alvarez (City Engineer, City of Santa Monica); Dr. James Foxworthy (Engineering Department, Loyola Marymount University); Mr. Mark Gold (Staff Scientist, Heal the Bay); Dr. Rainer Hoenicke (Environmental Specialist, SMBRP); Mr. John Mitchell (Stormwater Engineer, Los Angeles County Department of Public Works); Mr. Jack Petralia (Director Environmental Protection, Los Angeles County Department of Public Health); and Dr. Michael Stenstrom (Engineering Department, UCLA). Sampling was completed in late 1990, the final project report accepted by the USEPA and SMBRP in June of 1992 and is enclosed here as Appendix I.

In early 1993, the internship with the City of Santa Monica was completed, the doctoral committee reconstituted, and the prospectus defense approved in February of 1993. A manuscript entitled "Ozone Disinfection of Urban Storm Drain Water" was prepared, based on the data assembled during the pilot plant study, and submitted to *Ozone Science and Engineering* in September of 1993 and accepted for publication in January of 1994. This manuscript is presented in Appendix II. A second manuscript, entitled "Design Considerations in Disinfection Urban Runoff Water With Ozone", was similarly prepared and has recently been submitted to the *Journal of Environmental Engineering*. The draft manuscript appears in Appendix III.

Dissertation Goals and Objectives

The four major sections of the dissertation are the introduction, institutional barriers, conclusion and technical appendices. In the introduction, point and nonpoint source pollution has been contrasted, urban runoff more fully defined, and genesis of this study described. In essence, this investigation was initiated because the regulatory mechanism for controlling urban runoff pollution is based on management practices, which are unlikely to achieve community environmental objectives. As an alternative to proposed effluent limitations, this study investigated the feasibility of constructing an ozone-based disinfection treatment facility to alleviate urban runoff contamination, during the summer dry season when the human health threat is most significant. This study is not an economic or exhaustive evaluation of alternative treatment processes, but the evaluation and proposal of one potential treatment train that could achieve these challenging environmental objectives.

The technical appendices include the project methods, summarize the data, and develop the scientific conclusions that have resulted from this study. They essentially describe the complete mechanics of the investigation, but have been summarized as the conclusion of this introductory chapter. The following chapter describes potential institutional barriers that have inadvertently been constructed and could prevent construction of facilities similar to the proposed treatment plant. While many of these hurdles can be overcome by reinterpreting existing agency polices the process should begin soon to minimize future delays in planning, design and construction. Finally the conclusions chapter summarizes the major findings of this investigation and suggests future work that could resolve some of the issues that developed during this study, but are beyond its scope.

Summary of the Technical Appendices

APPENDIX I: OZONE DISINFECTION AND TREATMENT OF URBAN STORM DRAIN DRY-WEATHER FLOWS: A PILOT TREATMENT PLANT DEMONSTRATION PROJECT FINAL REPORT

The primary objectives of this study were to determine if ozone could disinfect the dry-weather runoff in the Pico-Kenter storm drain and to identify and characterize the concentration variability of any contaminants that were present. The disinfection results showed that ozone, at a geometric mean dose of 12 mg/L, effectively reduced total coliform, fecal coliform, enterococcus bacteria, and attenuated polio virus counts by a geometric mean of 3.4 log. This is equivalent to 99.96% of the microorganisms being killed or inactivated. At high ozone dosages, and optimal treatment conditions, disinfection reached 6 log or 99.9999% bacteria elimination. Disinfection was slightly inhibited by moderate (< 100 NTU) turbidity levels, and if the suspended solids were inorganic clays or cement dust, ozonation proceeded virtually unaffected. At 10-20 mg/L, ozone dosages was three times greater than typically used in potable water; however, the geometric means for suspended solids and organic carbon were 22 and 15 mg/L respectively, about ten times predisinfection potable water concentrations. The arithmetic means for these contaminants were 103 and 19 mg/L, emphasizing the second major study finding, which was the extreme pollutant concentration variability. Most were geometrically (logarithmically), not arithmetically (normally), distributed.

The geometric mean is the antilogarithm of the mean of the logarithmically transformed raw data. This statistic reduces the skewing due to a few extreme values that may be orders of magnitude above the median. For organic carbon, the minimum and maximum samples concentrations were 2.2 and 124 mg/L and the 90th percentile values for the geometric and arithmetic distributions respectively, were 35 and 40 mg/L. Using D'Agostino's test for normality (Zar 1974) either distribution adequately characterizes the sample population. In contrast, suspended solids ranged between 0.6 and 6,540 mg/L and the 90th percentile values were 129 and 740 mg/L respectively, for the geometric and normal distributions. These values are indicative of extremely different levels of water quality and demonstrate the affect of contaminant variability.

The study also found that many of the ozonated effluent water samples met the California wastewater reclamation standard, for limited access landscape irrigation, of 23 total coliform organisms per 100 ml. In water deficient Southern California, this suggests a valuable application that conserves the treated effluent and may warrant the inclusion of additional treatment processes, such as biologically active filtration (BAF). This process should reduce the concentration of assimilable organic carbon (AOC) disinfection by-products, which include aldehydes, alcohols, carboxylic acids, and ketones, that are formed at moderate levels (low to mid μg/L) during treatment. Although the limited number of analyses and high sample variance limit the statistical significance, the mutagenicity of the effluent was less than that of the influent.

Many organic contaminants, including the phthalates and PAHs, were detected in the sediments at concentrations four orders of magnitude above that of the liquid phase. Removing these suspended solids and sediments could facilitate treatment and significantly reduce the mass of contaminants emitted with the effluent. In the water phase, the mean concentration of most chemical contaminants was well below drinking water maximum contaminant levels (MCL) and state Ocean Plan discharge objectives. Exceptions to this statement include lead, which exceeded both standards but has since been eliminated from gasoline, zinc and chromium, which approximated the Ocean Plan objectives, and two "spills" when first chlordane then o-xylene were detected at high μg/L concentrations. Paradoxically, while the mean concentrations of copper and regulated polycyclic aromatic hydrocarbons met potable water maximum contaminant levels, they greatly exceeded the Ocean Plan discharge objectives. Therefore, with respect to these contaminants, runoff which was "potable" should not be discharged.

During experiments regarding the ozonation of added organic chemicals, and incidentally during the chlordane spill, high ozone dosages oxidized over half of the compounds tested; sometimes reducing concentrations by two orders of magnitude. Based on the observations for pyrene and naphthalene, which were both spiked into and natively found in the runoff, these results were most apparent when contaminants composed a significant fraction of the total organic carbon, as might happen during a spill. At lower, more typical concentrations, competitive organic carbon reactions appeared to predominate. These chemical oxidation tests were limited in scope and number and these observation are both tentative and require further validation.

APPENDIX II: OZONE DISINFECTION OF URBAN STORM DRAIN WATER

This manuscript introduced the conclusions from the pilot plant project into the literature and further analyzed the relationships among effluent bacteria counts, process variables and contaminant concentrations that can be monitored during treatment. The results were graphically and numerically summarized, showing that while temperature and pH were normally distributed, conductivity, turbidity, organic carbon, bacteria counts, and settleable, suspended, and dissolved solids were geometrically distributed.

A correlations matrix, characterizing effluent bacteria counts as a function of contaminant concentrations and process controls values, like ozone dose and residuals, was prepared. Due to the prevalence of detection limit data for fecal coliforms and limited data for enterococcus bacteria, the most successful correlations were related to effluent total coliform counts, which are also the primary wastewater reclamation standard. Effluent total coliforms were negatively correlated to the log of effluent dissolved ozone residuals by the formula:

$$\text{Log } TC_e = 1.784 - 0.622 \text{ Log } (O_{3r})$$

where: TC_e is the total coliform count per 100 ml of effluent water
O_{3r} is the ozone residual in the effluent water in mg/L

This formula, based on over 400 samples covering a wide range of flow, dosage, and contaminant concentrations, explained 41% of the variation in effluent coliform count.

While the existence of a dissolved ozone residual indicates that disinfection is occurring, control of the treatment process would be facilitated by a predictive estimate of the dosage of ozone required to achieve an effluent bacterial goal. This measure is the reacted (absorbed minus residual) ozone, which was then correlated against various influent parameters that are suitable for monitoring. The resulting regressions indicated that the logarithm of reacted ozone was a function of the logarithm of the total organic carbon as characterized by the formula:

$$\text{Log } O_{3d} = 0.514 + 0.427 \text{ Log TOC}$$

where: O_{3d} is the estimated reacted ozone or demand in mg/L
TOC is the influent water total organic carbon in mg/L

Under the same highly variable conditions as the previous equation, this formula was found to explain 34% of the variation in ozone demand. Both of these correlation had F ratios (mean square to error mean square) that were highly ($P << .001$) significant.

The required, or absorbed, ozone dosage is the sum of the reacted and residual ozone, which can be estimated by rearranging the previous equations and solving to obtain the following formula:

$$O_{3a} = 740\ TC_e^{-1.6} + 3.3\ TOC^{0.43}$$

While these numeric values are likely to be treatment train specific, the derivation of these equations is an important finding. This formula suggests that on the basis of a predisinfection ozone demand measurement (TOC or COD) and an effluent bacterial target (discharge or reclamation standard), the disinfectant dosage can be estimated. Since the estimation of ozone demand is amenable to process monitoring, using TOC, and disinfection can be confirmed by monitoring the effluent dissolved ozone residual, these parameters can be used in controlling and automating the treatment process.

APPENDIX III: DESIGN CONSIDERATIONS IN DISINFECTION URBAN RUNOFF WATER WITH OZONE

Based on the results from the pilot plant project, the City of Santa Monica has proposed construction of a full scale ozone based treatment plant for disinfection and reclamation of the dry-weather runoff from the Pico-Kenter storm drain. Discussions with design consultants, have indicated that few appreciate the extreme variability of storm drain flows and contaminant concentrations, as well as the local preoccupation with protecting both the environment and public health. These observations led to preparation of the manuscript in Appendix III, which characterizes this variability and proposes a hypothetical treatment train for dealing with the urban runoff matrix.

The manuscript is a combination of scientific, design, and position paper, and contends that while urban runoff requires treatment, an unconventional process train, facility design, and operational strategy are required. The position that urban runoff is a serious environmental and public health threat is supported based on chemical and microbial contaminant data and the observation that proposed emission standards will be difficult to achieve without treatment. But, traditional regulated flow and dosage based treatments would improperly respond to the varying conditions of contamination and runoff flow. The manuscript responds by developing the proposed treatment train and operational control strategy based on flexible process-monitoring-based responses and an effluent quality dependent discharge that: 1) delivers by-product and difficult to treat flows to the wastewater system for extensive sewage treatment; 2) disinfects typical flows to eliminate any potential health risk; and 3) reclaims water that is suitable for reuse in landscape applications.

The proposed "straw man" design is both a conclusion, that urban runoff can be treated, and a hypothesis of what might be the preferred treatment train, against which other alternative hypotheses or treatments can be evaluated and tested. In this respect, the project is an extension of a previous report (JMM 1987) which advocated chlorination, which was unacceptable to the community, or UV disinfection, which predicated on unrealistic runoff quality expectations. Ozone was then investigated in anticipation that filtering to remove suspended solids would be unnecessary. While the results supported that hypothesis, they also indicated that runoff reclamation could be undertaken, creating a new benchmark objective with the proposed treatment train as the new model for comparison and evaluation.

INSTITUTIONAL BARRIERS

Although questions remain regarding the most practical process for treating the dry-weather urban storm drain runoff, the technology appears to be feasible and ready for development. Unfortunately, many contradictory public policy issues exist, and regulatory input and clarification are required to facilitate rational decision making about constructing the proposed runoff treatment facility. Among these questions is how the proposed treatment plant would integrate into the federal point and nonpoint source pollution control programs and what funding sources could become available for construction of the facility. At the state level, the California Ocean Plan requires points sources of pollution, like the proposed facility, to meet restrictive discharge objectives that greatly exceed drinking water standards for copper and polycyclic aromatic hydrocarbons. Since these objectives would require additional, prohibitively expensive, treatment processes, the standard for these effluents should be relaxed in order to reduce the public health threat from dry-weather flows. If effluent reuse is undertaken, can the title XXII regulations for wastewater be applied and how must they be modified? This chapter reviews and clarifies some of issues that have lead to these contradictory and undesirable policy implications.

Federal Policies

Municipal storm drain systems have received contradictory management under the Clean Water Act. In mandated assessments of water quality (EPA 1990) "urban runoff was considered to be a diffuse source or nonpoint source pollution." However, section 502(14) of the act clearly defines point source as "any discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, ... from which pollutants are or may be discharged." Based on *Regulations for Storm Water Discharges* (EPA 1990) municipal separate storm water systems are point sources that convey both point and nonpoint source pollution. However, unlike industrial point sources, which must implement Best Conventional Pollutant Control Technology (BCT) and Best Available Technology (BAT), municipal storm systems are primarily required to "reduce the discharge of pollutants to the maximum extent practicable". This is to be achieved using nontraditional management practices that include best management practices (BMPs) public awareness/education programs, land conservancy practices, and alternative paving materials. However, these regulations also allow discharge emission standards, and end-of-pipe technologies, to be required by the administrator, or local enforcement agency, as a permit condition.

The potential use of structural end-of-pipe treatments is frequently referred to in the municipal stormwater regulations, with direct reference to first flush diversions, detention/retention/infiltration basins and trenches, oil/grit separators, grassy swales, porous pavements and swirl concentrators. The unavailability of land in urban areas was also described as limiting these options, without reference to more sophisticated treatment facilities and despite the correlation between increased runoff contamination and impervious urban surfaces. The 1987 Water Quality Act amendment of the Clean

Water Act, added §1292(2)(B) to expand the definition of treatment works to include "any other method or system for preventing, abating, reducing, storing, treating, separating, or disposing of municipal waste, including storm water runoff..." This provision appears to facilitate and endorse fabrication of such a facility through the publicly owned treatment works (POTW) construction grants program.

Probably the most efficient solution for eliminating the health threat from dry-weather runoff and storm flows is to proceed through a graded response. Large urban areas should continue to implement the municipal storm water program, with emphasis on effective best management practices and sanitary surveys, but concentrate on those drains that have the greatest pollution potential. The benefits of this nonpoint source type program should rapidly accrue and be distributed throughout the permit area. Then, using the collected dry and wet weather flow and contaminant data, the most problematic storm drains could be targeted for further actions. The construction of storm drain and urban runoff treatment plants could then be one of the more drastic solutions available and reserved only for those drains that discharge where the public or environmental health threat is significant. The dry-weather urban runoff must also be significant and not associated with upstream NPDES permitted point sources.

In the Santa Monica Bay, only a handful of the over 70 storm drains would fit into this category. Chief amongst these are Ballona Creek, Malibu Creek, Topanga Canyon, and Pico-Kenter Canyon. The 1993 study by Stenstrom and Strecker split the Santa Monica Bay drainage into 28 sub-basins by lumping together many of the smaller storm drains, and modeled pollution emissions from the 28 catchments. The Ballona Creek drainage encompasses over 83,000 acres, almost one third of the entire Santa Monica basin, and drains extensively developed areas west of the Los Angeles civic center. Almost half of all storm water runoff from the basin, discharges through this drain and into the ocean off the popular Dockweiler, Playa and Marina del Rey beaches. Correspondingly, over half of the basin's total runoff emission of chemical oxygen demand, phosphorous, copper, lead, and zinc are also believed to discharge from this drain. Over 60% of the basin's 5-day biological oxygen demand and almost 70% of the oil and grease from the basin discharge from this creek alone. The mean annual runoff has been estimated at over 40,000 acrefeet, with flows during the 6 dry months amounting to 16% of the flow during the wet months. Since it usually rains on less than 20 days per year, the dry-weather flow probably amounts to over 20% of the total discharge.

The Malibu and Topanga catchments encompass 70,000 and 12,600 acres respectively, and comprise 26.5% and 4.8% of the total basin drainage. But, unlike Ballona Creek, they are both over 88% open and undeveloped areas which greatly reduces the runoff and pollutant emissions potential of these basins and suggests that treatment is probably unwarranted. This determination should be considered tentative pending the development of further information regarding leaky septic systems, camping and the microbial emissions potential of these drainage basins.

The next largest basins are the Santa Monica Canyon and Pico-Kenter Canyon drainages at 10,500 (4%) and 8,900 (3.4%) acres respectively. The former is similar to the Malibu and Topanga watersheds, with 77% open and undeveloped areas, while the latter is primarily urban residential, commercial, and industrial areas, with only 20% remaining open. Most pollutant parameters associated with the Pico-Kenter are at about 10% of the Ballona Creek value, based on the model developed by Stenstrom and Strecker (1993), and contaminant emissions should be about 5% of those for the entire Santa Monica Basin. The remaining urban sub-basins are significantly smaller and, given present knowledge about their effluents, probably do not warrant treatment as point sources. In reality, the value from treating the Pico-Kenter probably revolves more around its use as a prototype for larger facilities, such as Ballona Creek, and the interest of its community in controlling pollutant emissions and reclaiming runoff. The proposed plant is significantly different from other water treatment facility and further research and testing should be conducted at this intermediate design flow.

In conclusion, the Clean Water Act recognizes municipal separate storm drains as point sources that convey both point source and nonpoint source pollution, such as urban runoff. While the storm water regulations stress the use of best management practices to reduce emissions from municipal storm runoff, they include provisions to require structural and end-of-pipe treatments when necessary to achieve water quality objectives. Agencies regulated under the Municipal Storm Water Runoff National Pollutant Discharge Elimination System Program, should first implement system wide best management practices, but anticipate the future addition of structural treatments. This is especially true for storm drains with significant pollutant mass emissions. Where possible, land should be reserved for the construction of first flush diversions, detention/retention/infiltration basins and trenches, porous pavements, grassy swales, oil/grit separators and swirl concentrators. When these structures cannot be built, the proposed urban runoff treatment facility may provide an acceptable means for treating storm drain discharges and reducing pollutant emissions.

State Policies

The most critical institutional barrier to an agency considering construction of the proposed treatment facility is ascertaining what standard will be used in regulating it. Based on the wording of the Clean Water Act, storm drains are point sources, and the restrictive California Ocean Plan (SWRCB 1990) applies. However, since storm drains convey discharge from nonpoint source pollution, they are also regulated under the municipal stormwater NPDES program, which primarily utilizes best management practices. Finally, the contention could also be supported that a treatment works for dry-weather runoff is a point source subject to Ocean Plan objectives, while flows that by-pass the facility are only subject to best management practices. Clearly, the State and Regional Water Quality Boards could, through their interpretations, alter the goals of the proposed treatment process and the feasibility of the construction decision.

The California Ocean Plan appears to be guiding document with regards to the standards that could be applied to the proposed facility. It includes limitations on the release of microbial, chemical, radioactive, and physical contaminants and is designed to protect the beneficial uses of the near ocean areas of the state. It generally applies to facilities that have control over their production processes and can apply treatments to eliminate any generated pollutants. The permits for public owned sewage treatment works are typically negotiated with the Water Quality Board to arrive at reasonable emission objectives, based on the available treatment process, while requiring further treatment processes to meet future pollutant reduction goals.

As with most flowing storm drains, if Ocean Plan standards were applied to the Pico-Kenter discharge, almost continuous noncompliance would be observed for all bacterial standards, several metals (lead, copper, and zinc) and many organics, especially phthalates and polycyclic aromatic hydrocarbons (Greene 1992). For zinc, copper, and the aromatic hydrocarbons, the Ocean Plan Objectives are 250, 333 and 200 times more restrictive then potable water maximum contaminant levels. Although dilution reduces the magnitude of these estimates, it is inconceivable that any agency would voluntarily undertake any action that could endanger the nonpoint source status of its storm drain discharges.

A similar result would probably occur if the Ocean Plan were applied to the effluent from the facility. Although the incidence of noncompliance would probably be reduced, the proposed treatment train may be vulnerable to enterococcus counts that exceed standards and high instantaneous concentrations of chemical contaminants.

The Ocean Plan requires mean bacterial counts for total and fecal coliforms, and enterococcus to be below 1,000, 200, and 12 organisms per 100 ml respectively at the boundary of the zone of initial dilution. During the pilot study, the influent mean geometric counts were 520,000, 19,000, and 69,000 organisms per 100 ml, while the effluent averaged 160, 7, and 30. Assuming a 5 fold level of dilution, the coliform counts would remain well under the standard, while enterococcus counts are at 50% of their objective. However, if reclamation is undertaken, the ocean discharge would consist primarily of runoff that was unsuitable for reuse and may have higher bacteria counts. While this should not cause the coliforms counts to exceed standards, the status of enterococcus numbers is far less assured, even with additional treatments such as flotation and filtration.

Maintaining low concentrations of chemical contaminants will also be difficult, especially for metals and some strongly regulated organics. During the pilot study, a chlordane spill occurred and concentrations as high as 5700 ng/L were detected. Filtering would remove most of the sediments, where organics generally concentrate, and the biologically active carbon would absorb much of what remains dissolved in solution. Even ozone would oxidize some of this contaminant. However, it would be difficult to assure anyone that these process would reduce concentrations below the standard of 0.1 ng/L. Likewise, metal chelating resins would be mandatory in order to achieve the 6 month median values required for zinc, copper, and lead, or the instantaneous maximums for almost any of the regulated heavy metals. These resins have never been evaluated for use in urban runoff and it is unlikely that any agency would be willing to risk their use without prior access to regulatory relief.

Relief from restrictive California Ocean Plan Objectives could come from sections VI B., which provide for relaxed standards to encourage water reclamation, and IV F., which grants exceptions when they will not compromise protection of the ocean and best serve the public interests. A second more practical option would be to permit the facility within the confines of the municipal storm water program, which included provisions for best management practices that include structural treatments (USEPA 1990). While numerical standards are not required under this program, they can be issued if required to achieve objectives. Informal standards could be adhered to during preliminary facility testing, then, as information on the process effectiveness is developed, more appropriate standards could be issued and implemented.

In California, reclamation of wastewater is covered under Title 22, Division 4, Chapter 3, of the Administrative Code. While stormwater is not strictly equivalent to wastewater, these regulations provides a reasonable engineering standard against which the proposed treatment process can be gauged. These regulations become more restrictive with increasing likelihood of human exposure, but, for the restricted access landscape irrigation category, the water is only required to be oxidized and disinfected to a mean effluent coliform count of less than 23 organisms per 100 ml. Individual samples must remain below 240 total coliforms per 100 ml. These standards appear to be achievable using the proposed treatment train, but disinfection would be through ozone, rather than chlorine as typically occurs with Title 22 wastewater reclamation. With the exception of water source and disinfectant, most of the other requirements are fundamental to the design of the proposed treatment plant and should complement the Title 22 requirements.

CONCLUSIONS AND FUTURE STUDIES

The results from this and other studies of the Pico-Kenter Canyon storm drain, clearly demonstrate that urban runoff can be contaminated with a variety of pollutants, including trash, hazardous heavy metal and organics, and human enteric pathogens. This ozone pilot plant study established the feasibility of disinfecting the dry-weather urban runoff to eliminate these pathogens and reduce the perceived public health threat associated with surfing, ocean bathing, and typical summer recreational beach use. In response to proposals that a full scale facility be constructed to eliminate much of this pollution, a prototype treatment process train and control strategy are developed to stimulate further discussions and proposals of alternative treatment processes. Governmental policies, that act as institutional barriers to construction of this facility, were identified, so that policy reviews can be initiated by the appropriate agencies. The major conclusions from this study include:

- The mean ozone dosage of 12 mg/L reduced bacteria and virus counts 99.96%
- Ozone dosages approaching 20 mg/L reduced bacteria counts up to 6 log
- Screening (1.5 mm mesh), but not filtering, was the only pretreatment utilized
- Heavy metals, phthlates, and PAHs were consistently present at low levels
- Runoff flow and contaminant concentrations varied widely and changed rapidly
- Metals, chlordane and o-xylene appeared episodically at high concentrations
- Ozone dose was correlated with total organic carbon (TOC)
- Effluent Coliform counts were correlated with dissolved ozone residuals
- The ozonated effluent frequently met landscape irrigation reclamation standards

The major handicap to evaluating the alternative design options, is determining the true range and distribution of the dry-weather flows. Visual estimates from 1987 indicated that the flow averaged 1,800 GPM. During the 1990 pilot plant study, flows were visually estimated at around 200 GPM. During the summer and fall of 1992, the fourth year of an extended drought, a pump station used to divert the runoff to the sewer, discharged at an average of 120 GPM, although flows between 220 to 70 GPM were common. On one occasion, a dry-weather flow estimated at over 4,000 GPM, continued for over an hour. The pump station was inactive following the winter of 1993, which ended the drought and no flow monitoring information is available.

While this research has demonstrated that ozone can effectively disinfect urban runoff, it has also raised the issue of storm drain water reclamation, which in turn has resurrected the question of ultra-violet irradiation versus ozone disinfection. Previous investigations (JMM 1987) had proposed ultra-violet light disinfection of the runoff, provided that a 3 mm mesh screen would reduce suspended solids below 20 mg/L. That assumption was invalidated during the ozone study, which used a finer (1.5 mm) mesh, but still observed a mean suspended solids concentration of over 100 mg/L. Obviously, without further treatment, UV irradiation would have often produced an inadequately treated effluent. Since then, the recent drought, ozone study results, and elevated interest in pollution control, has suggested the inclusion of filtration to allow reclamation of dry-weather urban runoff. The improved water quality, which would result from filtration, necessitates a comparison of ozone and UV light disinfection.

Although there is little information relating to the use of ultra violet light on separate storm systems, tests on combined sewer overflows have been encouraging (O'Shea and Field 1992) and conceptually the method should be effective. Although the effectiveness of ozone is diminished by organic turbidity, it is little effected by inorganic suspended solids, while UV irradiation efficacy decreases dramatically if turbidity and suspended solids are not tightly controlled. Ozone benefits several water treatment processes such as, preozonation, ozone flotation, and disinfection, while UV is an effective disinfectant. By varying gas flow and corona discharge strength, ozone generator output is rapidly adjustable within a 10 fold output range. Irradiation output is not adjustable and treatment is essentially on or off. Both methods require several minutes for a "cold" start up, but inability to adjust output forces UV disinfection to better anticipate erratic flow conditions. Ozone oxidizes some recalcitrant organics into forms that are assimilable and when combined with biologically active filtration, reduces the emission of total organic carbon. Ultra violet light reacts by different mechanisms with recalcitrant compounds and, while little is known about the resulting by-products, they do not include bromate and the peroxides that are formed by ozone. Ozone is effective against protozoans such as giardia and cryptosporidium at typical contact times, while UV disinfection of protozoans employs contact times that exceed those typical used against other pathogens.

In a per unit treated analysis, ultra violet disinfection is far more cost effective because of lower capital, operating and maintenance costs. However, the analysis is likely to become more equal when one considers that an ozone generator designed for a flow of 200 gallons per minute can increase output to disinfect 3 to 5 times that flow. In contrast, irradiation systems would require either additional storage capacity or infrequently used redundant system to control erratic increases in flow.

Despite the preceding discussion, ultra-violet light is a reasonable alternative to ozone disinfection for urban runoff, and it is capable of producing a high quality reclaimable effluent (Darby, Snider and Tchobanoglous 1993). However a precise analysis of the treatment goals must first be prepared to facilitate a fair comparison. The analysis must include: 1) design and peak treatment flow rates; 2) the importance of reclamation; 3) what are the target pollutants (soaps, organic carbon, protozoans, etc.) ?; and 4) is partial treatment of storm flows desirable ? Even with this analysis, it may prove virtually impossible to adequately delineate the attributes of each process train, when applied to treating urban runoff. It may well prove that the final answer will require construction of a hybrid full scale facility that allows either disinfectant to be applied. The operation and control of either process train will be challenged by the variable flow and contamination present in urban runoff from storm drains.

APPENDIX I

OZONE DISINFECTION AND TREATMENT OF URBAN STORM DRAIN DRY-WEATHER FLOWS: A PILOT TREATMENT PLANT DEMONSTRATION PROJECT ON THE KENTER CANYON STORM DRAIN IN SANTA MONICA

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OZONE DISINFECTION AND TREATMENT OF URBAN STORM DRAIN DRY-WEATHER FLOWS

A PILOT TREATMENT PLANT DEMONSTRATION PROJECT ON THE KENTER CANYON STORM DRAIN SYSTEM IN SANTA MONICA

(Dissertation Format)

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EXECUTIVE SUMMARY

The Pico-Kenter Canyon storm drain has become the archetype for assessing the problems and possible solutions that can be associated with many of the urban storm drains in the Santa Monica Bay region. While known events of chemical contamination are few, the drain has long been known to be contaminated with indicator bacteria such as Total and Fecal Coliforms. More recently, the consistent identification of Human Enteric Viruses, F-male Specific Coliphage, and high densities of Enterococcus bacteria have indicated that a potentially serious public health threat exists. The City of Santa Monica, with the assistance of the Santa Monica Bay Restoration Project (SMBRP), the United States Environmental Protection Agency (EPA), and the UCLA Laboratory of Biomedical and Environmental Sciences (LBES), recently completed an evaluation of ozone for the treatment of dry-weather storm drain flows. The primary goals of this study were to establish if ozone could be used to disinfect the water that typically flows from the Pico-Kenter storm drain and determine if some known hazardous chemical contaminants were present at significant levels.

Recently, ozone has become renowned in the drinking water industry as an alternative to chlorine that rapidly disinfects water while forming few halogenated by-products. This study demonstrated that ozone was an effective disinfectant, reducing bacterial and viral populations by 3-5 log (99.9 to 99.999% of the microbes killed or inactivated). In many of the 438 effluent samples, coliform concentrations were sufficiently reduced to qualify the water for reclamation projects such as landscape irrigation along the Santa Monica Freeway, suggesting a possible useful role for the treated effluent. Ozonation by-products (aldehydes) were detected in the plant effluent at low (<100 PPB) concentrations. No significant increases in halogenated by-products, or mutagenicity, were observed following ozone disinfection. During a test of the ozonation process, twelve organic chemicals were added to the influent water and the effluent monitored. While some refractory compounds passed through the pilot facility intact, the concentrations of most were reduced.

In comparison to State Ocean Plan Water Quality Objectives and Federal Drinking Water Maximum Contaminant Levels, the primary hazardous chemical constituents in the influent storm drain water were metals (primarily copper and lead) and polynuclear aromatic hydrocarbons (PAHs). While lead levels were significantly above both standards, the concentration of copper was well under drinking water standards. The mean observed level of six major PAHs were approximately equal to their proposed phase V drinking water MCL standard (100-400 ng/L or PPTr). Isolated samples were found to contain organic contaminants, such as ortho-xylene and the pesticide chlordane. This did not appear to be a pervasive problem and can be attributed to isolated events that cannot be anticipated and will only be prevented through an informed and concerned public.

While the metal content of the water cannot be reduced using ozone, this study found that high concentrations of some organics, including PAHs, can be reduced during the ozonation process. This remediation probably occurs by oxidation and hydroxylation to less hazardous forms. Irregardless of further ozonation investigations, additional more sensitive and definitive PAH analyses are warranted in future studies of the storm drain water and sediments.

Based on the results of this investigation, the City of Santa Monica is investigating construction of a disinfection facility that would reclaim high quality water for landscape irrigation, use low quality for sewer flushing, and disinfect the remainder prior to releasing it into the Santa Monica Bay. Construction of the proposed facility would be encouraged by the support of the Santa Monica Bay Restoration Project in goal definition and consensus building among the member and non-member agencies.

Summary Conclusions

1) Ozone at moderate doses (10-20 mg/L) was an extremely effective disinfectant of dry-weather storm drain flows.

2) Bacterial and viral levels were reduced 3-5 log (99.9% to 99.999% of the microbes killed or deactivated).

3) Much of the effluent was sufficiently disinfected to meet the landscape irrigation standard of 23 coliforms per 100 ml.

4) Based on California Ocean Plan Water Quality Objectives, heavy metals and polynuclear aromatic hydrocarbons appear to be the primary contaminants of concern in the pilot plant effluent.

5) While ozone disinfection by-products were detected (aldehydes), their concentration was low and, in contrast to what would be expected from disinfection by chlorination, no increase in mutagenicity was observed following ozonation.

Summary Recommendations

1) The SMBRP should encourage further evaluation of the ozone disinfection process, by promoting the City of Santa Monica in its effort to design and construct a full scale facility.

2) Since construction and operation of the proposed facility will require interagency consent and permitting, the City of Santa Monica solicits the continued assistance of the SMBRP in consensus building, policy direction, and technical support.

3) Further investigations into the use of the ozone technology should include provisions for the evaluation of Advanced Oxidation Processes (AOPs), using hydrogen peroxide and ozone, for the control of organic pollutants such as PAHs.

INTRODUCTION

In contrast to the success achieved in controlling point sources of water pollution, storm drains and other non-point sources of pollution remain a significant threat to the environmental and public health of our national waterways (GAO 1990 and Water-2000 1991). The popular perception of these conveyances is expressed by the antiquated, but still prevalent, descriptive phrase "storm sewers", suggesting a pipe that conveys wastewater to a treatment facility that purifies the water into a non-polluting effluent. However the Civil Engineer knows, and the public is being educated to the fact, that storm drains are only tubes meant to rapidly convey rainfall to a nearby lake, river, or bay, without significant treatment to remove the pollutants that maybe present.

Rain falling in urban areas becomes contaminated by scavenging pollutants such as Polynuclear Aromatic Hydrocarbons (PAHs) even before reaching the ground (Tsai et al, 1991). The runoff is further contaminated by passing through fields or lawns that contain fertilizers, pesticides, and decaying organic matter. Urban areas are also significant sources of additional pollutants including construction site suspended solids, transportation-derived metals, particulates, oils and previously deposited aerial fallout. Even hazardous substances, which may be present at outdoor storage and manufacturing facilities, find their way into storm drain water. While urban runoff, groundwater infiltration, and National Pollutant Discharge Elimination

System (NPDES) permitted facilities, produce a steady stream of contaminated water, spills and illegal releases of hazardous chemicals continue to regularly occur with potentially disastrous implications (SCAG 1988). Additional sources of urban storm drain pollutants include illegal sewer and floor drain connections, sanitary sewer overflows, swimming pool drainage, lawn over-watering, human and pet fecal matter, vehicular and structural washdown, leaking cooling systems, and automotive repair shop off-site drainage.

A second aspect of the storm drain pollution problem, is attempting to economically deal with the volume of water that must be conveyed. In many regions of the United States, precipitation is evenly spaced throughout the year and undeveloped land is relatively affordable. In these areas, management practices, such as open spaces and park-like detention basins, can help to detain water on-site, provide additional area for infiltration, and reduce the stormwater pollutant loading (Davenport 1990). Unfortunately, in Southern California rainfall and runoff are observed on one or two dozen days each winter and the large percentage of impervious surface assures that a immense volume of water must be processed in an exceedingly short time. Furthermore, the high value of land in Southern California ensures that little open space remains for the installation of treatment or detention facilities, especially when usage is limited to few dozen days per year and the adjacent developed areas might become susceptible to periodic flooding.

The City of Santa Monica, California, located just west of Los Angeles, is an extreme example of a populated urban community with a resident population of 86,900 (1990 census), a significantly larger business population, and a surface area of only 8.147 square miles. Santa Monica was founded in 1875 and is mainly zoned for residential and commercial use, with confined industrial areas. The municipal infrastructure is well developed and most of the storm drain system was constructed prior to 1960. Since then, numerous multistory buildings, parking lots, roofs, roadways and other impervious surfaces have been added, covering an estimated 70% of the total municipal surface area and exceeding the drainage capacity of the system. Eight, of the fourteen storm drains in the City, discharge onto municipal beaches, while the remaining six drains pass through adjacent portions of Los Angeles before entering Santa Monica Bay. Although originally constructed to seasonally empty into the ocean, accretion of beach sand has resulted in some drains discharging directly onto public beaches where trash and other debris accumulates and ponding occurs. Several of these areas have been identified as major sources of biological and chemical contamination during both wet (rainy) and dry-weather conditions. While incidents of chemical contamination are few, the drainage water often contains high levels of indicator organisms that pollute the adjacent marine environment and are associated with human and animal fecal input (PLC 1988).

The Kenter Canyon, Pico Boulevard, and Santa Monica Freeway or Caltrans (California Department of Transportation) storm drains all terminate under Pico

Boulevard at The Promenade, entering a concrete lined channel before spilling onto the beach. The latter two are completely within the City of Santa Monica and join approximately one kilometer upstream of the beach, but have significantly different source characteristics and should be considered independently. The Kenter Canyon Storm drain enters Santa Monica along its northeast boundary, after having drained canyon, suburban and commercial areas of Los Angeles City. Two thirds of the total Kenter Canyon drainage area of 6.28 square miles is in the City of Los Angeles. Approximately one third of the total City of Santa Monica area is discharged at the combined three drain outlet. While the California Department of Transportation is responsible for the Santa Monica Freeway drain, the Pico and Kenter Canyon drains are maintained and operated by the Los Angeles County and City Departments of Public Works and City of Santa Monica Department of General Services.

The dry and wet weather flow, from the Pico-Kenter Canyon storm drain outfall, primarily consists of water conveyed by the Kenter Canyon storm drain. During dry weather, the Pico and Caltrans drains usually contain little water and the flow is generally less than a few thousand gallons per day. In contrast, the Kenter Canyon Storm drain has a dry-weather flow estimated at between one hundred thousand and three million gallons per day (SCCWRP 1973), most of which enters Santa Monica from the upper drainage basin. Low flows during this study were normally estimated at between one and three hundred thousand gallons per day (70-210 GPM). During a significant storm, this stream swells to an estimated hundred million gallons per day, fills the enclosed 10 by 12 foot Kenter Canyon storm drain, and lifts manhole covers.

For decades, the effluent from the mouth of the Kenter Canyon storm drain has formed large ponds on the beach, where young children would play away from the surf, and wildlife would find a source of freshwater. Over a dozen years ago, the outfall became suspect as a source of carcinogens which may have affected the health of lifeguards stationed near it. Since then, the Pico-Kenter has become one of the most heavily investigated storm drains in the country. The beach adjacent to it is now posted to warm bathers to avoid the area and storm drain water in general.

While the evidence of chronic chemical contamination is mixed, it appears that few recognized hazardous contaminants are present in significant concentrations (PCR 1988). Among those that are present, most are found in low concentrations and at levels that are comparable to other storm drains (SCAG 1988b). Assuming a five fold initial dilution, and comparing the mean values reported in State of the Bay report (SCAG 1988b) with the 1990 California Ocean Plan, several pesticides exceeded the water quality objectives given in the Plan. In particular, the DDT, DDE, and DDD group was several hundred times above the 1990 objectives. The endrin and endosulfan (including heptachlor) groups also exceeded objectives by 6 to 20 times. Copper was determined to be at about six times the water quality objectives while lead, chromium, zinc, and nickel were all slightly above their respective goals.

Significant spills of hydrocarbons, probably vehicular fuels, were observed in the outfall in September 1980, December 1985, and September 1986, and caused beach closures and the posting of warning signs (PCR 1988).

The problem of microbial contamination in the Pico-Kenter effluent is more clear than that of chemical contamination and has warranted significant attention from various agencies and advocacy groups. Biological standards are based on the enumeration of benign indicators, such as enterococcus and total and fecal coliform bacteria, because of the difficulty in estimating the number of human pathogenic (disease causing) organisms, such as enteric viruses. Unfortunately, as was extensively reviewed in the State of the Bay report (1988b), all of the standard indicators have sources other than human fecal material. The California Ocean Plan standards for total coliform organisms can be summarized as 1,000 bacteria per 100 ml of water, yet this group of microbes are common constituents of soil and vegetation and are prevalent in the urban runoff found in storm drains. The criterion for fecal coliform and enterococcus bacteria are 200 and 24 organisms per 100 ml. respectively. Both of these groups are prevalent in the intestinal tract of endotherms and would be anticipated in the runoff from communities with large pet populations or where birds bathe and roost, as is observed in the beach ponds below the Pico-Kenter outfall. Not surprisingly, the Pico-Kenter outfall, even with ocean dilution, frequently exceeds the standards for these indicator bacteria. However, due to the prevalence of non-human sources, the presence of these indicator bacteria in storm drain effluent has been minimalized and not used as evidence of a public health threat for exposure to pathogenic organisms. The recent detection of human enteric virus in the mouth of the Kenter Canyon storm drain (Gold et al. 1990), indicates that a defined public health threat may indeed exist and that the storm drain low-flow may warrant treatment to control human pathogenic organisms.

In response to concerns for the public and environmental health, the City of Santa Monica has participated on commissions and undertaken studies and projects, with the goal of reducing exposure to contaminated storm drain effluents. The Cities of Santa Monica and Los Angeles have joined with Los Angeles County in directing the combined Pico-Kenter dry-weather effluent through a by-pass pipe, 600 feet into the ocean in an effort to reduce the exposure of terrestrial organisms to contaminants. As part of this project, the Consortium has also installed hydrocarbon sensors that warn authorities in case of a significant fuel spills. The Cities have begun construction of a temporary diversion to pump the dry-weather flow into a sanitary sewer for eventual treatment at the Hyperion Sewage Treatment Facility. The City of Santa Monica also commissioned a treatment orientated preliminary assessment for the Pico, Caltrans, and Kenter Canyon Storm Drains which concluded that chlorination could be successfully used to disinfect the dry weather flow (JMM 1987). However, chlorine is a hazardous chemical with significant storage and transportation risks. In addition, the chlorine gas disinfection process, requires long contact times, forms many carcinogenic disinfection by-products, and ocean release of the chlorinated water would require a dechlorination step. Furthermore, the proposed facility would have been placed on a heavily used public beach, adjacent to resort hotels, and would probably have encountered significant resistance from local environmental and neighborhood advocacy groups.

Recently, ozone has become renowned in the drinking water industry as an alternative to chlorine, that rapidly disinfects water while forming few halogenated, and toxicologically potent, by-products (Tate 1991). Unlike chlorine, ozone is generated from air or oxygen at the time of use and does not require the storage or transport of hazardous chemicals. During an emergency, electrical generation of ozone terminates and the ozone rapidly reverts back to oxygen. The process of ozonating water is easily monitored using off gas and effluent monitors, so that the dosage can be instantaneously increased to meet the challenge of contaminated material entering the treatment stream. The dissolved ozone residual in the plant effluent, rapidly degrades and introduces little environmental hazard. Off-gas ozone is rapidly returned to oxygen by passage through a heated metal catalyst.

The City of Santa Monica, with the assistance of the Santa Monica Bay Restoration Project (SMBRP), the United States Environmental Protection Agency (EPA), and the University of California Laboratory of Biomedical and Environmental Sciences (LBES), recently completed an evaluation of an ozonation pilot plant for the treatment of dry-weather storm drain flows. The major goal of this study was to determine if ozone could be used to disinfect the water that typically flows from the Pico-Kenter Canyon storm drain. Unlike drinking water, the storm drain effluent is high in suspended solids and organic carbon, factors that might be expected to significantly reduce the efficacy of ozone disinfection. Secondarily, this study was also intended to develop a comprehensive and long-term analysis of chemical constituents in both the influent and treated water and their variability. This information could then be used to determine if construction of a full scale facility was warranted, which pollutants would be amenable to treatment at the proposed plant, and what process train the facility should incorporate.

METHODS

A. Location, Design and Operation of the Ozone Pilot Plant

This project was facilitated, by the placement of the Santa Monica Municipal Bus Yard over the Kenter Canyon storm drain near the corner of 5th Street and Olympic Boulevard in Santa Monica. This facility provided security, utilities, and supportive staff that assisted in maintenance activities. Operation of the pilot plant began in November 1989 and continued through December of 1990, but was intermittent during June, July, and August due to organic contamination that was eventually traced to the rupture of a sanitary sewer into an upstream catch basin. Sampling was occasionally suspended due to plant modifications or monitoring device failures. Generally three sample runs were conducted during each day of operation. Each run consisted of an influent/effluent sample pair with the treated sample collected after a time delay sufficient to allow the influent sample plug to reach the effluent port. This time delay was equivalent to the contactor tower volume (12 gallons) divided by the flow rate (1- 6 GPM) which yielded delays of 2 to 12 minutes. Feed gas flow ranged from 2-18 Standard Cubic Feet per hour (SCFH) with an ozone concentrations of up to 4.5%. Effluent dissolved ozone residuals of up to 10 mg/L (PPM) were observed. Although dosages of up to 40 mg/L (PPM) ozone were delivered, operation was generally in the 5-20 PPM range.

In general, all materials exposed to ozone were constructed of either stainless steel, polyvinyl chloride (PVC), borosilicate glass, or teflon. Swagelock® fittings and valves were utilized for lines smaller than ½ inch, while PVC valves were used on the water lines. Most of the samples were collected with the flow design shown in figure 1 and the schematic plant configuration shown in figure 2. The daily operating schedule commenced with provision of compressed gas and warming up of the ozone generation and monitoring systems. Compressed air was prepared using a Dayton Speedaire® oil-less air compressor (model 3Z852) equipped with aftercooler, air filter, and relief valve. Later in the study, standard cylinders of industrial grade compressed oxygen were obtained from the Liquid Air Corporation. The use of compressed oxygen, rather than air, doubled the ozone production in the influent gas and effectively doubled the applied dose, but does not significantly influence the disinfection process or basic treatment parameters. For all but the largest ozone facilities, generation from air is more economical than first separating oxygen from air. The submersible pump (Goulds #3885) was secured in a large plastic housing, with 1.5 mm aluminum mesh screen, lowered into the storm drain, upstream of a temporary weir, and the screened water pumped to the surface and into a 110 gallon polyethylene holding tank. Once the level in the tank reached the return overflow, water was pumped through an Ace-50 swimming pool-type pump through an RMC-145 flow meter (1-9 GPM) and into the top of the contactor tower.

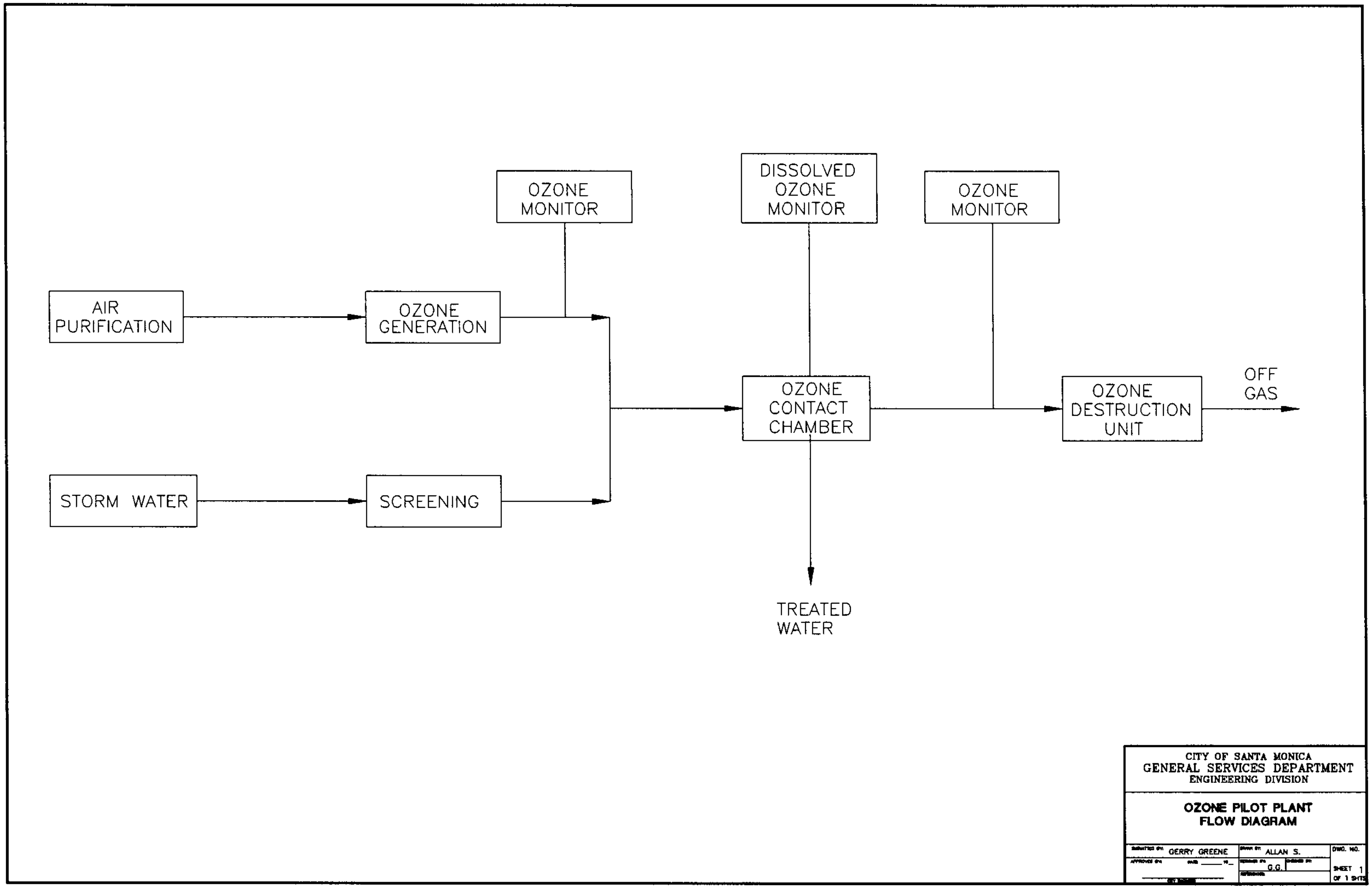


Figure 1. Ozone Pilot Plant Process Flow Diagram.

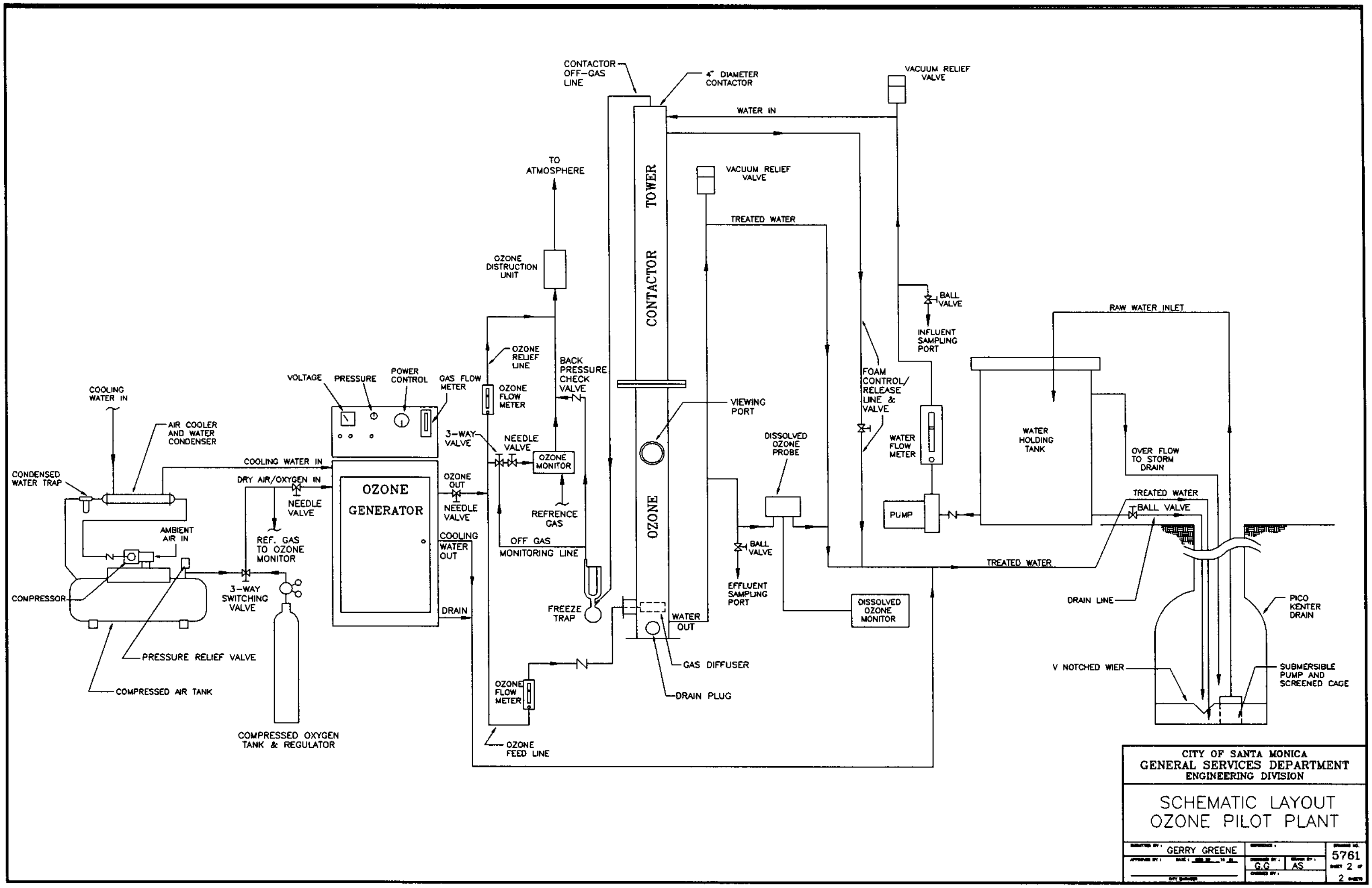


Figure 2. Ozone Pilot Plant Schematic Diagram.

The contactor tower, ozone generator, and flow meters were generously supplied by the Hankin Ozone Company of Scarborough, Canada and San Francisco, California. The stainless steel contactor tower was composed of two section with a 10 cm inside diameter and total height of 6 meters. The gas flow meters were rotameter type and calibrated to deliver the specified flow (1-18 scfh) with the 6 meter water head pressure. The ozone generator was a Hankin dual Ozotec® lab unit with cabinet. The bulk of the feed-gas leaving the ozone generator was passed through the flow meter and into the bottom of the contactor tower through a cylindrical ceramic diffuser (bubbler) to increase transfer efficiency. A side stream from the generator could be passed through a 3-way valve to a PCI HC® ozone gas monitor, which determines ozone concentration on the basis of UV light absorbance. After the flows of water and gas were initiated, the process was monitored and allowed to stabilize for at least 15 minutes prior to each sample collection. Samples were taken as influent/effluent pairs, with an appropriate delay for flow through the treatment train. The delay was determined based on the assumption that the influent water would travel through the tower as a plug. An Orbisphere dissolved ozone probe was installed adjacent to the effluent sampling port and operated based on the manufacturer's instructions. During each sampling period, the dissolved ozone residual was recorded twice. Following treatment, the pilot plant effluent was returned to the storm drain downstream of the weir.

The tower off-gas was passed through a water vapor trap, a check valve, and then the remaining ozone was catalytically reverted to oxygen by passage through a Carulite® 200 (Carus Corp.) manganese dioxide ozone kill unit. The water vapor trap was a Dewar type condenser (Ace glass # 5964-14), with Claisen adapter (Ace Glass # 5055-10), and 50 ml boiling flask. It was utilized, as described below, to prevent water vapor from passing into the ozone gas monitor. Prior to pilot plant installation, the vapor trap was tested in a by-pass loop between the generator and gas monitor to insure that the device would not directly influence ozone concentration. No difference in ozone gas concentration was observed after passage through the trap. During normal operation, the trap condenser was filled with a dry-ice/butanol mixture and the contactor tower off-gas passed in through the adapter side arm. While water, and sloughed off ice crystals, collected in the boiling flask, the off-gas would pass through the condenser where the water vapor would freeze out. Between the vapor trap and back pressure/check valve, a "T" led to the three-way valve and into the ozone gas monitor. During the sample run time delay, the 3-way valve was switched between influent and off-gas lines, the flow rate adjusted, and the ozone concentrations recorded. Normally, both ozone feed- and off-gas concentrations were measured twice per sample. The difference between these two values was used to calculate the absorbed or consumed ozone dose. If foam was noted in the vapor trap, holding tank or influent sampling port, sampling was generally suspended and the tower either drained or the top of the tower "skimmed" via a foam release line and valve. When foam was present, the tower was observed to pressurize and water would be forced out, shortening the contact time and interfering with dosage estimation.

At the conclusion of each sampling day, the ozone generator was turned off, the ozone off-gas concentration allowed to fall to background, and the tower and holding tanks drained. The submersible pump and screen were then removed from the drain and the screen cleaned. The ozone generator, flow meters, and monitors were maintained as per manufacturers recommendations. On several occasions the tower was not promptly drained and the check valves failed. The ozone unit would then require extensively cleaning, after which it would take several days for the full ozone generating potential to return. This is probably associated with water vapor in the generator dielectric and illustrates the need for dry feed gas. The catalyst in the off-gas kill unit was also noted to "combust" organics when, during an incidental test of a sensor, water contaminated with gasoline (50-100 PPM) passed through the contactor tower and began reacting in, and melting, the plexiglass kill unit. During spiking tests, when the influent water was artificially contaminated, the effluent was collected in barrels and subsequently passed through a carbon filter (organics spiking tests), or chlorinated and dechlorinated (virus spikes), prior to release back to the drain. Following the summer 1990 sewage shut down, the ozone transfer efficiently was observed to be greatly reduced and the diffuser was eventually found to be contaminated with organic matter. The diffuser was subsequently cleaned in concentrated sulfuric acid and found to operate more efficiently then during earlier parts of the project.

B. Sampling Design

The sampling design basically followed that given in the Project Quality Assurance Plan which was approved by Kent Kitchingman of the EPA in November of 1989. Most of the deviations from the proposed plan were related to the additional analyses that were undertaken at the request of the project review board. Some changes were the result of concerns with the external certified laboratory analyses and are more fully elaborated in appendix A (Quality Control and Assurance Report). The basic goal of the analytical design was to identify those water quality and disinfection parameters which most substantially influenced the treatment process. In particular, we were concerned with those parameters which could be effectively monitored and controlled in a full-scale automated facility. The secondary goal was to identify known hazardous chemicals, in both the plant influent and effluent, and determine if they would constrain future operations or induce significant public health or environmental harm.

Because the storm drain environment can be subjected to relatively small plugs of contaminants moving through the system, this study analyzed pre- and post-ozonation sample pairs, with an appropriate contact-time delay between them. The analyses were split into physical, biological, and chemical groupings. The physical analyses were performed at the pilot plant site and at the University of California Los Angeles (UCLA) Laboratory of Biomedical and Environmental Sciences (LBES).

Biological analyses were performed at the site and at a certified contract laboratory. Chemical analyses were undertaken at UCLA and at the certified laboratory. While the intent of using both research and contract labs was to insure the quality of the results from the University labs, several difficulties arose in interpreting the contract laboratory results, which are elaborated in appendix A. Since this study was primarily concerned with disinfection, the staff utilized the minimal media Most Probable Number (MPN) method to analyze each of the 438 sample pairs for the number of total and fecal coliform organisms. The certified lab performed 48 duplicate coliform analyses and all of the Enterococcus analyses.

While the analytical chemical methods were chosen to provide a thorough screen of emissions into the Santa Monica Bay, the individual analyses were selected for specific secondary purposes. The concentrations of the individual metal analytes, including sodium, calcium, and magnesium, were critical to evaluating the potential usefulness of the water for reclamation. The formation of hexavalent chromium during ozone treatment was a concern of the SMBRP steering committee. Total Organic Carbon (TOC) can be correlated to bacterial counts and may be a indicator of sanitary contamination. Chlorinated pesticides, like DDT, have previously been detected in this drain and were a likely source of health or environmental risk that could be compared to previously published data. Volatile organic analysis was used to screen for gasoline components and previously reported chlorinated solvents, but also estimated the concentration of short chain aldehydes, a known ozonation by-product. The semi-volatile, or base-neutral acid extractable (method 625), analysis was included to screen for heavier hydrocarbons, such as polynuclear aromatic hydrocarbons (PAHs), and other significant, but non-traditional contaminants.

C. Analytical Methods

The analytical methods followed those given in the Project Quality Assurance (QA) Plan which was approved by Kent Kitchingman of the EPA and the other project officers in November of 1989. Following the validation described in appendix A, the duplicate sample spiking concentrations were reduced in several of the methods, in order to facilitate interpretation of the analytical results at the low contaminant levels observed during this study.

The analyses can be split into process, physical, chemical and biological groups. Among the process analyses, were the various flowmeters and ozone monitors previously described. Rotameter-type flowmeters were checked daily for accumulations of oil or debris that would inhibit free travel of the metering ball, and cleaned as needed. Water and gas flow rates were always verified immediately prior to, during, and following each sampling run. The gas and water ozone monitors were both solid state and self calibrating. The monitors were maintained as recommended by their manufacturers and repaired when indicated by the monitor or by questionable performance. The gas monitor generally failed catastrophically, while the dissolved ozone monitor failed both catastrophically and occasionally by degraded performance over the matter of a few hours. During occasions of degraded performance, the collected samples were discarded and repeated after repairs were completed.

The physical analyses included temperature, pH, conductance, turbidity, settleable solids, suspended solids, dissolved solids and total solids. The measurement of conductance was initiated in mid-January, 1990, using an ICM model 71250 portable, temperature correcting, conductivity meter and the analysis conformed to EPA Method 120.1 (EPA 1983). Fresh calibration standards were prepared monthly and the unit calibrated before each analysis. The measurement was taken within 15 minutes of sample collection, from the one liter samples used for pH, temperature, settleable solids and turbidity analyses, which were collected in polycarbonate graduated cylinders. The measurement of pH was initiated using a pocket meter, but by January, analyses were being made using a portable ICM model 41250 unit. Commercial prepared temperature corrected buffer solutions were used to calibrate the unit before each sample. Measurement was made within 15 minutes of sample collection, from the 1 liter sample, and conformed with EPA method 150.1 (EPA 1983). Temperature was measured using a standard glass laboratory thermometer that was checked weekly against a precision thermometer. Measurement was made within 15 minutes of sample collection from the 1 liter sample and conformed to EPA method 170.1 (EPA 1983), except that the thermometer was not mercury filled. This deviation did not appear to influence the results.

Turbidity measurements began in early January 1990 and were made using a Monitek model 21PE Nephelometer. The unit was calibrated between samples and the initial measurement was made within 15 minutes of sample collection. Influent samples exceeding 100 NTU were diluted until the desired working range was reached. The corresponding effluent sample was then identically diluted. Although method 180.1 was followed, two notable analytical difficulties arose. First the 1-10 and 10-100 NTU scales did not completely overlap i.e. a sample could read greater than 10 units on the lower scale, but less than 10 on the higher range. Careful analysis of standards indicated that both scales were in error by about 10% on a 10 NTU sample, with the error decreasing to 0% for values below 8 and above 15 NTU. Analyses that were observed to be within this range, were estimated from the readings on one or the other scale and the paired sample measured on the same scale. The second problem related to effluent samples which were observed to form gas bubbles on the wall of the turbidity cuvette. After "bumping" the bubbles free, the turbidity was found to be lower. It appeared that micro bubbles of dissolved ozone/oxygen aggregated or came out of solution during the delay between repeated sample analysis. Unfortunately, it is unknown whether the reduction in turbidity is due to aggregation of micro bubbles or settling of suspended material. Both of these difficulties are not expected to effect a full scale treatment facility and only trivially corrupt the results of this analysis.

After the completion of the above physical test, the remainder of the 1 liter samples were used to determine the quantity of settleable solids in poly carbonate Immhoff cones as per EPA method 160.5. It should be noted that occasionally material would settle on the walls of the cone, but not fall to the bottom. Usually a rapid rotation of the cone would cause much of the material to dislodge and fall downward for inclusion in the measurement.

The analysis for total solids (total residue, Method 160.3), dissolved solids (filterable residue, method 160.1) and suspended solids (non-filterable residue, method 160.2) followed basic EPA methodology except that the volume in the latter analysis varied between 50-1000 ml based on passage through the filter, rather than the anticipated residue weight. Residue measurements were made at LBES using a 1.25 liter sample collected in a clear Wheaton media bottle. After collection, the bottle was chilled on blue ice and transported to LBES for processing. Residue samples were generally processed within 6 hours of collection, although approximately 10% of the samples required up to 12 hours for completion, due to scheduling conflicts. Samples held for more than 4 hours were refrigerated until analysis was undertaken. All samples were allowed to dry overnight in a standard laboratory oven. Poor balance performance during the first 3 weeks led to unreliable results and required that the balance be repaired. Enumerations during this period are accurate to only about 10 mg. rather than the 1 mg observed during the bulk of the study.

The analytical chemistry methodologies employed during this study were Inductively Coupled Plasma Atomic Emission Spectrometric (ICP-AES) analysis of metals (EPA method 200.7), hexavalent chromium (EPA method 218.5 modified for ICP-AES analysis), total organic carbon (EPA method 415.2), organochlorine pesticides (EPA method 608), purgeable or volatile organics (modified from EPA method 624) and extractable or semi-volatile organics (modified from EPA method 625). The first three methods are taken from Methods for Chemical Analysis of Water and Wastewater (EPA-600/4-79-020 rev. March 1983), while the latter three are from Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (EPA-600/4-82-057). As anticipated in our QA plan, several changes were undertaken to better utilize our instruments in the low analyte concentration ranges which were observed during this study. These changes were minor and primarily served to increase and evaluate our sensitivity in the observed matrix.

The analysis for metals was conducted by Mr. Leon McAnulty, a senior staff technician at the Laboratory of Biomedical and Environmental Sciences of UCLA, using a research grade simultaneous Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES), with a 1.5 meter focal length. Samples collected during 1989 were analyzed with a meinhard nebulizer, while samples collected after that time were analyzed using the more sensitive ultrasonic nebulizer. Since acid digestions using ultra-high purity acids, new acid washed fleakers, and milli-q water, resulted in unacceptable levels of metal contamination, digestions were undertaken only on those samples that had greater than 100 mg/L of suspended solids. The detection limits reported in appendix B (Data Summary and Comparison to Relevant Standards) were determined using the method of the International Union of Pure and Applied Chemistry.

The primary change in the hexavalent chromium method (218.5) was analysis by the ICP-AES, rather than graphite AA, in order to utilize the sensitive ultrasonic nebulizer. Sample preparation was undertaken by project staff. During early March, the author became aware that hexavalent chromium blanks were contaminated at around 7 PPB. While this was above the method detection limit of 5 PPB, it was below the Ocean Plan Water Quality Objective (with 5:1 initial dilution) of about 10 PPB and did not warrant the significant time and financial expenditures required to find and replace the contaminant source. Reported values are not adjusted.

Because of equipment scheduling conflicts the analysis for Total Organic Carbon (method 218.5) could not begin until late December. Samples collected prior to this time were acidified and refrigerated, then analyzed, out of holding time compliance. The carbon concentrations in these non-compliance samples were typical of values seen during most of the study and were included in the data base. TOC analyses were undertaken by project staff under the supervision of the QA officer. Some samples containing high dissolved solids (salt) concentrations gave erroneous results due to chloride interferences and were excluded from the data base.

The delays encountered in performing organochlorine pesticides analyses was one of the more significant frustrations of the project. Fortunately, the purchase of a service agreement ensured that it was not one of the more costly aspects. Upon initiating the laboratory phase of this project, the Varian 3500 gas chromatograph with dual electron capture detectors was found to be severely malfunctioning. After a dozen service visits, the unit was returned to Varian and completely refurbished. It was only after a second certified lab unit failure, that the detector insulation was found to degrade over time. Following the return and evaluation of the GC in mid-April, pesticide analyses were begun, using both DB-5 and DB-1701 30 meter capillary columns hooked in parallel through a chromafit zero dead volume Y splitter, and integrated on a Spectrophysics 4270. Analyses was made using 4,4'-dibromooctafluorobiphenyl (DBOFBP) as an internal standard and hexabromobenzene as a surrogate. The choice of hexabromobenzene was made due to the unavailability of dibutyl-chlorendate, but it was found to be a poor substitute. The compound precipitated out of the spiking solution during freezer storage, then was slow to re-enter solution when returned to room temperature. This information became available after many analyses were completed and the bulk of the pesticide samples had been extracted. Fortunately, the recoveries from spiked samples indicate that extraction efficiencies were generally good. Sample extraction from the complex and organically rich matrix, was accomplished through the use of centrifuging and glass wool filtering. Concentration was performed using a combination of hot water baths, tube and block heaters. After analyses had begun, it was determined that alumina (neutral super III) clean-up was routinely required. Even with this step, most samples contained a significant number of false positives that would appear on one or the other, but not both, chromatograms. As discussed in appendix A, sample spikes were prepared using surplus EPA QA samples diluted to about the CLP detection limit. The extracted samples were stored at about -20°C until analysis, at which time they received alumina clean-up and were reconstituted to a volume of 1 ml. Due to the delays in starting this analysis, one fourth of the total number of pesticide samples were analyzed out of holding time compliance.

The analysis of volatile compounds was performed at the Institute of Geophysics and Planetary Physics under the direction of Mr. Edward Ruth, a senior staff technician with over 4 years experience with the GC/MS and an extensive analytical chemistry background. The analysis was conducted using a Tekmar purge and trap unit with cryofocusing interface to a Finnigan gas chromatograph with DB-624 capillary column and mass spectrometer. The analysis was a hybrid of the 624 wastewater and 524 drinking water methods, using a 25 ml water volume to increase sensitivity. Six hazardous substance list compounds were also simultaneously analyzed and the results are included in the data summary appendix. The surrogate spiking compound, 4-Bromofluoro-benzene, was utilized during the analysis and the priority pollutants quantified by addition of three internal standards to the water sample.

The extraction of semi-volatile (method 625) compounds was performed at LBES by the QA officer. The only substantial change in methodology, was the combining of acid and base neutral extracts prior to concentration and analysis as a single GC/MS extract. The results given in the QA supplement (appendix A) demonstrate the validity of this modification. Extraction was conducted in groups of eight: 3 sample pairs, a travel blank and a spiked duplicate sample. As with the pesticide extraction, centrifugation and filtering was required to separate the aqueous/organic emulsion. A third "humic" layer formed between the two normal layers and was returned to the separatory funnel between extractions. Spikes were at either 20 or 40 PPB rather than the 100 PPB used in the method description. The analysis of extractable compounds was performed at the Institute of Geophysics and Planetary Physics under the direction of Mr. Edward Ruth using a Finnigan gas chromatograph with a DB-5 capillary column and mass spectrometer detector. Each sample contained 6 extraction surrogates and 6 internal standards.

During the brief spiking study, organic test compounds of interest were prepared at various concentrations, in 50 ml of acetone, then mixed into the holding tank just prior to beginning the treatment process. Methanol was originally used as the diluting solvent, but was found to have a significant ozone demand as a free radical scavenger. After the treatment process had run for approximately 10 minutes and was nearing equilibrium, normal influent and effluent samples pairs were taken for biological and chemical analyses. The effluent water was held in holding tanks and slowly pumped through granulated activated carbon (GAC) to remove the offending spiked compounds before being release back to the storm drain. The chemical analysis was performed using liquid-liquid micro-extraction and the pesticide method analytical instrumentation. To summarize the method, 30 ml of water was combined with 2 ml of hexane and vigorously (vortex) mixed for 1 minute. The organic layer was removed using fresh disposable pasteur pipettes and added to the 1 ml mark on an autosampler vial. The internal standard (DBOFBP) and a few anhydrous sodium sulfate crystals (to prevent water from contaminating the GC) were added to the extract, which was then analyzed. Since funding for the spiking study was not provided for in the agreement, it was not included or cleared in the QA/QC plan, but was described to the project review board and SMBRP technical advisory committee. Due to the carrier solvent, TOC analyses are only available for the pre-spike influent waters.

Information regarding the methodology for the mutagenicity extraction and assay can be obtained from the project QA officer or Dr. John Froines of the UCLA School of Public Health. The basic method called for resin extraction of influent and effluent waters, followed by extraction and concentration in hexane and acetone. The extracts were serially diluted and plated, following the EPA Interim Procedures for Conducting the Ames Mutagenicity Test (EPA 1983). Extractions and mutagenicity analyses were undertaken by staff under the direction of Dr. John Froines.

The bacteriologic analyses were undertaken by project staff working at the pilot plant site and by the certified laboratory. The methodology proposed in appendix B of the pre-project Quality Assurance plan was followed with minor adjustments for correct bracketing of the bacteria numbers and collection of the effluent samples in recently emptied dilution bottles. All of the 438 samples collected during this study were analyzed by project staff for the most probable number (MPN) of total and fecal coliform organisms in both the influent and effluent water. The analysis was undertaken using the Minimal Media Ortho-nitrophenyl-beta-D-galactopyranoside 4-Methyl Umbelliferyl-beta-D-Glucuronide method, also referred to by the specific generic name of Minimal Media O-MUG or MMO-MUG as in the EPA final ruling on its use (EPA, 1989). The supplier was Environetics (formerly Access Analytical) which markets the product under the Colilert® brand name. Briefly, a potentially contaminated water sample, is mixed, in a test tube with a sterile powder consisting of growth media, the two sugar dye complexes listed above, and antibiotics to inhibit the growth of competing organisms. The tube is then sealed, mixed and incubated at 36°C for 24 hours. Coliform organisms produce the enzyme beta-galactosidase, which cleaves the ONPG sugar dye complex, causing the culture to become yellow. Similarly, Escherichia coli, the primary fecal coliform, produces the enzyme beta-glucuronidase, which cleaves MUG releasing a greenish fluorescent dye that is clearly visible under ultraviolet light.

Using the same statistical methods developed for the Multiple Tube

Fermentation (MTF) method, it is them possible to take the results from the MMO-MUG analysis and estimate the number of total and fecal coliform organisms per volume of the original sample. The certified laboratory initially used the Membrane Filtration (MF) method 9222A-E (APHA 1989) for total and fecal coliform analyses, but shifted to the MMO-MUG method mid-way through the project. The enterococcus analyses were only undertaken by the certified laboratory which always used the membrane filtration standard method 9230 A,C (APHA 1989). While the results were decipherable, the project QA officer found that the bacterial analyses from the certified laboratory were frequently erroneous and that their results required some interpretation. This difficulty is further elaborated in appendix A.

The virus spiking study was conducted by Charles McGee and staff of the Sanitation Districts of Los Angeles County on June 5, 1990, using a modification of Standard Method 9510-B (APHA 1989). Attenuated, vaccine strain type 1, poliovirus was added to about 85 gallons of water pumped from the storm drain into the surface holding tank. The tank was then mixed for about 5 minutes prior to being pumped into the treatment system. Influent samples were taken at the beginning and termination of each run. Effluent samples were collected after 20, 40, and 60 gallons of seeded water had been treated. The quantity of virus in the samples was determined at the County Sanitation Districts Laboratory. Samples were assayed on Buffalo Green Monkey Kidney cells using the plaque forming unit technique (EPA 1984).

RESULTS

The database is fully summarized and tabulated in appendix B, and includes comparisons to drinking water standards and California Ocean Plan standards and objectives. The following results are taken from the database, and appendix B, and consists of that information which the author believes is most pertinent to this report and future research and policy issues. Since the intent of the study was to provide research information, the reported values are often well below normal CLP (Contract Laboratory Program) reporting levels and the concentrations and detection limits should be judiciously noted. Both the arithmetic and geometric means were calculated, and if the geometric was less than about 75% of the arithmetic mean, the data was assumed to be skewed and the log normal distribution and geometric statistics are both reported. The observation of skewed data is common in the environmental field (APHA, 1989) and the use of the log normal distribution acts to decrease the overwhelming influence that a small number of high samples can have on the overall sample group. As an extreme example, the sanitary sewage spill resulted in water with an ozone demand that exceeded the generating capacity of the pilot plant and high bacterial counts were observed in the effluent. The overall project arithmetic mean and 90th percentile for the total coliform count in the disinfected water were 7,600 and 13,200 organisms per 100 ml. respectively, while the log-normal or geometric values were only 160 and 5,600. While the geometric mean is only 2.1% of the arithmetic mean, the high values converge in each distribution. Skewed data were prevalent in the metals, biological and "significantly" detected organics, but the distribution was normal among the remaining organics where "noise" below the detection limit predominated.

The mean absorbed, or effective, ozone dose was around 12.5 mg/L (PPM), although exposures of twice that concentration were occasionally utilized. Although higher values are often used to control specific problems such as color, taste, odor or chemical contamination, the drinking water industry typically disinfects with ozone concentrations below 5 mg/L (Tate, 1991). The geometric mean of the effluent water ozone residual was 0.31 mg/L, although many samples of greater than 2 mg/L were produced. Dissolved ozone rapidly degrades and residuals will drop within a few minutes of treatment. Since ozone is not used to provide distribution system disinfection, it is not closely monitored in the water industry.

Among the physical parameters, the ozone treatment appears to have caused an increase in temperature and decrease in pH. The former result was due to the compression of air during the first part of the study, and was not observed after switching to bottled oxygen. The maximal temperature increase was about 1.5°C and should not be sufficient to constrain the release of the effluent. The mean pH was normally reduced from 8.1 to 7.8 and the value of well ozonated effluent water was generally a half pH unit below that of the influent. Only a few of the influent samples exceeded the Ocean Plan Water Quality Objective of 6.0-9.0 pH units and none of the effluent samples were in violation.

Ozonation had little effect on solids or conductance which are primarily inorganic characteristics. The geometric mean of both influent and effluent dissolved solids (690 mg/L) and conductance (1070 μmho/cm) were about 80% of the arithmetic mean and the data approximated a normal distribution. The geometric mean of suspended (22 mg/L) and settleable (<0.1 ml/L) solids were both significantly below the Ocean Plan Water Quality Objectives and about 20% of the arithmetic mean, indicating that the data were highly skewed. The data for suspended solids is plotted on a log scale in figure 3. The plots of both influent and effluent data are virtually identical, indicating that ozone had little influence on this parameter. The results are characterized by normally low values punctuated by brief periods of contamination, when values would rise above the 240 mg/L objective. At concentrations between 60 and 240 mg/L the Ocean Plan calls for a reduction in suspended solids to no more than 60 mg/L. At levels above 240 mg/L the source is required to remove 75% of the suspended material. The skewed distribution is primarily associated with brief upstream events (construction and sewer break) when values rose to levels 100 times greater than the Water Quality Objectives.

OZONE DISINFECTION OF URBAN STORM DRAIN DRY-WEATHER FLOWS

Suspended Solids Before and After Ozonation (Log mg/L versus Sample Number)

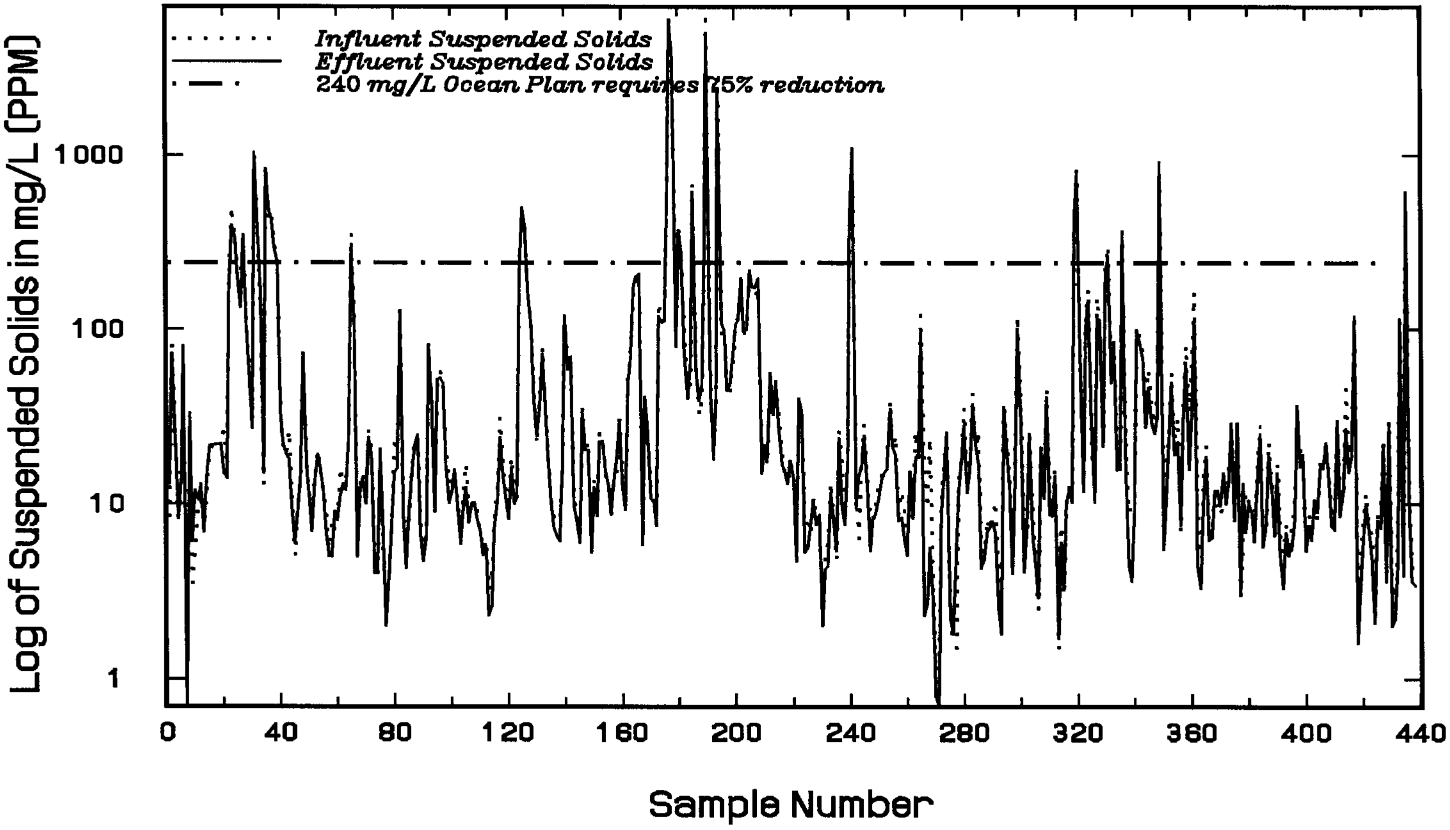


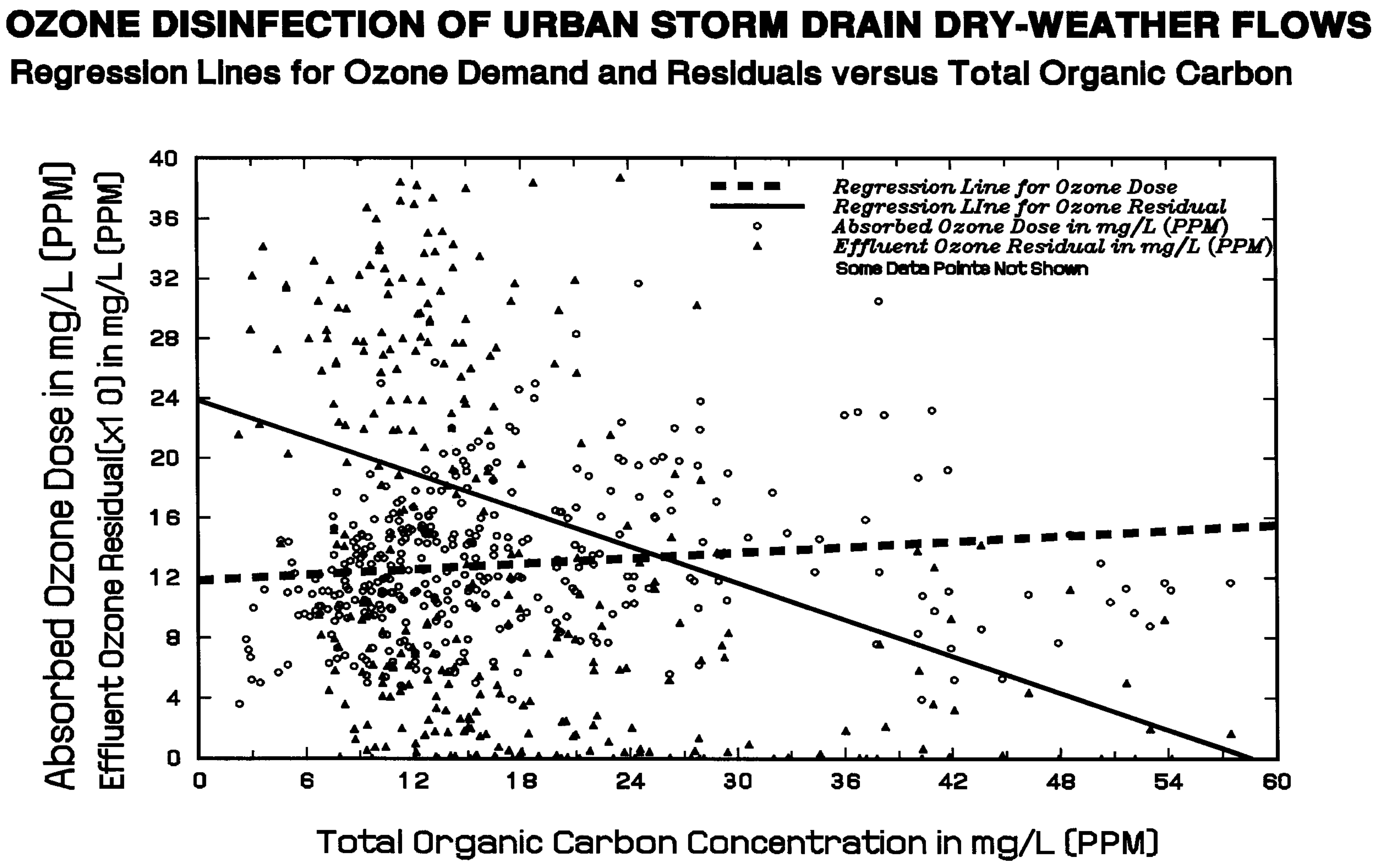
Figure 3. Suspended Solids Before and After Ozonation (Log mg/L Versus Sample Number).

The influence of ozone on turbidity was difficult to assess, since freshly treated water contained light scattering micro-bubbles, while settling could be expected to occur in seasoned samples. Paired samples checked 10-20 minutes after collection, generally showed a slight (10-20%) decrease in turbidity, but it would be speculative to suggest that ozone was the causative agent. Color was not monitored during the study, but it was visually evident that ozonation decreased the orange brown color associated with the dissolved humic and fulvic acids that result when water passes through decaying organic matter. In Myrtle Beach, South Carolina highly organic influent water containing 150-450 color units, is reduced to as little as 5 units using ozone doses of up to 10 mg/L (Ferguson, Gramith and McGuire, 1991).

Bacterial and viral analyses conclusively demonstrated that ozone was an extremely effective disinfectant of storm drain dry-weather flow, reducing microbial counts by a geometric mean of 3.4 log (99.96%). The remainder of the biologic results will be elucidated in the discussion section in conjunction with a discussion of the goals and conclusions of this study.

The Total Organic Carbon (TOC) content of the influent and effluent waters ranged from 2.2 mg/L, the day after a rain storm, to 124 mg/L when the sewer break was flowing maximally. While most values were between 7 and 30 mg/L, the mean TOC level was 19 mg/L and the distribution was only slightly skewed. While ozone can mineralize moderate levels of some organic compounds (Glaze and Kang 1988), the high TOC levels observed in this study assure that most was consumed in breaking cellular material and humic and fulvic matter into simpler organic units. As observed in this study, this would not result in a net TOC decrease. While the source and treatment variability assure that the data is widely scattered, the regression lines in figure 4 show that ozone demand increased, and observed ozone residuals decreased, with TOC concentration as would be intuitively expected.

There were significant differences between the arithmetic and geometric mean concentrations of most metals, especially the heavy or non "salt" metals. The "salt" metals, such as calcium, magnesium, sodium, phosphorus, silicon, and potassium, were generally in the mid to high PPM levels, normally distributed, and are not regulated. In contrast, the industrially valuable metals, such as aluminum, iron, manganese, chromium, lead, titanium and molybdenum were normally at low concentrations, which episodically rose orders of magnitude higher resulting in a skewed distribution. Many of these elements are toxic and closely regulated. The mean concentration of selenium, which is both an essential element and highly toxic, was below the drinking water standard of 10 PPB, but numerous samples above this level were observed. The highest observed value of 112 μg/L was well below the Instantaneous Maximum Ocean Plan Water Quality Objective, with 5:1 dilution, of 750. Barium, nickel, and silver were always well below standards.


OZONE DISINFECTION OF URBAN STORM DRAIN DRY-WEATHER FLOWS

Regression Lines for Ozone Demand and Residuals versus Total Organic Carbon

Figure 4. Regression Lines of Ozone Demand and Residual With TOC Concentrations.

The mean values of arsenic and cadmium were well under the Ocean Plan and drinking water standards, but occasionally samples exceeded one or both sets of limitations. Mean chromium, copper, lead and zinc concentrations exceeded Ocean Plan Water Quality Objectives and will be subject to further discussion in later sections of the report. While the results from the hexavalent chromium analyses are complicated by contamination in the reagents, both the arithmetic and geometric mean, before (31 and 12.9 μg/L respectively) and after (29 and 11.7 μg/L) ozonation, show that no increase in concentration was observed.

Only 4 organochlorine pesticides were detected among the 86 sample pairs analyzed. The high concentrations of both lindane (τ-HCH or hexachlorocyclohexane) and endosulfan I were about 30 ng/L (PPTr) or just slightly above our detection limit and about half of the Contract Laboratory Program detection/reporting limits. Both high values were an order of magnitude below Ocean Plan Water Quality Objectives. Heptachlor is a contaminant in chlordane, that has a double bond instead of a chlorine and hydroxyl group. It was only detected in the three samples having the largest chlordane concentrations and its detection is obviously incidental. The sample containing the highest chlordane concentration also included heptachlor at 2.5 times the 30 day Ocean Plan objective of 36 PPTr.

The detection of the pesticide chlordane, was the only significant finding among the pesticide analyses. This compound was used against termites and ants and was sprayed or injected adjacent to residential foundations. While now recognizedas a probable human carcinogen, it was commercially available early in the decade and manufactured until 1988. The pesticide was first detected on 12/14/89 and concentrations diminished during the next two weeks. Following an intense rain storm, no additional detections were observed. The arithmetic mean concentration in the plant influent was 133 ng/L and in the effluent 59 ng/L. The influent geometric mean was 0.86 ng/L, while the effluent value was 0.78 ng/L. The 30 day Ocean Plan objective for chlordane is 1.15 ng/L (PPTr). In the most contaminated sample, an ozone dose estimated at between 15-20 mg/L, with no residual, reduced the chlordane concentration from 5700 PPTr to about 1900 PPTr. While it is impossible to accurately estimate the efficiency of removal, ozone appeared to significantly reduce the concentration of chlordane in the plant effluent. This is especially evident at the highest chlordane concentrations when it made up a significant fraction of the TOC. As pesticide concentrations decreased toward the detection limit, and chlordane became a smaller fraction of the carbon pool, the removal efficiency appeared to drop. Although speculative and based on trace concentrations (given in ng/L or PPTr) and few data points, ozone may have also reduced heptachlor (90, 30, and 24 to 55, 24, and not detected) and Endosulfan I (30 to 24) concentrations, but probably not lindane (34, 26, and 21 to 28, 27, and <20), which is an extremely stable compound.

The analysis of volatile organic compounds showed that the maximum observed values were mostly more than an order of magnitude below either drinking or Ocean Plan standards, and the means were generally less than 1 μg/L (PPB). The primary exceptions to this assertion, is that one sample contained ortho xylene at levels in the 1,000 to 100 PPB range, which was sufficiently high to saturate the detector and invalidate the accuracy of the results. By the time the instrument was returned to service, the samples were of little value due to volatilization. The second exception was that butanone, 2-hexanone, and 4-methyl-2-pentanone were all observed in the ozonated effluent at less than 4 PPB as maximum observed values. Standards do not exist for these compounds. The drinking water ozonation process is known to form aldehydes, ketones, and carboxylic acids, generally in the low PPB to PPTr range (Glaze et al., 1989), and the detection of these compounds is to be expected. Among the other observed ozonation by-products were aliphatic aldehydes such as hexanal, heptanal, octanal etc., which appeared individually in the 10-50 PPB range. There are no water standards for aldehydes, but they are found in fermented beverages (wines).

With the exception of Polynuclear Aromatic Hydrocarbons (PAHs or PNAHs) and phthalates, the results from the base-neutral-acid extractable or semi-volatile analyses were inconsequential. The maximal value of most compounds was orders of magnitude below any Ocean Plan or drinking water standards and less than 1 μg/L (PPB). Benzyl alcohol, naphthalene, 2-methylnaphthalene and nitrobenzene had maximal values in the 1-5 PPB range, but means of less than 0.5 μg/L. Benzoic acid was detected at 13, but the mean value was less than 4 PPB. Cresols (methyl phenols) were detected in the spiking run, probably as contaminants of one of the spiked compounds. Phthalates were occasionally detected at levels over 100 PPB, but the mean values were generally in the low PPB levels. These plasticizers are ubiquitous in surface waters and laboratories, and with the exception of bis 2-ethylhexyl phthalate, the values observed in this study are not untypical of the results seen in laboratory extractions. In the case of bis 2-ethylhexyl phthalate, the high value of 122 μg/L was well above the 30 day Ocean Plan dilution objective of 17.5 PPB, but the arithmetic and geometric mean were only 12 and 7.1 PPB respectively. These values are noticeably above the Phase V proposed drinking water maximum contaminant level (MCL) of 4 μg/L.

The most significant finding among the extractable analyses, was the level of Polynuclear Aromatic Hydrocarbons or PAH's. The California Ocean Plan treats PAH's as a group and the objective is based on the sum of 13 PAHs that are commonly analyzed. The Ocean Plan 30 day average, with a 5:1 dilution, requires that the sum of these 13 PAHs remain below 0.044 μg/L. The sum of the maximum observed values, for each PAH analyte, was 17 PPB and was associated with samples containing significant amounts of suspended sediment. The arithmetic and geometric means of both the influent and effluent streams ranged from 1.9 to 1.3 μg/L (PPB) indicating that a normal distribution existed and that levels were about 35 times the

Ocean Plan Water Quality Objective. The sum of the mean travel blank PAH concentrations was equal to 0.22 PPB.

The results of the mutagenicity study are shown in table 1 and clearly reveal that the ozonation process did not form mutagens as measured by this extraction method and test. While ozone could conceivably be cleaving large mutagens into small volatile mutagens, that are lost during extraction, the results clearly show that mutagenicity was lower in the effluent for all Salmonella strains with, or without, S9 activation (a mammalian enzyme that makes some PAHs more mutagenic). This observation is in agreement with many of the papers cited in the review by Noot et al. (1989).

Table 1. Ames Assay Results for Ozonated Storm Drain Water.

Salmonella Strain	± S9	Influent Slope[1]	Effluent Slope[1]
TA 98	w/o S9	1498 ± 337	1165 ± 322
	w S9	2304 ± 496	2130 ± 397
TA 100	w/o S9	4655 ± 2718	3672 ± 1994
	w S9	8072 ± 2970	6153 ± 2958

[1] Slope of mean number of revertants per liter of sample water for five sample pairs with standard error.

Three sets of spiking runs were conducted during the latter phases of the project. In the first chemical study, available extractable compounds were added to the influent water then pre- and post-ozonation samples were analyzed using the standard GCMS method (625). The results for 2 sample runs are given in table 2 and clearly indicate that chemical remediation did occur when the contaminants were present in significant concentrations.

Table 2. Chemical Spiking Study 1, Values in μg/L (PPB).

Spiked Compound	MDL	Sample Pair 348		Sample Pair 349	
		Influent	Effluent	Influent	Effluent
2-Chloronaphthalene	.19	.69	<MDL	.42	.078
4-Methyl Phenol	.59	71.	.64	29.	<MDL
Naphthalene	.10	7.8	.103	10.6	.072
Phenol	.91	21.	.21	2.6	.31
Pyrene	.10	39.	2.1	40.	.79
1,2,4-Trimethylbenzene	NA	20.	.88	3.6	ND

In the second chemical study, 7 halogenated compounds were spiked into the treatment stream and samples taken before and after ozonation. The compounds were chosen as examples of a halogenated solvent (1,1,1-Trichloroethane), surrogate gasoline-like components (Benzyl Chloride or α-Chlorotoluene and 124-Trichlorobenzene), PAHs (9,10-Dibromoanthracene) and halogenated pesticides (Aldrin and Lindane). Calibration standards were prepared in milli-q water, then both standards and samples were extracted as described in the methods section. The calibration standards and samples were then analyzed using the pesticide analytical equipment, and the results are given in table 3. While no explanation for the anomalous increase in TCE concentrations is available, it is notable that the concentrations of most other compounds decreased. In retrospect, this was especially impressive given the relatively high concentrations of Benzyl Chloride.

Table 3. Chemical Spiking Study 2, Values in μg/l (PPB).

Spiked Compounds	Sample354		Sample355		Sample356		Sample 357	
	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
1,1,1-TCEthane	6.2	8.2	6.0	9.4	6.2	9.0	7.1	9.2
Benzyl Chloride	460	122	440	172	470	86	520	220
1,2,4-TCBenzene	10.8	.70	9.6	.83	9.8	.66	8.0	.98
Lindane	8.9	8.5	10.2	8.9	10.	8.5	13.7	12.8
Aldrin	7.4	ND	6.0	.43	6.8	.11	7.1	.012
9,10-DBAnthrac.	74	66	132	100	150	115	200	150

The third spiking study examined the disinfection of virus (attenuated polio) by ozone and was generously undertaken by the Los Angeles County Sanitation District. This study was conducted on June 5, 1990, just prior to the time when the sanitary sewage spill overwhelmed operations. While a negligible loss of virus occurred due to toxicity (20% reduction), each of three replicates taken during three separate sample runs, showed viral reductions of 99.96% (3.8 log) or greater.

Bacterial kill during these runs was unusually low and ranged between 1.7 and 3.6 log. Significant turbidity was observed during two of the three runs (8, 98, and 80 NTU). The applied ozone doses were moderately high at 15, 19 and 15 mg/L (PPM) and dissolved ozone residuals were negligible.

An analysis of the sediments contained behind the storm drain weir was undertaken and although this evaluation did not relate directly to the use of ozone, it does have implications for the disposal of sludge that might accumulate in a treatment facility. Coarse sediments were collected on 2/13/90 and both fine and coarse sediments were taken on 6/21/90. The extracts was analyzed for organochlorine pesticides and semi-volatile compounds and the estimated concentrations are given in table 4. The reporting of 4,4'-DDE should be viewed with suspicion, since the levels detected were at the limit of quantification, the extract contained numerous interfering peaks, and neither DDD nor DDT were detected. The levels of polynuclear aromatic hydrocarbons detected in the storm drain sediments is both significant and predictable given our knowledge of combustion particulates and aerial deposition.

Table 4. Contaminants in Storm Drain Sediments mg/gram (PPM).

Chemical Constituents	2/13 coarse		6/21 coarse		6/21 fine	
	WET	DRY	WET	DRY	WET	DRY
TOC (by combustion)	1.6%	2.0%	1.01%	1.12%	6.3%	14.2%
4,4'-DDE	.0043	.0054	.0040	.0044	.0129	.029
Acenaphthene	.052	.064	ND	ND	ND	ND
Acenaphthylene	.0142	.018	ND	ND	ND	ND
Anthracene	.17	.21	.024	.026	.24	.54
Benz(a)Anthracene	.33	.41	.145	.160	1.00	2.3
Benzo(a)Pyrene	.15	.19	.090	.099	.97	2.2
Benzo(b)Fluoranthene	.87	1.09	.29	.32	2.2	4.9
Benzo(ghi)Perylene	ND	ND	.027	.30	2.2	4.9
bis(2-ethylhexyl) Phthalate	.44	.55	.28	.30	ND	ND
Butyl Benzyl Phthalate	.040	.050	ND	ND	ND	ND
Chrysene	1.48	1.8	.38	.42	2.0	4.4
Dibenzo(ah)Anthracene	ND	ND	.051	.056	.21	.48
Dibenzofuran	.070	.087	ND	ND	.19	.43
Diethyl Phthalate	.026	.032	ND	ND	.046	.105
Di-n-Butyl Phthalate	.65	.81	.149	.160	.55	1.24
Di-n-Octyl Phthalate	.084	.104	.126	.138	.18	.41
Fluoranthene	2.6	3.2	.38	.41	2.4	5.4
Fluorene	.110	.137	.042	.047	.75	1.7
Indeno(1,2,3,4-cd)Pyrene	ND	ND	.074	.081	.86	1.9
2-Methyl Naphthalene	.029	.036	.15	.17	.72	1.6
Naphthalene	.016	.020	.053	.58	.19	.426
Phenanthrene	3.0	3.8	.30	.33	2.3	5.2
Pyrene	1.9	2.3	.31	.34	2.6	5.8
Σ PAH's	10.7	13.3	2.2	2.4	18.	40.
Σ Ocean Plan PAHs	8.0	10.0	1.7	1.9	15.	35.

DISCUSSION

The primary goal of this project was to demonstrate whether ozone would be an effective disinfectant for dry-weather storm drain flows, particularly those of the Kenter Canyon drain. The secondary goal was to characterize the variance, in concentration, of some low flow pollutants and determine whether the observed levels would inhibit disinfection or be beneficially reduced during ozonation. Others goals were to define the important treatment parameters, develop a prototype process train, estimate the cost of treatment, and elucidate the operational response to a sudden influx of contaminants. The answers to these questions would determine whether the project should continue beyond the pilot plant phase and what goals to set for that expanded facility.

The pilot plant study proved that ozone was extremely efficient in disinfecting the Pico Kenter Canyon storm drain dry-weather flow. As summarized in table 5, the overall reduction in bacterial numbers was over two and half log, or three and half log based on the more representative geometric mean. Furthermore, these statistics severely under-report disinfection for at least three reasons: First, the plant was not always operated optimally, many runs were performed to compare the relative importance of contact time and ozone concentration or some other parameter; Second, less than half of the samples were prepared using oxygen, rather than air, as the feed gas, so that during the first half of the study applied ozone dosages were relatively low; Third, the analytical method is insensitive to counts of less than two, so that 100% disinfection is still reported in the database as a most probable number of 2 organisms per 100 ml. As seen in figures 5, 6, and 7, disinfection was greatest during the latter phase of the project and a full scale facility should be able to maintain a 5 log (99.999%) reduction in bacterial and viral numbers, based on total coliform counts. Finally, while this study analyzed benign indicator bacteria counts, it should be noted that ozone has been used against a variety of pathogens (Ferguson, Gramith and McGuire 1991) and, while a few species are relatively resistant (Ferguson et al. 1990), the vast majority succumb to ozone more rapidly than other common disinfectants.

Table 5. Reduction in Microbial Counts Following Ozonation.

Micro Organism Type	Arithmetic	Geometric
Total Coliform	2.4 log (99.6%)	3.5 log (99.97%)
Fecal Coliform	2.5 log (99.7%)	3.4 log (99.96%)
Enterococcus sp.	2.9 log (99.9%)	3.4 log (99.96%)
Polio Virus (Vaccine Strain)	3.5 log (99.97%)	

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Total Coliform Counts Before and After Ozonation (Log MPN versus Sample Number)

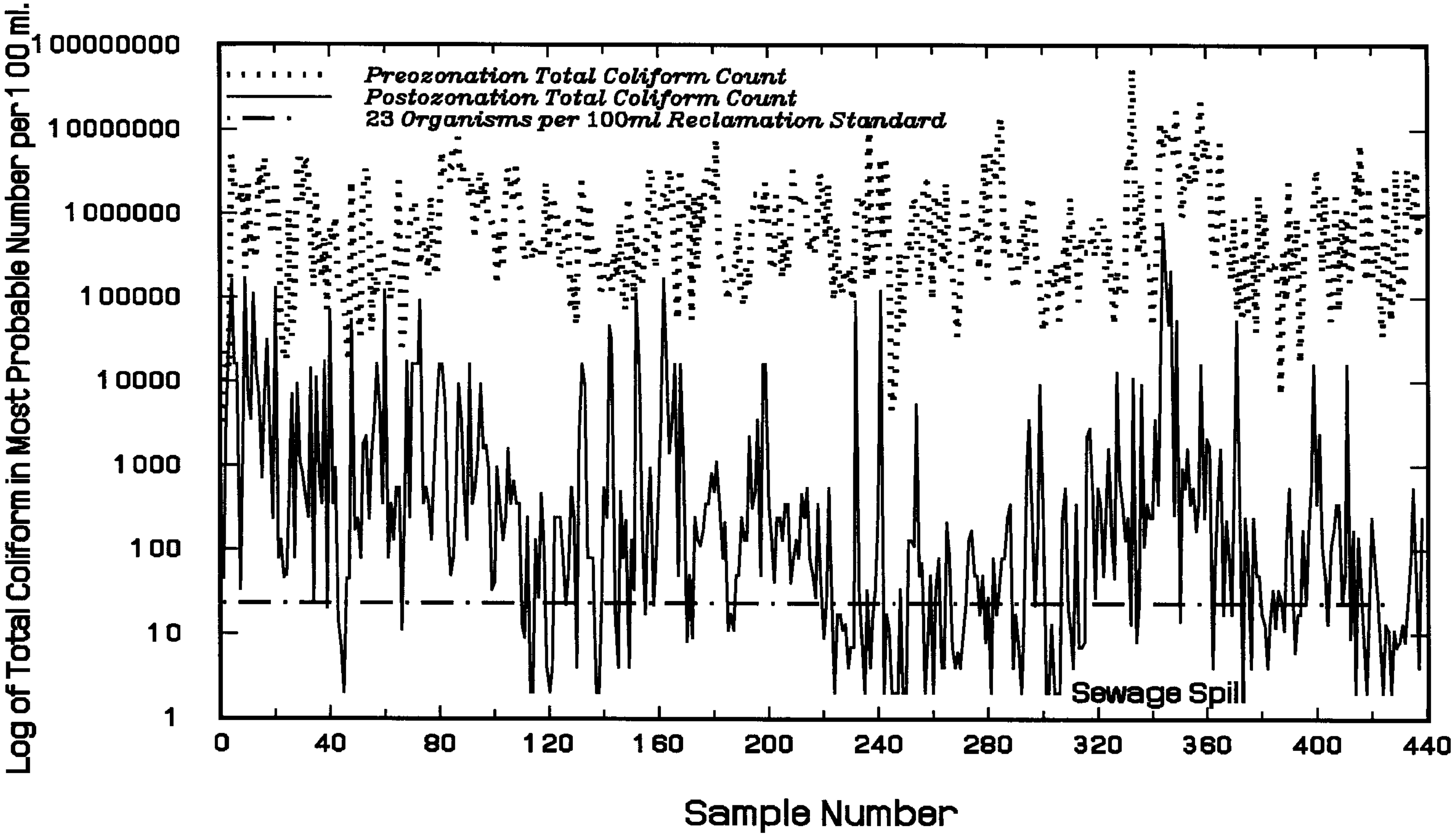


Figure 5. Total Coliform Counts Before and After Ozonation (Log MPN Versus Sample Number).

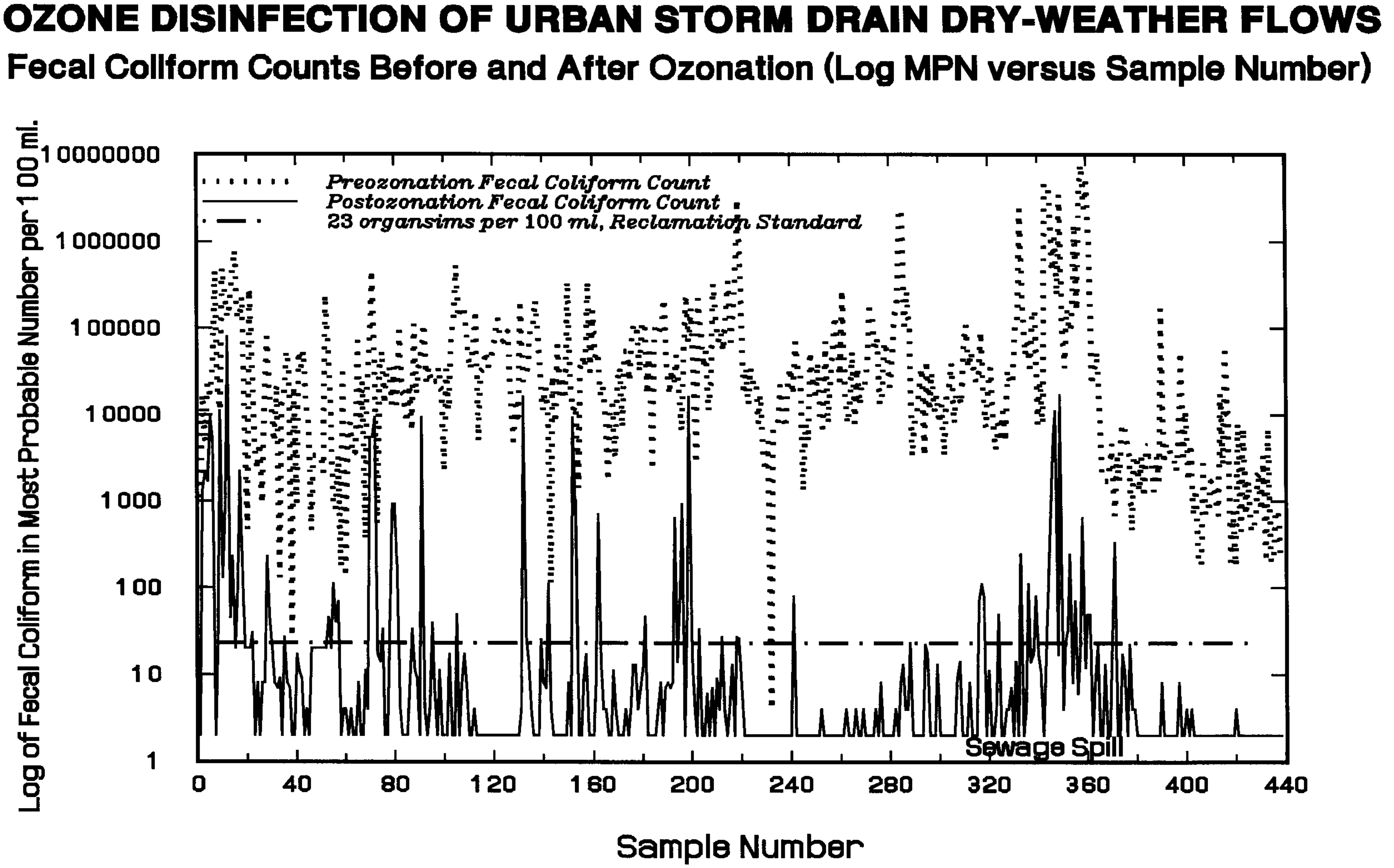
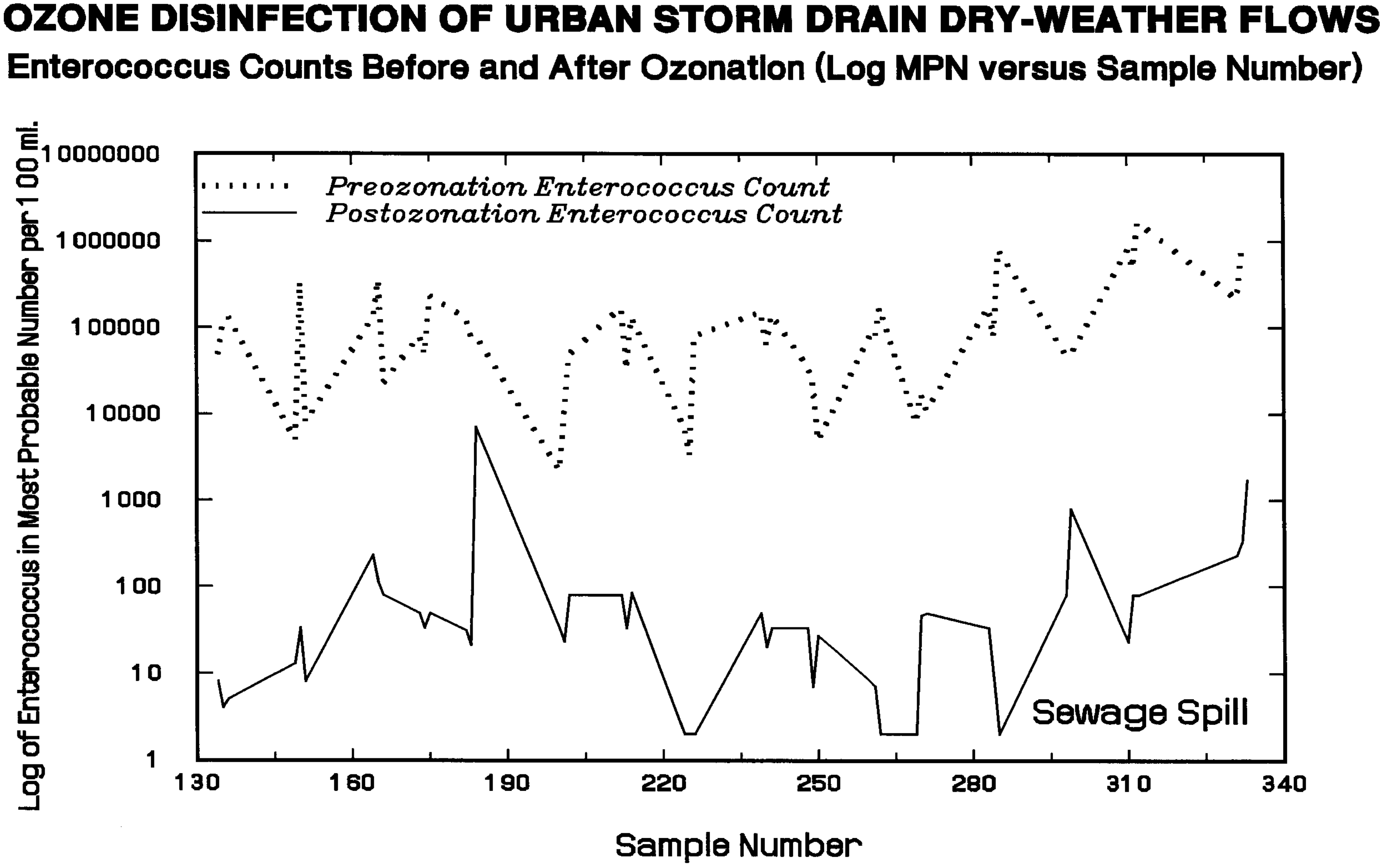


Figure 6. Fecal Coliform Counts Before and After Ozonation (Log MPN Versus Sample Number).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Enterococcus Counts Before and After Ozonation (Log MPN versus Sample Number)

Figure 7. Enterococcus Sp. Counts Before and After Ozonation(Log MPN Versus Sample Number).

Major economies of scale exist in sizing air preparation and ozone generation equipment and a full scale facility of this type should probably be sized at 5 to 10 times the anticipated mean ozone demand. The major variable expense of treatment, is the electrical ozone generation costs, which is directly proportional to the quantity of ozone produced and consumed and few penalties exist for over designing this aspect of the treatment train. While the pilot phase demonstrated that bacterial numbers were often reduced 5-6 log, a full-scale efficiently operated facility should be able to consistently achieve a 4.5 to 5 log reduction in bacterial counts. This compares with the experience of the drinking water industry which, while using more rigorous filtration processes, is able to achieve a 7-8 log bacterial reduction (Ferguson et al. 1990) using an ozone dose of only 4 mg/L.

The highly variable concentration of contaminants in the flow have confounded the statistical analyses of the parameters that influenced the disinfection process. Intuitively ozone dose and residual would be expected to correlate with disinfection. Contact time also appeared to correlate with disinfection, however, the exposures in this project were relatively short (2-6 minutes) and other research suggests that little correlation exists for periods greater than six minutes (Ferguson et al. 1990). While pH decreased with degree of disinfection, this is probably an artifact of ozonation rather than a direct contribution to sterilization. Total organic carbon was normally inversely proportional to disinfection efficacy, especially at high TOC concentrations. Since ozone indiscriminately reacts with both organismic and inanimate carbon, as the proportion of the latter increases, the amount of ozone acting on microbial carbon must correspondingly decrease. Turbidity, settleable solids, and suspended solids were generally correlated with each other, but appeared to have risen from both inorganic and organic sources. Disinfection generally continued, albeit at lower efficiencies, in the presence of inorganic material, such as was present when extensive upstream concrete cutting flushed large quantities of loamy sediments into the storm drain. In contrast, when the sanitary sewer ruptured into the drain, turbidity, solids and TOC all increased significantly and disinfection was reduced to one or two log. Fortunately these periods were exceptional and disinfection normally proceeded efficiently.

The treatment of storm drain water is hampered by two major constraints. First the integrity of the storm drain as a means of rainfall conveyance must not be hindered. Second, contamination is periodic, erratic and concentrations may change by orders of magnitude over a few moments. The variability was particular evident amongst the solids (Total Solids, Suspended Solids, Dissolved Solids, and Settleable Solids), bacterial, and metal contaminants, but instances also occur among the organic analytes. Chlordane (and heptachlor), lindane, endosulfan and o-xylene were each observed as single spill events and were probably released by a household or small business. While both chlordane and o-xylene were at significant concentrations during these periods, it is unlikely that these random events could have been anticipated. While a typical wastewater treatment facility would receive these individual releases diluted by volumes of wash water and organic sludge, a low- or base-flow storm drain treatment facility would be confronted by a significantly modified and contaminated flow. The proposed storm drain facility would require a smart process train capable of distinguishing between the normal water, that can be treated during the primary disinfection process, and heavily contaminated water that should be directed elsewhere. Depending on the costs, type of contamination, and societal goals, this second path could include on-site treatment, but would probably be more economically decontaminated at a wastewater facility where dilution and additional treatment processes would moderate the spill event.

The chronic Kenter Canyon low flow chemical contamination appears to be limited to some heavy metals and polynuclear aromatic hydrocarbons (PAHs). While an actual initial dilution factor (assumed to be 5:1) would need to be determined to calculate the exact limitations, table 6 indicates that the concentrations of several metals warrant concern. Fortunately, most of the high heavy metals concentrations came from only a few of the almost 200 samples analyzed, and their exclusion would have significantly reduced the mean concentrations. Excluding PAHs, these few easily detected samples, and the described hexavalent chromium contamination, only lead and copper appear to violate the Ocean Plan Objectives for ocean release of the water.

Table 6. Mean Concentrations of Heavy Metal Analytes, in μg/L, During Study and Comparison to Representative Water Standards.

Analyte Name	Analyte Concentration During the Study			Ocean Plan Objective 5:1 Dilution Assumed		Potable Water MCL
	Mean Values		Maximum	6 Month Median Value	Instantaneous Maximum	
	Normal	Geomet				
Arsenic	24	13	730	33	465	50
Cadmium	2.8	2.8	16	5	50	10
Chromium+6	31	13	1020	10	100	50
Copper	38	32	136	8	170	1000
Lead	90	42	740	10	100	15
Nickel	6.4	3.6	47	25	250	100
Selenium	7.8	2.2	112	75	750	10
Silver	0.6	0.3	14	3.4	41	50
Zinc	100	82	700	80	1160	5000

While the recent elimination of leaded gasoline may well bring emissions of this element under standards, a few years will be required to test the hypothesis. Copper represents a more difficult regulatory quagmire. While the mean concentration of copper was about 4 times the Ocean Plan Objectives, it is only one 30th of the drinking water MCL. While no one would advocate that the water is potable, we are faced with the dilemma that water fit to drink from the standpoint of copper contamination, could not be released to the ocean. Given the overall environmental benefits of disinfection, copper would be a prime candidate for regulatory relief if construction of the ozone facility is contemplated.

The major chronic organic contaminants were the polynuclear aromatic hydrocarbons (PAHs) which consist of variously linked benzene rings and include several known and probable human carcinogens. The California Ocean Plan treats PAHs as a group with the water quality objective being based on the sum of thirteen that are commonly analyzed. The Ocean Plan 30 day average for the sum of these 13 is 8.8 ng/L (PPTr) which, with a 5:1 dilution, is equal to an effluent objective of 0.044 μg/L (PPB). The arithmetic and geometric means of both the influent and effluent streams ranged from 1.9 to 1.3 μg/L (PPB) suggesting a normal distribution and indicating that levels were 35 times the Ocean Plan Water Quality Objective. The sum of the mean travel blank PAH concentrations was equal to 0.22 PPB. In the proposed phase V drinking water regulations, the EPA plans to set maximum contaminant levels (MCLs) for 7 of the PAHs specified in the Ocean Plan. For each of these 7 PAHs, the mean value observed during this study was slightly less than the proposed MCL. Furthermore, the sum of the seven proposed drinking water MCLs (1.6 μg/L) was essentially equal to sum of the observed project means (1.9 to 1.3 μg/L) for the 13 PAHs listed in the Ocean Plan Objectives. Consequently, for PAHs we again face the regulatory dilemma that water meeting proposed drinking water maximum contaminant levels would be prohibited for ocean release.

Polynuclear aromatic hydrocarbons are associated with combustion processes and are commonly found in the particulates emitted by diesel engines. These vehicular emissions are also significant sources of metals such as lead and chromium

(Manahan 1984). Although the pilot plant was located in the municipal bus yard, the runoff from the yard enters a second storm drain and the chronic contaminant concentrations observed in this study are probably attributable to basin-wide aerial deposition of particulates. This soot, which settle in street side curbs throughout the drainage basin, is probably carried by urban runoff into the storm drains and is unlikely to be effectively controlled in the immediate future. Water treatment technologies for the control of these chronic contaminants, at the mean concentrations observed in this study, include reverse osmosis/ultrafiltration and granulated activated carbon and are extremely costly with other potentially hazardous waste streams. Given the concentration of pollutants in the sediment (table 4), it is likely that much of the observed contamination was due to the submersible pump transporting sediments into the system. Future undertakings should explicitly segregate the sediments and utilize an alternative decontamination strategy, which may require some degree of administrative relief.

A secondary question relates to how the facility responds to chemical contamination and whether any chemical remediation of organic compounds would be observed. Given that metals cannot be "degraded", only isolated and removed, there were few instances in which to observe the action of ozone on hazardous substances. While the o-xylene event could not be analyzed due to saturation of the GCMS detector (the effect of air stripping would also have complicated the results), the chlordane spill provided an exciting validation that remediation does occur. At the highest concentration, 70% of the influent chlordane was apparently degraded to other, probably more polar and less toxic, compounds. This percentage dropped with influent concentration and was less than 40% when a storm washed out the contaminated sediments. The apparent loss in efficacy, with lower contaminant concentration, correlates with the simplistic concept of ozone randomly attacking and cleaving carbon macromolecules into less complex compounds that may still be susceptible to ozone directed attack.

When ozone susceptible compounds are present in the PPM level, and make up a significant fraction of the TOC, ozonation would be a meaningful remediation technology, but at sub-PPB levels in a PPM carbon soup, the removal efficacy could well be inconsequential. Automation and staging of the ozone treatment process should facilitate a rapid response to the challenge of an increase in TOC or drop in ozone residuals. Based on the results of this study, it appears that the concentration of many (trimethyl benzene, aldrin, phenol) compounds can be significantly (> 95%) reduced during disinfection. Others, such as benzyl chloride, naphthalene, 9,10-dibromoanthracene, and pyrene, are less reactive, but are still degraded when present in high concentrations. Finally some recalcitrant compounds, such as lindane and 1,1,1-trichloroethane are apparently resistent to ozone directed attack.

While the disinfection results exceeded expectations and the monitoring program found the water to be only modestly contaminated by chemicals, the question of disinfection by-products remains unresolved. The monitoring program detected mid PPB levels of aliphatic aldehydes, such as hexanal, heptanal, etc., compounds which are typical of ozone disinfection and whose environmental hazard at these levels are unknown. However, it is encouraging that in the Microtox® test, toxicity (EC_{50}) decreased with increasing carbon chain length from 1 PPM with formaldehyde to 5 mg/L for acetylaldehyde, 300 mg/L for butanal and almost 2 gr/l (PPTh) for Benzylaldehyde (Kaiser and Ribo, 1988). The smaller, more volatile, aldehydes are also likely to be stripped with the off-gas into a catalytic ozone destruction unit which is highly reactive with aldehydes and other volatile organics. As discussed in the methods section, this reaction is exothermic and a thermocouple must be included to monitor the unit for combustion. It is also clear that ozone disinfection formed few, if any, of the halogenated byproducts seen with disinfection by chlorine, chlorine dioxide and chloramines (Jacangelo et al. 1989). While all disinfection processes produce by-products, ozone and peroxzone (ozone combined with hydrogen peroxide) produce fewer mutagens then chlorine related processes (Noot et al 1989). Furthermore, as shown in table 1, ozonation clearly did not increase the mutagenicity of the dry-weather storm drain water.

The results obtained during this project, conclusively show that ozone was an effective disinfectant for the low-flow storm drain water. While ineffective in removing metals and trace organic contaminants, ozone disinfection appeared to produce few hazardous by-products, is amenable to automation, and has some chemical remediation properties. Based on the results of this study, it appears that disinfected water can be produced which meets the 23 coliform organisms per 100 ml standard and could be made available for landscape irrigation purposes as part of an integrated treatment and reclamation facility. The project-wide mean metal concentrations are within the guidelines suggested for trace elements in irrigation waters (CWQC 1968) for most metals on any soil. The only exceptions were molybdenum which, at the level found in this study could cause illness in ruminants, and boron which is well within the standard for use on fine textured soils. The other contaminants would not be expected to negatively impact the relatively hardy plants that tolerate growth along freeways.

A potential full-scale process train is diagrammed in figures 8 and 9 and could be based on construction adjacent to a section of storm drain or at a central locality with laterals carrying the flow from adjacent drains. The first station would be an automated trash rack to remove trash during low-flow, first flush, and light storm conditions. Water in excess of treatment system pumping capacity would pass through the 1/4 inch screen and be routed to the ocean through an overflow. The sluice gates (local and remote) and trash rack would be controlled by ultrasonic level detectors. Once the water had been de-trashed, redundant submersible pumps would bring the influent water to surface level and into a filtering device such as a back pressure activated auto strainer with 100 micron filter.

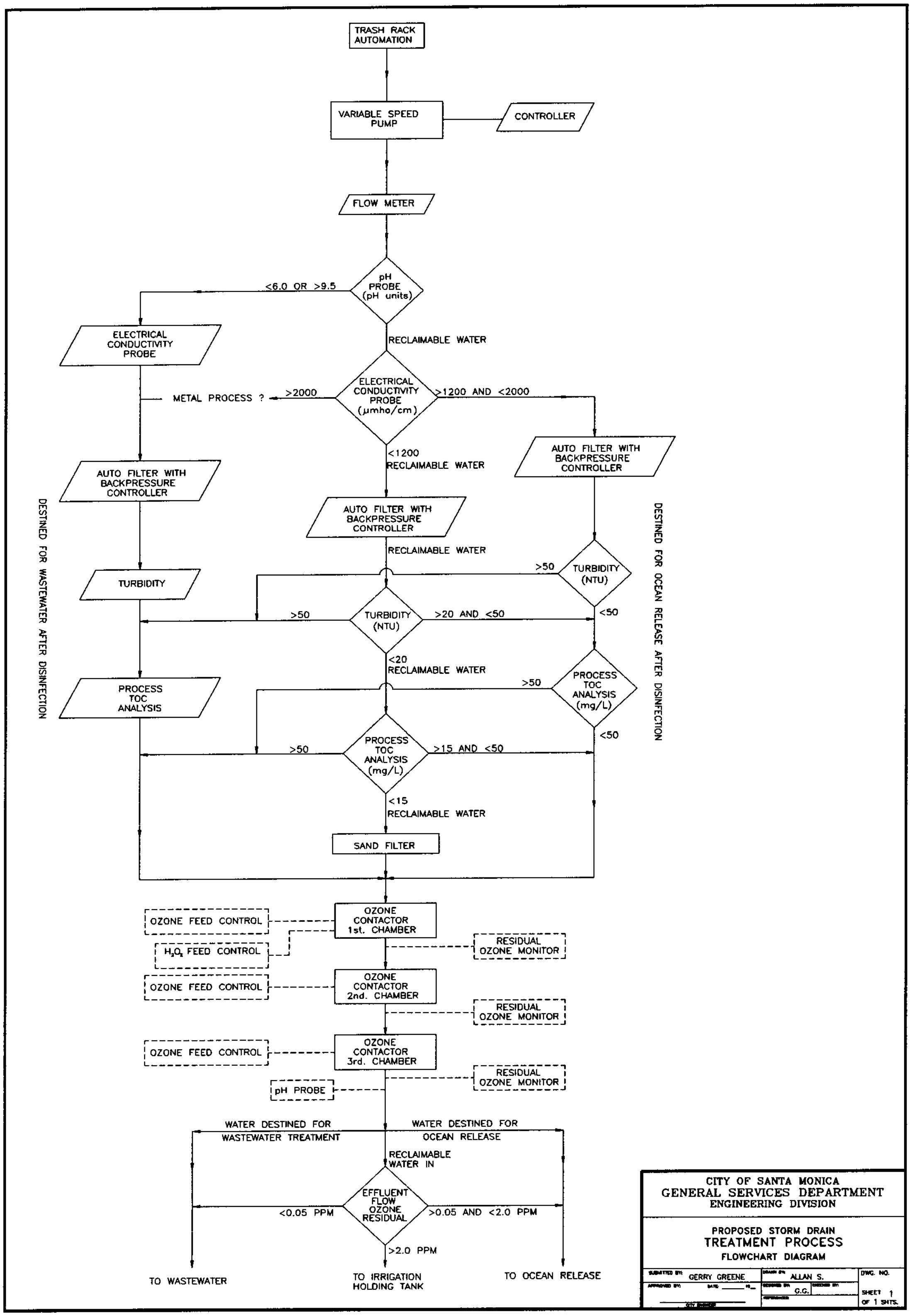

Figure 8. Proposed Storm Drain Treatment Plant Process Flowchart.

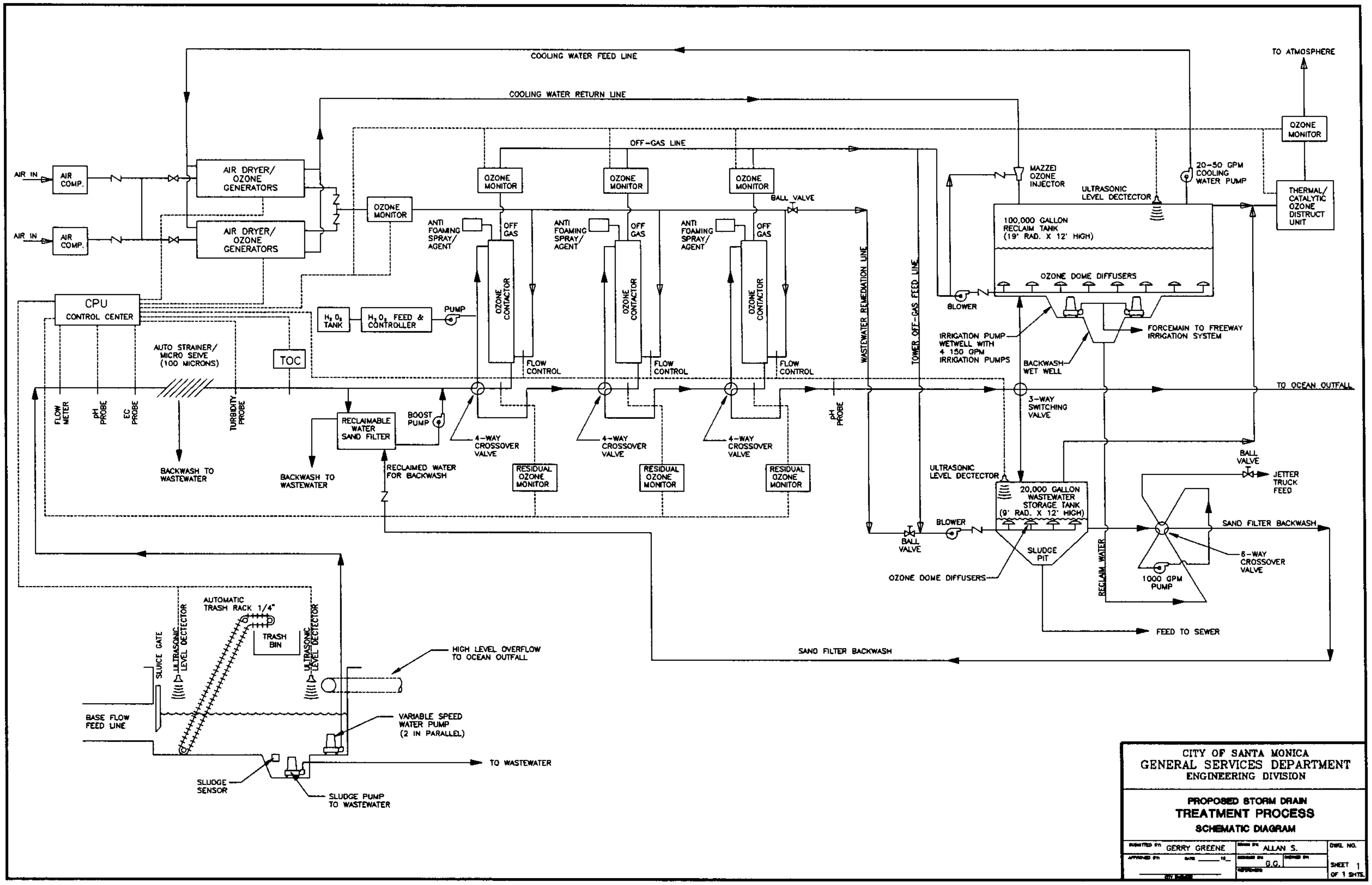

Figure 9. Proposed Storm Drain Disinfection Treatment Plant Schematic Diagram.

After filtering, the water would be monitored for flow rate, pH, conductivity, turbidity, TOC, and probably selected heavy metal ions, such as chromium and iron. Based on these results, the water would be tentatively categorized for potential end uses. Water low in contaminants would go through a sand filter with the intention of using the water for irrigation. Water that was moderate in contamination, or in excess of landscape needs, would be slated for ocean release. The most contaminated water could be directed to the sewer or used for sewer flushing.

Following sand filtration of the reclaimable water and characterization of the lower quality waters, the next step would be ozonation in a multichamber system. The separate towers permit maintenance and monitoring of the dissolved ozone residuals and off-gas concentrations. The addition of ozone would be correlated with tower effluent ozone concentrations and influent TOC. Assuming a design consisting of three sequential towers, the residuals would be monitored after each chamber. In response to low residuals, ozone gas flow or generation would increase to some optimum higher production point and be directed to the depressed chamber and its upstream companion. Finally, based on the cumulative sensor parameters, water would be directed one of three effluent streams: the storm drain and ocean; an irrigation reclamation holding tank; or a wastewater holding tank for sewer flushing. The reclamation holding tank would also be the source of backwash water for the sand filters and cooling water for the ozone generators and compressors. The contactor tower off-gas would be passed through both reclamation and wastewater holding tanks to maintain a disinfectant residual, with the off-gas from the tanks passing through the catalytic ozone destruction unit. An auxiliary line would be available to directly feed ozone into the wastewater holding tank if chemical remediation appeared to be warranted.

Initially, the bulk of the treated water would be directed back to the storm drain for ocean release. Later, as reclamation became more significant, only water that was in excess of reuse demand or highly conductive (salty) would be directed back to the drain. Water that was low in conductivity, turbidity, TOC and moderate in pH would be directed for landscape irrigation purposes if, it also contained a significant ozone residual. Water that failed the irrigation and ocean release criteria, such as water that was high in metals, organic matter, or turbidity, would be directed to the holding tank for contaminated or wastewater. The tank overflow and any water used in flushing sewers would then be directed to a typical wastewater treatment facility, but would arrive substantially diluted. Only the dry-weather flow that is within the wastewater treatment facility's capacity and requiring full treatment would receive it. The bulk of the dry-weather flow would receive only the warranted disinfection treatment before being reclaimed or released to the ocean. Finally, water that is highly contaminated and unacceptably for disposal to the sewer system because of metal content, gasoline, or oil and grease, could be held and treated by specific measures such as oil skimming, ozonation, or ion exchange, to reduce the contamination to acceptable levels. Thus the water would be treated in a manner appropriate to the degree of contamination observed.

The proposed treatment plant off-gas effluent stream is a potential source of cross-media contamination and it was therefore desirable to estimate the level of some contaminants that are likely to be released from the process train. In a study of automotive exhaust from traditional and oxygenated fuels, Hoekman (1992) calculated emissions in terms of milligrams of combustion by-products per mile driven, providing an easily understood standard for comparison. Estimates of treatment plant off-gas emissions of ozone, volatile organic carbon (VOC's), carbon dioxide, and carbonyl (aldehyde-like) compounds were prepared using best (manufacturer's claims), reasonable (generally observed), and worst (poor emission control performance) case scenarios. Based on the data from 6 late model California cars (1986 to 1990), the reasonable case scenarios resulted in 24 hour estimated emissions equivalent to between 10 and 20 miles of driving. With the exception of carbon dioxide, which is fixed at around 14 miles, the best case emissions estimates were less than 1 mile and worst case estimates were less than 160 miles. Therefore, the most likely estimate of treatment plant air emissions are about equivalent to one local commuter trip and represent an insignificant contribution to the local air quality problems.

While bacterial regrowth of the ozonated water in the irrigation pipeline is likely to occur, the bacteria are unlikely to include human pathogens and should not support replication of human enteric virus. The landscape irrigation system will initially require regrowth monitoring and it may become necessary to consider periodic flushing with heavily ozonated (or passed through a solid chlorinator) water with disposal to a modest injection well near the upstream terminus of the irrigation system.

SUMMARY AND CONCLUSIONS

The results proved that ozone was an extremely effective disinfectant and at doses in the range of 10-20 mg/liter was capable of reducing bacterial and viral populations by 3-5 log (99.9 to 99.999% of the microbes killed or inactivated) with contact times of less than 6 minutes. While high organic carbon (TOC) or suspended solids (turbidity) reduced the efficacy of ozonation, the process was not neutralized and samples high in inorganic solids were readily disinfected. In many effluent samples, coliform concentrations were sufficiently reduced to qualify the water for use in reclamation projects such as landscape irrigation along the Santa Monica Freeway, suggesting a possible useful purpose for the treated effluent. While ozonation by products, such as aldehydes, were detected in the plant effluent, their concentration was low (mid PPB range) and many would also be present in a chlorinated effluent. No significant increase in halogenated by-products or mutagenicity was observed following ozone disinfection. As a test of the ozonation process, a dozen hazardous organic chemicals were added to the influent water and the effluent monitored. While the four most refractory compounds passed through the facility unchanged, the concentrations of the other eight were greatly reduced during the disinfection process.

The primary hazardous chemical constituent in the influent water were metals, primarily copper, lead, zinc and chromium which are not removed by ozonation and polynuclear aromatic hydrocarbons which are at extremely low concentrations.

Isolated samples did contain organic contaminants, such as ortho-xylene and the pesticide chlordane, but this did not appear to be a pervasive problem and can be attributed to isolated events that cannot be anticipated and will only be prevented through an informed and concerned public. Data on the degradation of PAH's by ozone was mixed. The mean effluent sum of PAHs was 80% of the mean influent sum value, but during the first spiking study, when concentrations of Naphthalene and Pyrene were hundreds of time higher than normal, concentrations were reduced by <95%. This suggests that PAHs, and probably many other organics, are only degraded when their proportion of the total organic carbon becomes substantial in relationship to the large bacterial and biological carbon content. With the exception of some metals, the mean concentration of most of the chemical contaminants were below the levels allowed in drinking water, and only a few contaminants were above California Ocean Plan Water Quality Objectives.

In contrast to bacterial counts which were generally high and consistently present, sediments and suspended solids were generally low, then would suddenly, and unpredictably, rise to levels hundred of times greater than the mean value. This often appeared to coincide with increased dry-weather flows, which would resuspend deposited material, so that increased per gallon treatment demand coincided with higher flow rates through the treatment system.

RECOMMENDATIONS

The positive results from this study have lead the City of Santa Monica to consider construction of a full scale ozone based treatment facility, presently planned for construction near the Santa Monica Pier. While numerous institutional barriers will need to be surmounted, before a commitment to begin construction can be made, City staff is confident that any negative attributes will be greatly offset by the positive environmental outcome. The proposed facility is expected to be automated and intelligent with the capability to remove trash from all of the dry-weather flows and a least part of the first flush of wet-weather storm runoff.

In the proposed treatment train, after filtration, the influent dry-weather flows would be process monitored for parameters such as conductivity, turbidity, pH, and total organic carbon, the water would then ozonated, and the effluent retested for pH and ozone residual. Based on these parameters the effluent would be directed to the most appropriate disposition. Water that is low in conductivity (salts and metals), filtered and well disinfected (high ozone residual) would be slated for reclamation purposes. Initially, this could consist of a test section of the Santa Monica Freeway and other public works projects. If successful and warranted by the quantity and quality of the effluent, this project could then be expanded to other sections of the freeway. The bulk of the water, which is not initially needed for reclamation, would be screened, disinfected and released to the ocean. Filter backwash water and plant effluent water that is high in organic content (nominally 50 PPM as TOC) would be routed to a holding tank where oil water separators would remove floating contaminants. The contents of this tank could be utilized in municipal jetter trucks which use a high pressure stream to flush out sanitary sewers, thus routing the contaminated water to the facility traditionally designated to deal with water containing a high organic content. Water that is sufficiently high in organic content (perhaps 200 PPM) or heavy metals (based on detection with ion specific electrodes) would be investigated to determine if the contaminants would endanger downstream facilities and then either treated on-site or appropriately disposed of.

If the proposed Santa Monica facility is successful, the potential exists that the dry-weather flows from several of the adjacent storm drains could be transferred, through a new coastal interceptor, to a single treatment plant near the Santa Monica pier. The effluent from this hypothetical facility could then be distributed for use in public works projects, irrigation of neighboring freeways, released under the pier and into the ocean, or pumped into the adjacent Moss Avenue sewage pumping station for eventual treatment at the Los Angeles City Hyperion Facility.

The primary constraint on development of this facility is for the various agencies to determine the level of treatment which is compatible with the various effluent goals. As an example, the content of heavy metals and PAHs could occasionally exceed Ocean Plan Objectives for ocean release of the effluent. However, the reduction in uncontrolled and microbial emissions would be greatly reduced by construction of the facility. The reclaimed water will contain contaminants, but freeways are already the primary source of these pollutants and the landscaping flora has apparently adapted to a soil containing high concentrations of heavy metals and particulates. The treatment facility solids and sludge stream will need to be disposed of. While Santa Monica will be able to deal with "trash" from the screening process, the filter backwash, sediments, and sludge would require further processing. Assuming that ocean release is unacceptable, Santa Monica is faced with the costly choice of de-watering and disposing of the material or directing it to the sanitary sewer and perhaps being considered as an industrial point source. The cost of becoming a point source, that is treating nonpoint contaminants, may be prohibitively expensive, especially if aerial deposition is the primary source of contamination and two thirds of the drainage basin is in another jurisdiction. Unfortunately, it is possible that concerns regarding the unknown disposal costs of the these waste streams may prevent treatment of a known and potentially significant biohazard. While testing, evaluating, and operating this prototype facility, it is important that all parties be prepared to deal with some unanticipated excursions. It is vital that the known public health "big" picture remain consistently clear and not become distorted over contaminant variability and episodic spill events.

The various arms of the Santa Monica Bay Restoration Project can expedite the development of the proposed facility by continuing to contribute its group expertise on the individual policy issues. The advice of the technical advisory committee, has already been invaluable in directing the progression of this study and will hopefully continue to participate in designating the major contaminants and waste streams of concern. The public advisory committee has volunteered to translate this report into a format that can be understood and supported by the general public and will continue to reduce the level of storm drain pollution by educating the populace. Finally, the management committee and foundation wield significant authority and prestige among responsible agencies and regulators. As a consensus forming group, its support represents an essentially neutral opinion regarding the broad environmental good of the Santa Monica Bay Region. While Santa Monica gratefully acknowledges the support of the SMBRP in funding the demonstration project, the City requires the continued support and influence of the Santa Monica Bay Restoration Project to successfully commission and evaluate the proposed facility.

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The conclusions and recommendations contained in this report, represent the views of the author and do not necessarily represent the views of the City of Santa Monica, the Santa Monica Bay Restoration Project, the State and Regional Water Quality Control Boards, or the US Environmental Protection Agency. Any errors or omissions are the responsibility of the author.

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OZONE DISINFECTION AND TREATMENT OF URBAN STORM DRAIN DRY-WEATHER FLOWS

A PILOT TREATMENT PLANT DEMONSTRATION PROJECT ON THE KENTER CANYON STORM DRAIN SYSTEM IN SANTA MONICA

TECHNICAL AND DATA APPENDICES

(Dissertation Format)

APPENDIX IA

QUALITY CONTROL AND ASSURANCE REPORT

SUMMARY

Given the scope and resources of this project, the quality assurance and control were generally excellent. The primary QA/QC failure was associated with analyses conducted out of holding time compliance primarily for pesticide and TOC analyses. Lesser problems also developed in interpreting the results from the outside (state certified) laboratory, poor choice of pesticide internal standard, and contamination in the hexavalent chromium reagents. None of these difficulties compromised the analytical value of the data. To the contrary, the analytical accuracy of the analyses exceeded that anticipated in the project Quality Assurance Plan and, with only two exceptions, significantly more analyses were undertaken, then were originally planned.

A summary of the compliance and analytical information is given in Table A1. The only reductions, from the proposed number of analyses, were among the purgeable and mutagenicity assays. This was necessitated by a doubling in anticipated analytical cost of the mutagenicity work and was approved by the project review board. The other additional analyses were financed by a combination of unmatched municipal funds, lower personnel costs, and reduced costs of the bacterial analyses. The number of analyses performed by the certified laboratory remained unchanged. Differences between the sample number collected and number included in the database were generally due to analytic problems such as salt in TOC analyses, and detector saturating concentrations of ortho-xylene in the purgeable analyses.

Table 7. Sampling and Compliance Numerical Assessment by Method.

Analysis Name	# of Samples		Number in Extraction Compliance	Number in Analytical Compliance	Samples Added to Database
	Planned	Taken			
Total Coliform	360	438	N/A	438	438
Fecal Coliform	360	438	N/A	436	436
Metals-ICP	96	208	N/A	156-193	156-193
Chromium +6	96	96	95	95	95
TOC (wet)	312	438	N/A	425	425
Organochlorine Pesticides	72	86	86	64	86
Volatile Organics	24	22	N/A	20	20
Extractable Organics	18	21	21	21	21
Resin Accumul. Mutagenicity	6	5	N/A	N/A	5
Electrical Conductance	Not planned	332	N/A	332	332
pH	N/P	438	N/A	401	401
Temperature	N/P	430	N/A	430	430
Turbidity	N/P	349	N/A	349	349
Settleable Solids	N/P	438	N/A	438	438
Total Solid	N/P	435	N/A	435	435
Dissolved Solids	N/P	435	N/A	435	435
Suspended Solids	N/P	434	N/A	434	434
Off-gas O3	N/P	387	N/A	387	387
Dissolved Ozone Residual	N/P	430	N/A	430	430
Virus Spike	N/P	3	N/A	N/A	N/A
Sediments	N/P	3	N/A	N/A	N/A
Chemical Spike	N/P	6	6	6	N/A

The ozone pilot plant spiking studies and sediment sample results are contained in the text and were incompatible with inclusion in the database. The complete database, draft report, and alternative database formats have been submitted to, and should be available through, the EPA Oceanographic Data Evaluation System (ODES) network. The Data is available from the author in ODES, ASCII, and Dbase III+ formats.

The accuracy of the analyses for total solids (total residue, Method 160.3), dissolved solids (filterable residue, method 160.1) and suspended solids (non-filterable residue, method 160.2) were confirmed using EPA Residue Quality Control Samples (Lot RES 489). The results are given in Table A2.

ANALYTICAL QUALITY CONTROL PROCEDURES

Methodological problems that occurred during the project are included in the main report, this appendix is primarily devoted to describing the efforts undertaken to insure and demonstrate the accuracy and quality of the data obtained during the study.

The electrical conductivity meter was calibrated prior to each analysis using a 1,000 μmho/cm standard prepared using a calcium chloride solution as specified by the manufacturer. Samples were collected in polycarbonate Immhoff cones and any that measured above 3,000 μmho/cm were compared to a 10,000 μmho/cm standard. Fresh standards were prepared monthly and compared to the "expired" standards to insure that they agreed to within 5%. The meter was temperature corrected and the readout was directly recorded.

The pH meter was calibrated daily using pH 7 and 10 buffers corrected for the anticipated water temperature. The buffers were obtained from Fisher Scientific and were within expiration date. The calibration was checked just prior to use, or when the water temperature differed from the expected by more than 2°C.

Temperature was measured using a standard glass laboratory thermometer, that was checked weekly against a precision thermometer.

The nephelometer (turbidimeter) was calibrated between samples using a 40 or 5.0 NTU Amco® AEPA-1 standard. As discussed in the methods section, the 0-1, 1-10 and 10-100 scales did not completely overlap. Sample pairs that fell between the scales were compared on the same scale and could be accurately estimated up or down 1 NTU. The accuracy of the instrument and analyst was also checked using an EPA Turbidity Quality Control Sample (Lot WS 289). The 1.00 NTU sample read 1.02 on the 0-1.0 scale and 0.95 on the 1-10 scale, as compared to performance evaluation mean of 1.05 with 95% confidence interval ranging from 0.81 to 1.29. The 5.0 NTU sample was read as 5.5 NTU while the performance mean was 4.94 with a 95% confidence interval of 4.26 to 5.62 NTU. Since the samples were always measured as influent/effluent pairs, any error introduced by the scale misalignment would affect both samples and introduce a relatively neutral bias.

Immhoff cones are standardized at the factory and no calibration of the settleable solids analysis is possible.

The use of the sensitive ultrasonic nebulizer, presented a metals analysis quality assurance problem, since the standard inductively coupled plasma QC samples (ICP-19 and ICP-7) were far too concentrated. Secondly, the report included with these QC samples (Lot WP988) did not include interlaboratory mean, standard deviation and 95% confidence interval for each metal. The analyst responded by diluting the ICP standards 1:50 and 1:500 respectively.

Table 8. Evaluation of EPA Residue Quality Control Standards.

Analyte	True Value	Interlaboratory Mean	Standard Deviation	Tech. #1	Tech. #2	95% Confidence Interval
Dissolved Solids #1	408	411	27.0	455	381	361-470
Dissolved Solids #2	287	290	21.7	319	287	247-333
Suspended Solid #1	31.5	31.5	1.82	28.8	31.2	27.7-35.1
Suspended Solids #2	278	267	8.70	255	259	250-284
Total Solids #1	439	442	29.1	443	391	384-500
Total Solids #2	565	557	37.4	551	526	490-632

The QA officer has taken interlaboratory data from trace metal analysis by atomic absorption (Water Pollution Control Sample Trace Metal I Lot WP287) and prepared table A3. The concentration of metals in the diluted ICP standards were mostly at 200 μg/L, while the interlaboratory comparison was for samples containing 100 μg/L for most metals (Al was at 500, V was at 250, Cd and Se were at 25). The 95% confidence interval in table A3 have therefore been normalized to 200 PPB. With the exception of those metals not analyzed in the interlaboratory study, it appears that the results obtained in this study are comparable to those expected using graphite furnace atomic absorption analysis.

Two samples were collected in duplicate, one being handled by project staff, while the second was sent to a certified laboratory (International Technology) for analysis. As shown in table A4, the results for sample 200B are in reasonable agreement, with the exception of magnesium, which is at concentrations only four times their detection limit. Less correlation is observed in sample 331A, especially for arsenic, chromium, lead, and selenium, which were in significantly lower concentrations in the commercial lab results. While it is impossible to determine the source of disagreement at this time, this sample was noted by project staff to have required the most acid, during digestion, of any sample prepared, and included matter that was not digestible. A lab that prepared water samples in bulk, could easily have under-prepared this sample resulting in undissolved particulate matter, that would have escaped analysis.

Because hexavalent chromium is subject to valence changes during transport and handling, quality control is generally performed using samples prepared at the user laboratory. Both staff and the commercial laboratory experienced methods development problems due to contamination in the reagents. Staff, with review board approval, choose to tolerate the 7 ppb level of contamination rather than suffer the expense of locating the source. The commercial lab eventually located and replaced their contaminated reagents. Based on the method of standard additions, staff found that recovery of Cr_{+6} averaged 70%.

Table 9. Evaluation of Analytes Quality Control Standards.
All analyte concentrations are given in μg/L (PPB), n=15.

Analyte	ICAP-19 1:50 True Value	Normalized 95% Confidence Interval (Atomic Absorption)	Project Results	
			Mean	Stand. Dev.
Aluminum	200 ICAP7	170.8-234.0	228	28.4
Arsenic	200	160.0-236.0	208	14.3
Barium	200	NA	202	10.7
Beryllium	200	177.4-220.0	198	5.2
Boron	200	NA	186	60.7
Cadmium	200	169.6-221.6	201	9.0
Calcium	200	NA	262	28.3
Cobalt	200	173.6-224.0	198	6.2
Chromium	200	168.8-230.0	199	6.7
Copper	200	188.8-218.0	200	8.5
Iron	200	165.4-236.0	207	8.8
Magnesium	200	NA	195	10.4
Manganese	200	176.8-218.0	195	7.4
Molybdenum	200	NA	200	9.5
Nickel	200	176.0-226.0	206	9.9
Lead	200	170.2-230.0	203	10.5
Potassium	2000	NA	2840	640
Selenium	200	139.2-226.4	204	13.9
Silicon	106	NA	120	14.9
Silver	200	NA	200	9.2
Titanium	200	NA	197	8.5
Vanadium	200	176.0-225.6	193	8.2
Zinc	200	178.0-222.0	200	9.2

Table 10. Interlaboratory Metal Analytes Comparison.
All analyte concentrations are given in μg/L (PPB).

Analyte	Detection Limit		Sample 200B		Sample 331A	
	SM	IT	SM	IT	SM	IT
Arsenic	6.4	10	13	<10	160	<10
Barium	0.2	200	76	<200	169	200
Cadmium	1.1	5	2	<5	7	<5
Calcium	5.2	5000	41200	61000	53800	44000
Chromium	1.0	10	5	10	31	20
Lead	4.9	3	32	40	79	27
Magnesium	0.4	5000	11400	21000	16000	21000
Nickel	1.5	40	7	<7	17	<40
Selenium	5.0	5	<5	<5	53	7
Silver	0.2	10	3	<10	5	<10
Sodium	29	5000	77500	95000	126000	120000
Zinc	0.5	20	100	140	280	270

Five of the six samples analyzed by both laboratories were in basic agreement, while the sixth was reported at 45 PPB by staff while the certified lab reported 6 μg/L. A sample collected 90 minutes earlier, contained a moderate (32 PPB) concentration of total chromium. The project arithmetic and geometric mean trivalent chromium concentrations were 14.4 and 3.5 μg/L respectively.

Quality control was integral to the project Total Organic Carbon (TOC) analysis. Following instrument warm up, staff injected both 100 and 10 PPM standards and would proceed to the laboratory blank only if agreement was within 2%.

Table 11. Interlaboratory Total Organic Carbon Comparison in mg/L.

Sample #	Santa Monica Results	Commercial Laboratory Results
134A	8.3	12
149A	9.2	10
164A	7.9	8
174A	13.9	12
200A	13.9 (resin run)	21
213A	25	19
248A	23	29
285A	13.6	29
298A	25	37
311A	20	33
332A	72 (resin run)	46

If the blank was at less than 0.5 mg/L, the analysis would proceed, otherwise, the unit was recalibrated using a 5 to 7 injection standardization, then rechecked as above. If sample pairs differed by more than 10%, they were re-injected to verify variation or until a majority showed that an error had occurred during the initial injections. With the exception of samples collected during the long resin runs, sample pairs were normally in agreement. As shown in Table A5, little agreement was observed in the split samples sent for commercial analysis. Initially this was traced to the samples not being acidified and purged of carbon dioxide by the certified labs. Following this discovery, the samples were reanalyzed and the results are reported here. Samples 200 and 332 were collected during resin accumulation runs, when each type of analysis was undertaken and sampling could require 30 or more minutes. In both cases the effluent TOC sample agreed with the commercially tested sample and neither of those agreed with the influent sample. This disagreement is undoubtedly a sampling artifact associated more with coordinating sampling during the resin runs and demonstrates the variability of the flow. Although both laboratories were using the same model of instrument, efforts to improve the analytical correlation were unsuccessful during the latter part of the study. In an effort to verify internal quality assurance, the author did find that if the instrument ran too long between samples, or dilute samples followed more concentrated ones, high results were observed.

Although pesticide analyses were delayed due to instrumental failure, few quality control problems were encountered. During the initial phase of the study, samples were spiked using EPA Water Pollution Quality Control Sample, Chlorinated Hydrocarbon Pesticide III (Lot WP185) at the designated concentration. As presented in table A6, the results were well within the interlaboratory acceptance criteria, even though the samples were <u>all</u> analyzed out of holding time compliance. During the second half of the pesticide analyses, samples were spiked with EPA WQPQCS CHP I (Lot WP385), but at 1/20th the concentration used for the acceptance criteria. In both cases, quality control protocols call for spikes to be added to laboratory water rather than the more challenging field samples utilized here. The results from 13 (=n) spiked samples is presented in table A7. The acceptance criteria was taken from the report issued with the sample, but divided by 20 to normalize for the concentrations used in this series. While some of the mean recoveries were low, this is to be expected given the dilute concentrations spiked and utilization of the difficult storm drain matrix.

Table 12. High Concentration Pesticide Quality Control Samples.
Results taken from seven samples (n=7) and are given in ng/L (PPTr).

Analyte	True Value of Spiked Samples	EPA Accept.Criteria		Project Results	
		Mean Range	S	Mean	S
ß-BHC	2000	780-2600	640	1440	180
Heptachlor epoxide	2000	1130-2630	410	1470	121
Endosulfan I	2000	1140-2820	490	1500	123
Endosulfan II	10000	2200-17100	6100	5600	710
Endrin Aldehyde	10000	mean 8280	3540	4200	960

Table 13. Low Concentration Pesticide Quality Control Samples.
Results taken from 13 samples (n=13) and are given in ng/L (PPTr).

Analyte	True Value of Spiked Samples	Acceptance Crit.		Project Results	
		% Recovery	S	% Recovery	S
Heptachlor	100	42-122	20	62	11.9
Aldrin	100	34-111	21	49	11.3
4,4'-DDE	100	30-145	28	34	9.0
Dieldrin	100	36-146	38	39	10.1
4,4'-DDD	500	31-141	140	32	70
4,4'-DDT	500	25-160	180	30	56

Thirteen of the 14 pesticide samples analyzed by both staff and the certified laboratory, were negative for all analyzed pesticides. Sample 284A was determined by the contract lab to contain Endosulfan Sulfate at their detection limit of 100 PPTr. Since the staff analysis did not detect this pesticide at 20 ng/L, the certified lab was requested to verify the analysis and send copy of the pertinent chromatograms. While the detection was "confirmed" by the certified lab, the project QA officer's review of the chromatograms found a false positive. This determination is based on the pre- and post-sample standard injections of Endosulfan sulfate which had a retention time of 23.03 minutes, while the suspect sample peak was observed at 22.93 minutes. As shown in table A8, 3 spiked samples were shipped to the certified lab, with their mean recovery being comparable to those observed by project staff (table A7).

Table 14. Contract Laboratory Recovery of Spiked Pesticides.
Results are given in ng/L (PPTr).

Analyte/Sam.#	Det.Lim.	200AS	224A	260AS	$\bar{X}$Recovery
Spiking Level	ng/L	200	200	400	N/A
Aldrin	50	100	100	100	42%
α-BHC	50	200	200	300	92%
ß-BHC	50	100	200	200	67%
Γ-BHC	50	200	200	300	92%
δ-BHC	50	200	200	300	92%
4,4'-DDD	100	100	100	100	42%
4,4'-DDE	100	100	80	200	47%
4,4'-DDT	100	100	80	200	47%
Dieldrin	100	100	200	400	83%
Endosulfan I	50	100	200	200	67%
Endosulfan II	100	100	100	<200	<50
Endo. Sulfate	100	ND	100	300	42%
Endrin	100	100	200	200	67%
Heptachlor	50	100	100	100	42%
Hep. Epoxide	50	100	200	300	75%

As proposed in the project quality assurance plan, laboratory control standards were utilized to verify the analytical results for the analysis of purgeable compounds. The mean, standard deviation and range of recoveries, were all well within the EPA 624 method acceptance criteria and shown in table A9, with a comparison to the results obtained during this study. Because of the difficulty in reliable spiking low concentrations of purgeable compounds, no spiked samples were prepared for the certified laboratory.

Table 15. Evaluation of Purgeable Laboratory Control Standards.
Results taken from 3 samples (n=3) and are given in μg/L (PPB).

Analyte	Acceptance Criteria		Project Results	
	Range of Mean	S	Mean	S
Benzene	3.04-5.20	1.38	4.19	0.25
Bromodichloromethane	2.02-5.60	1.28	3.96	0.07
Bromoform	2.28-6.22	1.08	3.95	0.26
Bromomethane	D-8.24	3.58	4.16	0.50
2-Butanone	N/A	N/A	3.81	0.04
Carbon Disulfide	N/A	N/A	3.77	0.61
Carbon Tetrachloride	3.44-4.70	1.04	4.02	0.07
Chlorobenzene	3.28-5.48	1.26	4.02	0.09
Chloroethane	1.68-8.08	2.28	4.30	0.33
2-Chloroethyl Vinyl Ether	D-10.8	5.18	2.77	1.70
Chloroform	2.74-4.84	1.22	3.78	0.18
Chloromethane	D-9.18	3.96	3.94	0.19
Dibromochloromethane	2.76-5.32	1.22	4.00	0.12
1,1-Dichloroethane	2.84-5.70	1.02	3.87	0.05
1,2-Dichloroethane	2.86-5.48	1.20	3.87	0.04
1,1-Dichloroethene	0.74-8.46	1.82	3.88	0.33
trans-1,2-Dichloroethene	2.72-5.70	1.82	3.88	0.33
1,2-Dichloropropane	0.76-7.24	2.76	3.95	0.09
cis-1,3-Dichloropropene	0.20-7.80	3.16	4.78	0.12
trans-1,3-Dichloropropene	1.32-6.48	2.08	3.17	0.02
Ethyl Benzene	3.48-5.34	1.50	3.81	0.18
2-Hexanone	N/A	N/A	3.85	0.40

Table 15 continued. Evaluation of Purgeable Laboratory Control Standards. Results taken from 3 samples (n=3) and are given in μg/L (PPB).

Analyte	Acceptance Criteria		Project Results	
	Range of Mean	S	Mean	S
Methylene Chloride	D-8.20	1.48	3.68	0.22
4-Methyl-2-Pentanone	N/A	N/A	3.94	0.07
Styrene	N/A	N/A	3.91	0.19
1,1,2,2- Tetrachloroethane	2.70-5.44	1.48	4.00	0.12
Tetrachloroethene	3.40-5.32	1.00	4.03	0.10
Toluene	3.32-5.34	0.96	4.11	0.28
1,1,1Trichloroethane	2.74-6.02	0.92	3.93	0.10
1,1,2Trichloroethane	2.86-5.42	1.10	3.91	0.08
Trichloroethene	3.72-5.34	1.32	4.01	0.11
Trichlorofluoro-methane	1.78-6.30	2.00	3.81	0.84
Vinyl Acetate	N/A	N/A	3.58	0.54
Vinyl Chloride	D-8.70	4.00	3.97	0.18
o-Xylene	N/A	N/A	3.87	0.16

As with the other major analyses, the method 625 semi-volatile or extractable analysis was initiated using EPA Water Pollution Quality Control Samples spiked into duplicate field collected samples at the designated concentration of 100 μg/L (PPB). Three spiked samples were prepared using both GC/MS Base Neutral II (Lot WP586) and GC/MS Acids (Phenols) (Lot GAC489). As shown in tables A10 the mean and standard deviation were well within the reported acceptance criteria for all compounds except 2-Methyl-4,6-dinitrophenol, which appears to be due to a typographical error since the standard deviation (S=93.2) is twice the range of the mean (53-100).

Table 16. Evaluation of High Concentration Semi-Volatile Quality Control Stds. Results from 3 samples and are in μg/L (PPB).

Analyte	Acceptance Criteria		Project Results	
	Range of Mean	S	Mean	S
Acenaphthene	60.1-132.3	27.6	73	1.8
Anthracene	43.4-118.0	32.0	86	1.44
Benzo(b)fluoranthene	42.0-140.4	38.3	97	3.3
Benzo(a)pyrene	31.7-148.0	39.0	101	3.1
Benzo(ghi)perylene	D-195	58.9	106	23.
Benzyl Butyl Phthalate	D-139.9	23.4	90	4.6
Bis(2-ethylhexyl) Phthalate	28.9-136.8	41.1	81	3.8
4-Bromophenyl-phenyl Ether	64.7-114.4	23.0	87	1.7
4-Chloro-3-methylphenol	40.8-127.9	37.2	98	4.4
2-Chlorophenol	36.2-120.4	28.7	84	0.36
4-Chlorophenyl-phenyl Ether	38.4-144.7	33.4	85	1.6
Chrysene	44.1-139.9	48.3	95	1.7
Dibenzo(a,h) anthracene	D-199.7	70.0	147	3.5
1,4-Dichlorobenzene	37.3-105.7	32.1	67	2.0
2,4-Dichlorophenol	52.5-121.7	26.4	102	5.1
2,4-Dimethylphenol	41.8-109.0	26.1	86	1.5
Dimethyl Phthalate	D-100.0	23.2	69	4.0
2,4-Dinitrophenol	D-172.9	49.8	121	2.3
Fluoranthene	42.9-121.3	32.8	91	2.7
Fluorene	71.6-108.4	20.7	72	2.7
Hexachloroethane	55.2-100.0	24.5	75	3.1
2-Methyl-4,6-dinitrophenol	53.0-100.0	93.2	138	5.9

Table 16 continued. Evaluation of High Concentration Semi-Volatile Quality Control Standards. Results from 3 samples and are in μg/L.

Analyte	Acceptance Criteria		Project Results	
	Range of Mean	S	Mean	S
Naphthalene	35.6-119.6	30.1	56	6.4
Nitrobenzene	54.3-157.6	39.3	90	4.1
2-Nitrophenol	45.0-166.7	35.2	113	6.4
4-Nitrophenol	13.0-160.5	47.2	113	8.0
Pentachlorophenol	38.1-151.8	48.9	100	2.2
Phenol	16.6-100.0	22.6	50	1.22
2,4,6-Trichlorophenol	52.4-129.2	31.7	111	1.24

It should also be noted that combining, and simultaneously analyzing, the base neutral and acid extracts, a method modification used during this project, produced no discernable analytical artifacts, even with the vary concentrated spiked quality control samples.

During the second phase of the quality control assessment, three duplicate samples were spiked with all of the method 625 analytes, at either 20 or 40 μg/L. The resulting values were multiplied by 5 or 2.5 respectively and compared to method acceptance criteria, which are based on the spiking of laboratory water at 100 μg/L, and are presented in tables A11. As previously suggested, 2-Methyl-4,6-dinitrophenol appears to exceed criteria due to a typographical error. Three other compounds, 2-Chloronaphthalene, Hexachlorobenzene, and 2,4,6-Trichlorophenol,

Table 17. Evaluation of Low Concentration Semi-Volatile Quality Control Stds. Results from 3 samples and are in µg/L (PPB).

Analyte	Acceptance Criteria		Project Results	
	Range of Mean	S	Mean	S
Acenaphthene	60.1-132.3	27.6	94	18
Acenaphthylene	53.5-126.0	40.2	98	15
Aniline	N/A	N/A	8.9	6.8
Anthracene	43.4-118.0	32.0	88	16
Azobenzene	N/A	N/A	120	22
Benzidine	N/A	N/A	27	54
Benzo(a)anthracene	41.8-133.0	27.6	98	14.5
Benzo(b)fluoranthene	42.0-140.4	38.3	104	19
Benzo(k)fluoranthene	25.2-145.7	32.3	84	22
Benzo(a)pyrene	31.7-148.0	39.0	93	17
Benzo(ghi)perylene	D-195	58.9	114	34
Benzoic Acid	N/A	N/A	76	59
Benzyl Butyl Phthalate	D-139.9	23.4	108	13.8
bis(2-chloroethoxy) methane	49.2-164.7	34.5	97	16
bis(2-chloroethyl) ether	42.9-126.0	55.0	90	14.9
bis(2-chloro-isopropyl) ether	62.8-138.6	46.3	86	8.3
bis(2-ethylhexyl) Phthalate	28.9-136.8	41.1	81	3.8
4-Bromophenyl-phenyl Ether	64.7-114.4	23.0	87	1.7
4-Chloroaniline	N/A	N/A	26	23
4-Chloro-3-methylphenol	40.8-127.9	37.2	98	4.4
2-Chloronaphthalene	64.5-113.5	13.0	97	24
2-Chlorophenol	36.2-120.4	28.7	102	11.4
4-Chlorophenyl-phenyl Ether	38.4-144.7	33.4	85	1.6
Chrysene	44.1-139.9	48.3	98	19

Table 17 continued. Evaluation of High Concentration Semi-Volatile Quality Control Standards. Results from 3 samples and are in $\mu g/L$.

Analyte	Acceptance Criteria		Project Results	
	Range of Mean	S	Mean	S
Dibenzo(a,h) anthracene	D-199.7	70.0	112	33
Dibenzofuran	N/A	N/A	103	30
1,2-Dichlorobenzene	48.6-112	30.9	65	11
1,3-Dichlorobenzene	16.7-153.9	41.7	61	10.6
1,4-Dichlorobenzene	37.3-105.7	32.1	67	2.0
3,3'-Dichlorobenzidine	8.2-212.5	71.4	33	24
2,4-Dichlorophenol	52.5-121.7	26.4	107	18
2,4-Dimethylphenol	41.8-109.0	26.1	86	1.5
Diethyl Phthalate	D-100	26.5	89	8.3
Dimethyl Phthalate	D-100.0	23.2	69	4.0
2,4-Dinitrophenol	D-172.9	49.8	121	2.3
2,4-Dinitrotoluene	47.5-126.9	21.8	119	21
2,6-Dinitrotoluene	68.1-136.7	29.6	110	22
Di-n-octyl Phthalate	18.6-131.8	31.4	107	12.2
Fluoranthene	42.9-121.3	32.8	117	22
Fluorene	71.6-108.4	20.7	93	14.4
2-Fluorobiphenyl (Surrogate)	N/A	N/A	22	6.9
2-Fluorophenol (Surrogate)	N/A	N/A	13.7	1.9
Hexachlorobenzene	7.8-141.5	24.9	109	28
Hexachlorobutadiene	37.8-102.2	26.3	65	21
Hexachlorocyclopentadiene	N/A	N/A	62	21
Hexachloroethane	55.2-100.0	24.5	56	10.9
Indeno(1,2,3-cd) pyrene	D-150.9	44.6	108	30
Isophorone	46.6-180.2	63.3	93	12.9

Table 17 continued. Evaluation of High Concentration Semi-Volatile Quality Control Standards. Results from 3 samples and are in μg/L.

Analyte	Acceptance Criteria		Project Results	
	Range of Mean	S	Mean	S
2-Methyl-4,6-dinitrophenol	53.0-100.0	93.2	125	22
2-Methylnaphthalene	N/A	N/A	125	43
2-Methylphenol	N/A	N/A	84	11.0
4-Methylphenol	N/A	N/A	81	11.9
Naphthalene	35.6-119.6	30.1	90	26
2-Nitroaniline	N/A	N/A	142	46
3-Nitroaniline	N/A	N/A	98	65
4-Nitroaniline	N/A	N/A	142	43
Nitrobenzene	54.3-157.6	39.3	102	17
Nitrobenzene-d5 (Surrogate)	N/A	N/A	24	7.9
2-Nitrophenol	45.0-166.7	35.2	121	24
4-Nitrophenol	13.0-160.5	47.2	36	36
N-Nitrosodimethylamine	N/A	N/A	59	5.5
N-Nitrosodi-n-propylamine	13.6-197.9	55.4	90	14.5
N-Nitrosodiphenylamine	N/A	N/A	160	65
Pentachlorophenol	38.1-151.8	48.9	137	25
Phenanthrene	65.2-108.7	20.6	106	16
Phenol	16.6-100.0	22.6	55	6.5
Phenol-d6 (Surr)	N/A	N/A	10.4	1.12
Pyrene	69.6-100.0	25.2	96	12
4-Terphenyl-d14(Sur)	N/A	N/A	25	7.5
2,4,6-Tribromophenol(Surr)	N/A	N/A	27	7.6
1,2,4-Trichlorobenzene	57.3-129.2	28.1	73	17
2,4,5-Trichlorophenol	N/A	N/A	100	20
2,4,6-Trichlorophenol	52.4-129.2	31.7	129	34

are slightly out of acceptance criteria for the standard deviation. Given that acceptance criteria are normally based on 7 laboratory water extractions at higher concentrations, these variances do not warrant concern. Finally, sample 200A was collected in duplicate and both were spiked with 40 μg/L. They were then analyzed by either staff or the certified laboratory. The results are given in tables A12 and show a general agreement at levels above the CLP detection limits of 10 to 50 PPB. Sample 260A was analyzed by the contract laboratory and reported to contain 2-methyl phenol (o-Creosol) at 19 μg/L, while a duplicate analyzed by staff did not confirm the finding. The QA officers review of the contract labs analysis concurs with their findings. Since the two labs were in disagreement, only the staffs findings were reported in the report. However if this value had been included, the most significant change would have been in the total maximum value of phenols, which would have risen to 34 PPB while the Ocean Plan standard, with 5:1 dilution, is 150.

The quality assurance and quality control for the resin accumulation and ames assays were undertaken by staff under the direction of Dr. J. Froines. They generally followed EPA protocols and utilized blanks and controls. Further information on the specific efforts and results of those efforts can be obtained by contacting the author or Dr. Froines of the University of California at Los Angeles, School of Public Health.

Table 18. Interlaboratory Semi-Volatile Quality Control Evaluation.
Results are given in μg/L (PPB).

Analyte	Certified Laboratory			Project Results	
	D.L.	Conc.	% Recov	Conc.	% Recov
Acenaphthene	10	37	92	44	110
Acenaphthylene	10	35	88	44	110
Anthracene	10	32	80	29	73
Azobenzene	10	33	82	58	145
Benzidine	10	ND	<25	43	107
Benzo(a)anthracene	10	32	80	38	96
Benzo(b)fluoranthene	10	31	78	40	101
Benzo(k)fluoranthene	10	29	72	33	82
Benzo(a)pyrene	10	30	75	35	88
Benzo(ghi)perylene	10	28	70	37	92
Benzoic Acid	50	ND	<DL	ND	<DL
Benzyl Alcohol	10	37	92	42	106
Benzyl Butyl Phthalate	10	15	38	39	97
bis(2-chloroethoxy) methane	10	38	95	41	102
bis(2-chloroethyl) ether	10	40	100	43	108
bis(2-chloro-isopropyl) ether	10	36	90	36	89
bis(2-ethylhexyl) Phthalate	10	31	78	43	108
4-Bromophenyl-phenyl Ether	10	31	78	47	118
4-Chloroaniline	10	ND	<25	6.0	15
4-Chloro-3-methylphenol	10	41	102	36	89
2-Chloronaphthalene	10	34	85	48	120
2-Chlorophenol	10	37	92	43	108

Table 18 continued. Interlaboratory Semi-Volatile Quality Control Evaluation. Results are given in μg/L (PPB).

Analyte	Certified Laboratory			Project Results	
	D.L.	Conc	% Recov	Conc	% Recov
4-Chlorophenylphenyl Ether	10	ND	<25	4.7	12
Chrysene	10	32	80	40	99
Dibenzo(a,h) anthracene	10	30	75	37	92
Dibenzofuran	10	44	110	27	67
1,2-Dichlorobenzene	10	26	65	32	81
1,3-Dichlorobenzene	10	22	55	30	76
1,4-Dichlorobenzene	10	24	60	32	81
3,3'-Dichlorobenzidine	20	ND	<50	16	40
2,4-Dichlorophenol	10	36	90	41	103
2,4-Dimethylphenol	10	36	90	40	99
Diethyl Phthalate	10	ND	<25	37	92
Dimethyl Phthalate	10	ND	<25	34	85
2,4-Dinitrophenol	50	ND	<DL	29	71
Di-n-butyl Phthalate	10	18	45	49	122
2,4-Dinitrotoluene	10	28	70	48	121
2,6-Dinitrotoluene	10	39	98	39	97
Di-n-octyl Phthalate	10	26	65	37	92
Fluoranthene	10	32	80	58	145
Fluorene	10	38	95	42	106
Hexachlorobenzene	10	31	78	59	147
Hexachlorobutadiene	10	24	60	37	93
Hexachlorocyclopentadiene	10	ND	<25	23	57
Hexachloroethane	10	18	45	28	70
Indeno(1,2,3-cd) pyrene	10	25	62	38	94

Table 18 continued. Interlaboratory Semi-Volatile Quality Control Evaluation. Results are given in $\mu g/L$ (PPB).

Analyte	Certified Laboratory			Project Results	
	D.L.	Conc.	% Recov	Conc.	% Recov
Isophorone	10	40	100	34	86
2-Methyl-4,6-dinitrophenol	50	ND	<DL	51	126
2-Methylnaphthalene	10	46	115	73	182
2-Methylphenol	10	35	88	32	80
4-Methylphenol	10	34	85	29	73
Naphthalene	10	36	90	50	126
2-Nitroaniline	50	ND	<DL	56	139
3-Nitroaniline	50	65	162	46	115
4-Nitroaniline	50	69	172	54	135
Nitrobenzene	10	41	102	46	115
2-Nitrophenol	10	34	85	49	121
4-Nitrophenol	50	66	165	ND	<DL
N-Nitrosodimethylamine	10	ND	<25	25	62
N-Nitrosodi-n-propylamine	10	40	100	103	260
N-Nitrosodiphenylamine	10	40	100	34	85
Pentachlorophenol	50	ND	<DL	63	159
Phenanthrene	10	34	85	50	124
Phenol	10	42	105	21	53
Pyrene	10	31	78	36	91
1,2,4-Trichlorobenzene	10	30	75	39	97
2,4,5-Trichlorophenol	50	ND	<DL	46	115
2,4,6-Trichlorophenol	10	38	95	69	173

A major emphasis of this study, was the estimation of bacterial numbers. All of the bacterial densities are expressed in terms of the most probable number per 100 ml of water. While some of the certified laboratory analyses actually used a membrane filtration method (primarily the enterococcus analyses), the distinction is irrelevant for the purposes of analyzing the results. Routine quality control followed the recommendations of the manufacturer Environetics (formerly Access Analytical), and included weekly culturing of Pseudomonas aeruginosa (a non coliform organism), the total coliform bacteria Klebsiella pneumoniae, and the primary fecal coliform microbe Escherichia coli.

During the project, 48 influent/effluent pairs were analyzed by both project staff and the contract laboratory for both total and fecal coliform organisms. The contract lab also analyzed their 48 pairs for fecal streptococcus as shown in table A13. Thus, 192 pair-wise comparisons can be made between the staff and contract laboratory analyses. Early in the study (see sample #173-175), the project QA officer became disturbed with discrepancies in the outcomes of these comparisons. Initially, the contract laboratory responded by adding additional blue ice to further chill the samples or by supplying more sturdy sample collection containers. However, these changes were generally short lived and even with frequent remainders from the QA officer, shortages occurred.

In order to define the source of these errors, EPA Microbiological Quality

Control Samples were utilized. The Escherichia coli (lot series 121589), or fecal coliform, sample was diluted 1:99, then 7 sterile dilution bottles were inoculated with 1 ml from the first dilution bottle. Two of these seven were analyzed by each of the three staff members who performed the bulk of the bacterial analyses. The remaining seventh bottle was then poured into the whirl bag sample container and shipped to the certified laboratory marked as a spiked sample (300AS1). The analysis for total coliform was conducted using a Klebsiella pneumoniae quality control sample (lot series 060989) prepare in an identical fashion and marked as sample 300AS2. For both analyses the staff samples were all well within the 95% confidence interval for MMO-MUG type analyses. In the case of total coliforms, the staff mean was 490,000 organisms per 100 ml, compared to the EPA mean reported value of 510,000. The sample analyzed by the contract lab was reported to contain 2,400,000 organisms per 100 ml, and was outside of the 95% confidence interval. The results for fecal coliform were similar. The mean staff MPN was 320,000, with all enumeration in 95% confidence interval, while the EPA mean was 350,000 organisms per 100 ml. The certified laboratory analysis returned a value of 70,000 and was outside of the acceptance criteria confidence interval. It was also noted that after these results were reported back to the contract lab, the remaining analyses (sample numbers ≥310) more closely correlated with the results obtained by staff.

Table 19. Interlaboratory Bacterial Analyses.
Results are in terms of Most Probable Number (MPN) per 100 ml.

Sample Number	Total Coliform		Fecal Coliform		Enterococcus Contract Laboratory
	Santa Monica	Contract Laboratory	Santa Monica	Contract Laboratory	
134A	350,000	700,000	35,000	70,000	49,000
134B	79	33	14	11	8
135A	1,300,300	460,000	92,000	79,000	110,000
135B	79	49	4	4	4
136A	240,000	490,000	92,000	49,000	130,000
136B	79	<2	27	23	5
149A	1,600,000	230,000	17,000	13,000	4,900
149B	4	<2	<2	6	13
150A	920,000	70,000	350,000	7,000	330,000
150B	130	1,100	8	14	33
151A	92,000	230,000	24,000	4,300	7,900
151B	33	310	2	4	8
164A	3,500,000	490,000	22,000	11,000	130,000
164B	1,400	13,000	4	49	230
165A	2,400,000	230,000	11,000	22,000	350,000
165B	3,300	7,900	4	22	110
166A	210,000	2,800,000	1,700	7,600	23,000
166B	16,000	13,000	<2	5	79
173A	1,700,000	46,000	54,000	7,900	79,000
173B	240	<2	4	<2	49
174A	220,000	79,000	54,000	11,000	49,000
174B	130	8	<2	2	33
175A	1,700,000	33,000	24,000	3,300	230,000
175B	110	8	4	<2	49
182A	350,000	330,000	17,000	9,500	130,000
182B	350	790	<2	2	31
183A	220,000	110,000	54,000	7,900	79,000
183B	79	110	<2	2	21

Table 19 continued. Interlaboratory Bacterial Analyses.
Results are in terms of Most Probable Number (MPN) per 100 ml.

Sample Number	Total Coliform		Fecal Coliform		Enterococcus Contract Laboratory
	Santa Monica	Contract Laboratory	Santa Monica	Contract Laboratory	
184A	220,000	230,000	2,300	7,900	79,000
184B	210	490	<2	5	7,000
200A	790,000	79,000	170,000	33,000	2,200
200B	350	26	17	2	33
201A	220,000	490,000	24,000	23,000	11,000
201B	130	79	4	<2	23
202A	220,000	790,000	2,700	49,000	49,000
202B	41	22	2	<2	79
212A	1,600,000	490,000	92,000	46,000	170,000
212B	460	4,900	27	33	79
213A	1,700,000	230,000	54,000	49,000	33,000
213B	240	1,300	4	22	33
214A	920,000	330,000	160,000	22,000	130,000
214B	540	490	2	5	84
224A	92,000	130,000	35,000	22,000	7,000
224B	2	<2	<2	<2	2
225A	700,000	490,000	22,000	2,200	3,300
225B	17	5	<2	<2	<2
226A	160,000	230,000	24,000	700	79,000
226B	17	8	<2	<2	2
239A	350,000	49,000	22,000	7,900	150,000
239B	34	70	<2	5	49
240A	350,000	79,000	35,000	13,000	64,000
240B	260	<2	330	49	20
241A	4,600,000	1,300,000	17,000	79,000	140,000
241B	120,000	110	79	4	33
248A	350,000	230,000	54,000	14,000	35,000
248B	34	220	<2	2	33

Table 19 continued. Interlaboratory Bacterial Analyses.
Results are in terms of Most Probable Number (MPN) per 100 ml.

Sample Number	Total Coliform		Fecal Coliform		Enterococcus Contract Laboratory
	Santa Monica	Contract Laboratory	Santa Monica	Contract Laboratory	
249A	40,000	330,000	24,000	17,000	23,000
249B	2	49	2	5	7
250A	220,000	79,000	17,000	4,900	4,900
250B	<2	13	<2	2	27
260A	95,000	130,000	24,000	7,000	79,000
260B	<2	5	<2	<2	8
261A	1,700,000	490,000	280,000	22,000	70,000
261B	33	14	<2	7	7
262A	1,600,000	1,100,000	17,000	49,000	170,000
262B	79	14	4	5	2
269A	35,000	33,000	24,000	3,300	7,900
269B	6	8	4	<2	<2
270A	92,000	79,000	22,000	22,000	17,000
270B	4	23	2	5	46
271A	920,000	490,000	39,000	22,000	11,000
271B	11	46	<2	2	49
283A	2,400,000	4,900,000	170,000	79,000	170,000
283B	17	23	<2	5	33
284A	9,200,000	7,900,000	2,200,000	130,000	79,000
284B	31	79	8	8	8
285A	14,000,000	9,500,000	2,400,000	790,000	790,000
285B	79	49	13	17	2
298A	240,000	220,000	11,000	17,000	49,000
298B	140	22	<2	<2	79
299A	140,000	49,000	17,000	7,900	49,000
299B	9,200	1,700	13	21	790
310A	1,600,000	1,300,000	64,000	33,000	790,000
310B	11	33	<2	<2	23

Table 19 continued. Interlaboratory Bacterial Analyses.
Results are in terms of Most Probable Number (MPN) per 100 ml.

Sample Number	Total Coliform		Fecal Coliform		Enterococcus Contract Laboratory
	Santa Monica	Contract Laboratory	Santa Monica	Contract Laboratory	
300AS1	320,000*	70,000	320,000*	70,000	<2
300AS2	490,000**	2,400,000	<2	<2	<2
311A	540,000	490,000	110,000	33,000	490,000
311B	4	11	<2	<2	79
312A	540,000	790,000	35,000	79,000	1,700,000
312B	350	230	8	7	79
331A	4,600,000	17,000,000	110,000	49,000	220,000
331B	240	79	14	2	230
332A	3,500,000	11,000,000	110,000	33,000	790,000
332B	13	220	<2	2	330
333A	54,000,000	22,000,000	2,400,000	790,000	790,000
333B	11,000	790	240	330	1,700

* Sample 300AS1 is the mean of 540,000; 170,000; 240,000; 240,000; 540,000; & 170,000. EPA mean is 350,000; 95% CI 1,100,000-110,000.

** Sample 300AS2 is the mean of 920,000; 350,000; 170,000; 240,000; 1,100,000 & 170,000. EPA mean is 510,000; 95% CI 1,400,000-130,000.

In summary, all of the analyses in the Quality Assurance Plan were carefully evaluated to insure the quality of the results. Most of the analyses and analysts demonstrated their competence through the use of EPA Water Quality Control Samples. While any individual analysis maybe outside of the 95% confidence interval around the true value, there is no indication of any bias or significant inaccuracy. The data acquired by the project staff is of generally excellent quality and many of the primary conclusions of the study would not have been possible without the conscientious efforts of each analyst individually, and more importantly, as an analytical team.

OZONE DISINFECTION AND TREATMENT OF URBAN STORM DRAIN DRY-WEATHER FLOWS

A PILOT TREATMENT PLANT DEMONSTRATION PROJECT ON THE KENTER CANYON STORM DRAIN SYSTEM IN SANTA MONICA

TECHNICAL AND DATA APPENDICES

(Dissertation Format)

APPENDIX IB

DATA SUMMARY AND COMPARISON TO RELEVANT STANDARDS

Table 20A. Evaluation of Pilot Plant Process Parameters Before and After Ozonation.

Pilot Plant Operating Process Parameter	Units[1]	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\overline{X}$	σ	90%	$\overline{X}$	σ	90%	$\overline{X}$	σ	90%	$\overline{X}$	σ	90%
Water Flow Rate	GPM	3.1	1.11	4.5	2.9	1.48	4.8	NA	NA	NA	NA	NA	NA
Gas Flow Rate	SCFH	12.9	3.4	17.	12.3	1.35	18.	NA	NA	NA	NA	NA	NA
Influent Ozone	Wt.%	2.7	1.09	4.1	2.4	1.7	4.7	NA	NA	NA	NA	NA	NA
Off-gas Ozone	Wt.%	NA	NA	NA	NA	NA	NA	.61	.53	1.29	.32	4.7	2.3
Absorbed Ozone	mg/L	NA	NA	NA	NA	NA	NA	13.0	4.9	19.	12.0	1.48	20.
Ozone Residual	mg/L	NA	NA	NA	NA	NA	NA	1.47	1.60	3.5	.31	16.	11.0

Table 20B. Pilot Plant Process Parameters.

Physical Analysis or Analyte Name	Units[1]	MDL 3σ	LOQ 10σ	Travel Blanks $\overline{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Water Flow Rate	GPM	NA	0.5	NA	1.0	8.0	438	NA	NA
Gas Flow Rate	SCFH	NA	2.0	NA	4.0	18.	438	NA	NA
Influent Ozone	Wt.%	NA	.005	NA	.34	5.1	387	NA	NA
Off-gas Ozone	Wt.%	NA	.005	NA	<MDL	2.2	387	NA	NA
Absorbed Ozone	mg/L	NA	NA	NA	3.6	38.	414	NA	NA
Ozone Residual	mg/L	NA	.005	NA	<MDL	7.8	430	NA	NA

[1] Units are Gallons Per Minute (GPM), Standard Cubic Feet per Hour (SCFH), Weight Percent (Wt.%), and mg/L (PPM).

Table 21A. Evaluation of Pilot Plant Physical Parameters Before and After Ozonation.

Physical Analysis Name	Units	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Temperature	°C	18.5	1.7	20.7	18.2	1.10	20.5	18.8	1.8	21.1	18.6	1.10	21.0
pH	units	8.1	.29	8.5	8.1	1.04	8.5	7.8	.32	8.2	7.8	1.04	8.2
Conductance	μmho/cm	1310	2200	4100	1070	1.5	1900	1300	2100	4000	1070	1.5	1900
Turbidity	NTU	83	370	550	22	3.5	110	71	250	390	21	3.5	106
Settleable Solids	ml/L	.52	5.3	7.3	<LOQ	6.6	2.1	.52	5.0	6.9	<LOQ	6.6	2.2
Suspended Solids	mg/L	103	500	740	22	4.0	129	97	440	660	19	4.2	122
Dissolved Solids	mg/L	870	1650	3000	690	1.6	1250	900	1700	3100	710	1.7	1500
Total Solids	mg/L	1010	1800	3300	780	1.7	1500	1010	1800	3300	780	1.7	1500

TABLE 21B. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analyses.

Physical Analysis Name	Units	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Temperature	°C	NA	-10	NA	14.0	24.4	430	NA	NA
pH	units	NA	NA	NA	7.1	9.6	401	6.0 - 9.0	6.5-8.5
Conductance	μmho/cm	NA	NA	NA	470	36000	332	NA	1600
Turbidity	NTU	0.1	0.3	NA	2.3	5800	349	75	0.5
SettleableSolid	ml/L	NA	.20	NA	<LOQ	78	438	1.0	NA
SuspendedSolids	mg/L	1.2	4.0	NA	0.6	6540	434	60	NA
DissolvedSolids	mg/L	3.0	10.0	NA	190	30000	435	NA	1000
Total Solids	mg/L	3.0	10.0	NA	280	31000	435	NA	NA

Table 22A. Evaluation of Bacterial and Organic Analyses With Ozone Treatment.

Bacterial Group and Multiplier or Total Organic Carbon Analysis	Units[1]	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Total Coli.x10^6	MPN	1.49	3.4	5.9	.520	4.5	3.6						
Total Coli.x10^3	MPN							7.6	4.4	13.2	.160	160	5.6
Fecal Coli.x10^3	MPN	160	670	1020	19	7.8	260	.520	4.2	5.9	.007	7.2	.088
Enterococc.x10^3	MPN	190	310	590	69	4.8	510	.250	1.04	1.6	.030	5.9	.290
Total Organic C	mg/L	19	16	40	15	1.9	35	19	15	38	16	1.8	34

Table 22B. Bacterial and TOC Quality Assurance Parameters, and Standards, Before and After Ozonation.

Bacterial Group and Multiplier or TOC Analysis	Units[1]	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilu.	Drinking Water Standard
Total Coli.x10^3	MPN	NA	2	<LOQ	<LOQ	54000	438	5.	One
Fecal Coli.x10^3	MPN	NA	2	<LOQ	<LOQ	7900	436	1.	None
Enterococc.x10^3	MPN	NA	2	<LOQ	<LOQ	1700	47	0.12	None
Total Organic C	mg/L	.07	.20	<1.5	2.2	124	425	25 as Oil/G	NA

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[1] Units are Most Probable Number of organisms per 100 ml of water (MPN) and mg/L (PPM).

Table 23A-1. Evaluation of Metal Analytes (Method 200.7) Before and After Ozonation.

Chemical Analyte Name	Units[1]	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Aluminum	μg/L	1230	4100	6500	390	2.8	1470	1370	4100	6600	380	3.2	0.00
Arsenic	μg/L	23	56	95	10.2	3.8	61	25	58	100	13.1	3.2	63
Barium	μg/L	68	45	127	61	1.5	104	73	56	145	62	1.7	120
Beryllium	μg/L	.13	.41	.66	.090	1.29	.51	.16	.43	.71	.107	1.30	.19
Boron	μg/L	1170	1010	2500	870	2.1	2300	1120	830	2200	760	3.8	4200
Cadmium	μg/L	2.7	2.6	6.0	2.0	2.0	6.3	2.8	3.1	6.7	2.8	2.2	6.7
Calcium	mg/L	50	43	105	45	1.48	74	44	29	81	40	1.45	64

Table 23B-1. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Chemical Analyte Name	Units[1]	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Aluminum	μg/L	19	65	28	125	31000	156	NA	1000
Arsenic	μg/L	6.4	21	9.2	<MDL	730	193	33	50
Barium	μg/L	.20	.67	.75	25	400	193	NA	1000
Beryllium	μg/L	.06	.20	<.01	<MDL	3	193	NA	Prop. 1
Boron	μg/L	21	70	134	<MDL	6500	156	NA	NA
Cadmium	μg/L	1.1	3.7	1.00	<MDL	16	193	5	10
Calcium	mg/L	.005	.017	.018	20.4	540	193	NA	NA

[1] Concentrations are in gr/L (PPTh), mg/L (PPM), μg/L (PPB), ng/L (PPTr), and pg/L (PPQ).

Table 23A-2. Evaluation of Metal Analytes (Method 200.7) Before and After Ozonation.

Chemical Analyte Name	Units[1]	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Chromium	μg/L	14.4	70	104	3.5	4.0	20	21	95	144	2.2	4.7	22
Chromium (+6)	μg/L	31	107	170	12.9	2.6	43	29	102	160	11.7	2.6	41
Cobalt	μg/L	10.2	10.0	23	7.1	2.3	23	11.2	10.8	25	8.1	2.2	24
Copper	μg/L	34	22	62	29	1.7	59	38	24	68	32	1.7	66
Iron	μg/L	1490	5100	8000	470	3.0	1900	2100	5900	9600	600	3.3	2800
Lead	μg/L	59	82	164	33	3.2	148	89	127	250	42	3.8	240
Lithium	μg/L	28	11.5	43	27	1.45	42	28	11.4	42	26	1.5	45

Table 23B-2. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation.

Chemical Analyte Name	Units[1]	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Chromium	μg/L	.98	3.3	1.6	<MDL	700	193	10	50
Chromium (+6)	μg/L	6.0	20	4.0	<MDL	1020	95	10	50
Cobalt	μg/L	2.6	8.7	3.2	<MDL	92	193	NA	NA
Copper	μg/L	1.3	4.3	2.0	7.0	136	193	8	1000
Iron	μg/L	.75	2.5	14.0	60	40000	193	NA	300
Lead	μg/L	4.9	16	6.4	<MDL	740	193	10	$X<15$
Lithium	μg/L	.10	.33	1.8	10	72	193	NA	NA

[1] Concentrations are in gr/L (PPTh), mg/L (PPM), μg/L (PPB), ng/L (PPTr), and pg/L (PPQ).

Table 23A-3. Evaluation of Metal Analytes (Method 200.7) Before and After Ozonation.

Chemical Analyte Name	Units[2]	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Magnesium	mg/L	14.5	4.5	20	14.1	1.32	20	14.0	5.3	21	13.2	1.48	22
Manganese	µg/L	45	74	139	27	2.4	84	43	81	146	21	2.8	81
Molybdenum	µg/L	79	84	190	34	4.8	260	35	49	97	13.8	4.5	100
Nickel	µg/L	6.3	7.6	16	3.6	2.8	16	6.4	7.8	16	3.6	2.8	16
Phosphorus	µg/L	1900	1240	3500	1500	2.1	4000	2000	1400	3700	1600	1.78	3500
Potassium	mg/L	11.9	5.8	19	10.7	1.7	22	11.4	5.0	18	10.2	1.7	20
Selenium	µg/L	7.8	13.6	25	2.2	4.0	18	6.7	17	29	1.3	3.9	12.4

Table 23B-3. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation.

Chemical Analyte Name	Units[1]	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Magnesium	µg/L	0.4	1.3	2.1	940	41000	193	NA	NA
Manganese	µg/L	.013	.043	.13	<MDL	535	193	NA	50
Molybdenum	µg/L	2.4	8.0	4.9	<MDL	380	193	NA	NA
Nickel	µg/L	1.5	5.0	1.25	<MDL	47	193	25	100
Phosphorus	µg/L	51	170	69	<MDL	9900	193	NA	NA
Potassium	mg/L	.131	.440	.490	.62	55	193	NA	NA
Selenium	µg/L	5.0	16.7	7.8	<MDL	112	193	75	10

[2] Concentrations are in gr/L (PPTh), mg/L (PPM), µg/L (PPB), ng/L (PPTr), and pg/L (PPQ).

Table 23A-4. Evaluation of Metal Analytes (Method 200.7) Before and After Ozonation.

Chemical Analyte Name	Units	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Silicon	mg/L	11.8	2.3	14.8	11.5	1.29	16	10.9	2.4	13.9	10.5	1.45	17
Silver	μg/L	0.6	1.6	2.6	.29	1.7	1.6	.51	1.25	2.1	.29	1.7	1.47
Sodium	mg/L	144	78	240	132	1.50	220	126	82	230	102	2.8	390
Strontium	μg/L	350	260	690	320	1.48	520	330	320	740	290	1.5	490
Tin	μg/L	58	74	150	42	6.9	105	74	65	160	59	1.9	133
Titanium	μg/L	24	66	108	8.3	3.1	39	28	83	135	6.4	3.9	42
Vanadium	μg/L	11.4	12.0	27	9.2	1.7	19	12.2	13.5	30	9.2	1.9	22
Zinc	μg/L	86	93	200	61	2.1	160	100	80	200	82	1.8	170

Table 23B-4. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation.

Chemical Analyte Name	Units	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Silicon	μg/L	6.9	23	5.9	940	22000	193	NA	NA
Silver	μg/L	.14	.47	1.9	<MDL	14	193	3.4	50
Sodium	mg/L	.029	.097	.103	59	28000	193	NA	NA
Strontium	μg/L	.14	.47	.38	142	2600	193	NA	NA
Tin	μg/L	7.0	23	11.0	<MDL	576	193	NA	NA
Titanium	μg/L	.32	1.07	.88	<MDL	590	193	NA	NA
Vanadium	μg/L	.95	3.2	1.6	<MDL	101	193	NA	NA
Zinc	μg/L	.47	1.6	2.9	13	700	193	80	5000

Table 24A-1. Evaluation of Pesticides (Method 608) Analytes Before and After Ozonation.

Pesticide or Chemical Analyte Name	ng/L or PPTr	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Aldrin	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
α-BHC (α-HCH)	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
ß-BHC (ß-HCH)	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
δ-BHC (δ-HCH)	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Γ-HCH (Lindane)	ng/L	.94	5.1	7.5	.122	1.86	1.49	.64	4.2	6.0	.072	1.7	1.05
Chlordane	ng/L	133	670	990	.86	7.2	23	59	234	360	.78	6.2	17
4,4'-DDD	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
4,4'-DDE	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND

Table 24B-1. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Pesticide or Chemical Analyte Name	ng/L or PPTr	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilu.	Drinking Water Standard
Aldrin	ng/L	NA	20	ND	ND	ND	86	0.11	NA
α-BHC (α-HCH)	ng/L	NA	20	ND	ND	ND	86	Σ HCHs 20	NA
ß-BHC (ß-HCH)	ng/L	NA	20	ND	ND	ND	86	Σ HCHs 20	NA
δ-BHC (δ-HCH)	ng/L	NA	20	ND	ND	ND	86	Σ HCHs 20	NA
Γ-HCH (Lindane)	ng/L	NA	20	ND	ND	34	86	Σ HCHs 20	4000
Chlordane(tech)	ng/L	NA	200	ND	ND	5700	86	ΣChl 0.115	NA
4,4'-DDD	ng/L	NA	20	ND	ND	ND	86	ΣDDTs0.85	NA
4,4'-DDE	ng/L	NA	20	ND	ND	ND	86	ΣDDTs0.85	NA

Table 24A-2. Evaluation of Pesticides (Method 608) Analytes Before and After Ozonation.

Pesticide or Chemical Analyte Name	ng/L or PPTr	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
4,4'-DDT	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Dieldrin	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Endosulfan I	ng/L	.35	3.2	4.5	.040	1.45	.67	.26	2.4	3.3	.037	1.40	.60
Endosulfan II	ng/L	<LOQ	NA	<LOQ	<LOQ	NA	<LOQ	<LOQ	NA	<LOQ	<LOQ	NA	<LOQ
Endosu. Sulfate	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Endrin	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Endrin Aldehyde	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Heptachlor	ng/L	2.2	11.3	17	.19	2.2	2.3	1.33	7.4	10.8	.134	1.9	1.7

Table 24B-2. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Pesticide or Chemical Analyte Name	ng/L or PPTr	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilu.	Drinking Water Standard
4,4'-DDT	ng/L	NA	20	ND	ND	ND	86	ΣDDTs0.85	NA
Dieldrin	ng/L	NA	20	ND	ND	ND	86	0.2	NA
Endosulfan I	ng/L	NA	20	ND	ND	30	86	ΣEndo.s 45	NA
Endosulfan II	ng/L	NA	20	ND	ND	<LOQ	86	ΣEndo.s 45	NA
Endosu. Sulfate	ng/L	NA	20	ND	ND	ND	86	ΣEndo.s 45	NA
Endrin	ng/L	NA	20	ND	ND	ND	86	10	200
Endrin Aldehyde	ng/L	NA	20	ND	ND	ND	86	NA	NA
Heptachlor	ng/L	NA	20	ND	ND	90	86	ΣHept.s 3.6	NA

Table 24A-3. Evaluation of Pesticides (Method 608) Analytes Before and After Ozonation.

Pesticide or Chemical Analyte Name	ng/L or PPTr	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\overline{X}$	σ	90%	$\overline{X}$	σ	90%	$\overline{X}$	σ	90%	$\overline{X}$	σ	90%
Heptac. Epoxide	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Methoxychlor	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Mirex	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Toxaphene	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
PCB-1016,1221	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
PCB-1232,1242	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
PCB-1248	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
PCB-1254,1260	ng/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND

Table 24B-3. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Pesticide or Chemical Analyte Name	ng/L or PPTr	MDL 3σ	LOQ 10σ	Travel Blanks $\overline{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Heptac. Epoxide	ng/L	NA	20	ND	ND	ND	86	ΣHept.s 3.6	NA
Methoxychlor	ng/L	NA	20	ND	ND	ND	86	NA	NA
Mirex	ng/L	NA	20	ND	ND	ND	86	NA	NA
Toxaphene	ng/L	NA	1000	ND	ND	ND	86	1.05	5000
PCB-1016,1221	ng/L	NA	300	ND	ND	ND	86	ΣPCB0.095	NA
PCB-1232,1242	ng/L	NA	300	ND	ND	ND	86	ΣPCB0.095	NA
PCB-1248	ng/L	NA	300	ND	ND	ND	86	ΣPCB0.095	NA
PCB-1254,1260	ng/L	NA	300	ND	ND	ND	86	ΣPCB0.095	NA

Table 25A-1. Evaluation of Volatile Organic Analytes (Method 624) With Ozonation.

Volatile Organic Cmpds. Analyte or Chemical Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Benzene	μg/L	.051	.034	.095	.050	1.03	.094	.040	.038	.089	.040	1.04	.087
Bromodichloromethane	μg/L	.049	.063	.126	.047	1.06	.127	.068	.107	.21	.064	1.09	.190
Bromoform	μg/L	.19	.34	.63	.16	1.22	.51	.25	.44	.81	.21	1.27	.64
Bromomethane	μg/L	.085	.16	.30	.076	1.13	.26	.18	.20	.44	.17	1.17	.42
Butanone	μg/L	1.14	.96	2.4	.96	1.5	2.4	4.4	3.8	9.2	3.0	2.4	11.1
Carbon Disulfide	μg/L	.22	.25	.55	.20	1.18	.49	.17	.18	.40	.16	1.14	.37

Table 25B-1. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Volatile Organic Cmpd. Chemical Name	Units μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilu.	Drinking Water Standard
Benzene	μg/L	.030	.100	.019	<LOQ	.143	20	29.5	1
Bromodichloromethane	μg/L	.070	.20	ND	<MDL	.25	20	ΣHalomethane 13	Σ THMs 100
Bromoform	μg/L	.100	.300	2.0	<MDL	1.6	20	ΣHMET 13	Σ THMs 100
Bromomethane	μg/L	.080	.25	.011	<MDL	.73	20	ΣHMET 13	NA
Butanone	μg/L	.120	.35	.092	.145	3.7	20	NA	NA
Carbon Disulfide	μg/L	.060	.20	.144	.047	1.18	20	NA	NA

Table 25A-2. Evaluation of Volatile Organic Analytes (Method 624) With Ozonation.

Volatile Organic Cmpds. Analyte or Chemical Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Carbon Tetrachloride	μg/L	.001	.004	.006	.001	.002	.003	ND	ND	ND	ND	ND	ND
Chlorobenzene	μg/L	.004	.007	.013	.004	1.01	.012	.002	.003	.006	.002	1.00	.006
Chloroethane	μg/L	ND	.002	.003	ND	1.00	.001	.012	.031	.052	.012	1.03	.051
2-Chloroethyl-vinyl Ether	μg/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	μg/L	.107	.072	.20	.104	1.07	.20	.105	.063	.19	.104	1.06	.19
Chloromethane	μg/L	.30	.36	.75	.26	1.26	.69	.29	.32	.70	.26	1.21	.32

Table 25B-2. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Volatile Organic Cmpd. Chemical Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Carbon Tetrachloride	μg/L	.08	.25	.001	<MDL	<MDL	20	4.5	0.5
Chlorobenzene	μg/L	.03	.30	.001	<MDL	<MDL	20	2850	30
Chloroethane	μg/L	.09	.30	ND	<MDL	<MDL	20	NA	NA
2-Chloroethyl-vinyl ether	μg/L	0.6	2.0	ND	<MDL	<MDL	20	NA	NA
Chloroform	μg/L	.045	.15	.018	<MDL	.25	20	650	Σ THMs 100
Chloromethane	μg/L	.06	.21	.110	<LOQ	1.21	20	ΣHMET13	NA

Table 25A-3. Evaluation of Volatile Organic Analytes (Method 624) With Ozonation.

Volatile Organic Cmpds. Analyte or Chemical Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Dibromochloro-methane	μg/L	.24	.67	1.09	.16	2.3	.71	.17	.34	.61	.138	1.23	.48
1,1-Dichloroethane	μg/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	μg/L	.028	.038	.077	.028	1.04	.078	.020	.035	.065	.019	1.04	.065
1,1-Dichloroethene	μg/L	.002	.005	.008	.002	1.00	.009	ND	.001	.001	ND	ND	ND
trans 1,2-Dichloroethene	μg/L	ND	.001	.002	ND	1.00	.002	ND	ND	ND	ND	ND	ND

Table 25B-3. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Volatile Organic Cmpd. Chemical Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilu.	Drinking Water Standard
Dibromochloro-methane	μg/L	.08	.25	.004	<MDL	3.0	20	Σ HMETH 13	Σ THMs 100
1,1-Dichloroethane	μg/L	.08	.25	ND	<MDL	<MDL	20	NA	NA
1,2-Dichloroethane	μg/L	.08	.25	.021	<MDL	<LOQ	20	650	0.5
1,1-Dichloroethene	μg/L	.08	.25	ND	<MDL	<MDL	20	36000	6.0
trans 1,2-Dichloroethene	μg/L	.08	.25	.001	<MDL	<MDL	20	NA	NA

Table 25A-4. Evaluation of Volatile Organic Analytes (Method 624) With Ozonation.

Volatile Organic Cmpds. Analyte or Chemical Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Dichloromethane	μg/L	1.44	3.9	6.5	.73	1.8	2.8	.59	.43	1.14	.55	1.27	1.11
1,2-Dichloropropane	μg/L	.001	.003	.005	.001	1.00	.004	.001	.002	.003	ND	1.00	.002
cis 1,3-Dichloropropene	μg/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
trans 1,3-Dichloropropene	μg/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethyl Benzene	μg/L	.24	1.00	1.5	.102	1.46	.79	.146	.59	.90	.081	1.34	.57
2-Hexanone	μg/L	.039	.18	.26	.030	1.14	.22	.63	1.17	2.1	.42	1.6	1.6

Table 25B-4. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Volatile Organic Cmpd. Chemical Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Dichloromethane	μg/L	.08	.25	4.6	<MDL	18	20	2200	Proposed 5
1,2-Dichloropropane	μg/L	.004	.015	ND	<MDL	.011	20	NA	NA
cis 1,3-Dichloropropene	μg/L	.045	.15	ND	<MDL	<MDL	20	44	0.50
trans 1,3-Dichloropropene	μg/L	.08	.25	ND	<MDL	<MDL	20	44	0.50
Ethyl Benzene	μg/L	.015	.05	.006	<MDL	4.5	20	20500	680
2-Hexanone	μg/L	.09	.30	ND	<MDL	.79	20	NA	NA

Table 25A-5. Evaluation of Volatile Organic Analytes (Method 624) With Ozonation.

Volatile Organic Cmpds. Analyte or Chemical Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
4-Methyl-2-Pentanone	μg/L	.64	.96	1.9	.47	1.6	1.6	1.6	1.47	3.5	1.31	1.7	3.5
Styrene	μg/L	.087	.15	.28	.079	1.14	.27	.17	.34	.61	.135	1.26	.52
1,1,2,2-Tetrachloroethane	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Tetrachloroethene	μg/L	.026	.034	.070	.026	1.03	.069	.018	.018	.041	.019	1.02	.040
Toluene	μg/L	.31	.35	.76	.27	1.28	.75	.30	.38	.79	.26	1.30	.76
1,1,1-Trichloroethane	μg/L	.036	.038	.085	.035	1.04	.085	.029	.034	.073	.028	1.03	.071

Table 25B-5. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Volatile Organic Cmpd. Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
4-Methyl-2-Pentanone	μg/L	.08	.25	.002	<MDL	3.2	20	NA	NA
Styrene	μg/L	.017	.050	.050	<MDL	.43	20	NA	NA
1,1,2,2-Tetrachloroethane	μg/L	.06	.20	ND	<MDL	<MDL	20	6000	1
Tetrachloroethene	μg/L	.05	.15	.007	<MDL	.122	20	500	5
Toluene	μg/L	.017	.05	.25	<MDL	1.09	20	420000	NA
1,1,1-Trichloroethane	μg/L	.005	.015	.020	<MDL	.138	20	2700000	200

Table 25A-6. Evaluation of Volatile Organic Analytes (Method 624) With Ozonation.

Volatile Organic Cmpds. Analyte or Chemical Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
1,1,2-Trichloroethane	μg/L	.006	.025	.038	.005	1.02	.035	.006	.028	.041	.007	1.03	.043
Trichloroethene	μg/L	.006	.011	.020	.007	1.01	.022	.005	.006	.013	.005	1.01	.013
Trichlorofluoromethane	μg/L	.061	.046	.120	.060	1.04	.120	.052	.027	.087	.052	1.03	.087
Vinyl Acetate	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Vinyl Chloride	μg/L	.005	.023	.034	.005	1.02	.033	.001	.005	.007	.001	1.01	.008
ortho-Xylene	μg/L	2.4	10.6	16.	.28	2.4	2.8	2.9	12.7	19.	.27	2.5	4.1

Table 25B-6. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Volatile Organic Cmpd. Chemical Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
1,1,2-Trichloroethane	μg/L	.08	.25	ND	<MDL	<LOQ	20	220000	Proposed 5
Trichloroethene	μg/L	.05	.15	ND	<MDL	<MDL	20	135	5
Trichlorofluoromethane	μg/L	.11	.35	.105	<MDL	<LOQ	20	NA	NA
Vinyl Acetate	μg/L	.09	.30	ND	<MDL	<MDL	20	NA	NA
Vinyl Chloride	μg/L	.06	.20	ND	<MDL	<LOQ	20	18	NA
ortho-Xylene	μg/L	.015	.05	.010	<MDL	147.	20	NA	1750

Table 26A-1. Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Acenaphthene	μg/L	.22	.99	1.49	.089	1.45	.58	.20	.80	1.23	.096	1.41	.70
Acenaphthylene	μg/L	.005	.012	.021	.005	1.01	.021	.015	.051	.080	.014	1.05	.076
Aniline	μg/L	ND	.001	.002	ND	1.00	.002	ND	ND	ND	ND	ND	ND
Anthracene	μg/L	.034	.052	.101	.033	1.05	.097	.112	.34	.55	.082	1.23	.41
Azobenzene	μg/L	ND	ND	ND	ND	ND	ND	.013	.050	.077	.012	1.05	.072
Benzidine	μg/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	μg/L	.063	.18	.29	.052	1.15	.26	.072	.17	.29	.061	1.15	.27

Table 26B-1. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Acenaphthene	μg/L	.096	.32	ND	<MDL	4.6	21	NA	NA
Acenaphthylene	μg/L	.084	.28	ND	<MDL	.23	21	ΣPAHs.044	NA
Aniline	μg/L	1.05	3.5	ND	<MDL	<MDL	21	NA	NA
Anthracene	μg/L	.105	.35	.008	<MDL	<LOQ	21	ΣPAHs.044	NA
Azobenzene	μg/L	.096	.32	ND	<MDL	<LOQ	21	NA	NA
Benzidine	μg/L	39	129	ND	<MDL	<MDL	21	0.34	NA
Benzo(a)anthracene	μg/L	.093	.31	.043	<MDL	.73	21	ΣPAHs.044	Proposed 0.1

Table 26A-2. Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Benzo(b)fluoranthene	μg/L	.19	.26	.52	.17	1.20	.48	.18	.27	.52	.16	1.20	.47
Benzo(k)fluoranthene	μg/L	.132	.20	.39	.118	1.16	.36	.133	.22	.41	.118	1.18	.37
Benzo(a)pyrene	μg/L	.15	.23	.44	.137	1.18	.41	.130	.24	.44	.112	1.18	.38
Benzo(g,h,i)perylene	μg/L	.22	.49	.85	.17	1.33	.68	.16	.39	.66	.123	1.27	.52
Benzyl Alcohol	μg/L	.42	.80	1.44	.29	1.5	1.19	.49	.78	1.49	.36	1.5	1.29
bis(2-chloroethoxy) methane	μg/L	.002	.007	.010	.002	1.01	.011	.019	.064	.101	.017	1.06	.094

Table 26B-2. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Benzo(b)fluoranthene	μg/L	.16	.55	.040	<MDL	1.17	21	ΣPAHs.044	Proposed 0.2
Benzo(k)fluoranthene	μg/L	.17	.58	.068	<MDL	.90	21	ΣPAHs.044	Proposed 0.2
Benzo(a)pyrene	μg/L	.110	.36	.027	<MDL	1.06	21	ΣPAHs.044	Proposed 0.2
Benzo(g,h,i)perylene	μg/L	.22	.74	ND	<MDL	2.2	21	ΣPAHs.044	NA
Benzyl Alcohol	μg/L	.73	2.4	ND	<MDL	3.2	21	NA	NA
bis(2-chloroethoxy) methane	μg/L	.39	1.31	ND	<MDL	.28	21	220	NA

Table 26A-3. Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
bis(2-Chloroethyl) Ether	μg/L	ND	.002	.003	ND	1.00	.003	ND	ND	ND	ND	ND	ND
bis(2-Ethylhexyl) Phthalate	μg/L	11.7	19.	35.	7.1	2.5	25.	12.8	26.	46.	6.5	2.7	26
bis(2-Chloro-isopropyl)Ether	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
4-Bromophenyl phenyl Ether	μg/L	ND	NA	ND	ND	NA	ND	.070	.23	.37	.053	1.18	.31
Butyl benzyl Phthalate	μg/L	1.00	1.00	2.3	.82	1.5	2.1	1.16	1.39	2.9	.88	1.6	2.6

Table 26B-3. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Physical Analysis or Analyte Name	Units μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilu.	Drinking Water Standard
bis(2-Chloroethyl) ether	μg/L	.21	.69	ND	<MDL	<MDL	21	0.22	NA
bis(2-ethylhexyl) Phthalate	μg/L	.071	.24	.37	<MDL	122	21	17.5	Proposed 4
bis(2-Chloro-isopropyl)Ether	μg/L	.124	.41	ND	<MDL	<MDL	21	6000	NA
4-Bromophenyl phenyl Ether	μg/L	.93	3.1	ND	<MDL	<LOQ	21	NA	NA
Butyl benzyl Phthalate	μg/L	.18	.60	.037	<MDL	5.6	21	NA	NA

Table 26A-4. **Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.**

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
4-Chloroaniline	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
2-Chloronaphthalene	μg/L	.055	.17	.27	.045	1.14	.24	.009	.024	.040	.009	1.02	.039
4-Chlorophenyl phenyl ether	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Chrysene	μg/L	.148	.18	.38	.137	1.15	.37	.141	.15	.34	.131	1.14	.34
Dibenzo(a,h) anthracene	μg/L	.19	.41	.71	.146	1.28	.58	.16	.41	.68	.119	1.28	.53
Dibenzofuran	μg/L	.18	.76	1.16	.086	1.39	.65	.16	.59	.92	.093	1.34	.59

Table 26B-4. **Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.**

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
4-Chloroaniline	μg/L	.76	2.6	ND	<MDL	<MDL	21	NA	NA
2-Chloronaphthalene	μg/L	.19	.63	ND	<MDL	.69	21	NA	NA
4-Chlorophenyl phenyl ether	μg/L	.42	1.39	ND	<MDL	ND	21	NA	NA
Chrysene	μg/L	.103	.34	.042	<MDL	.71	21	ΣPAHs.044	Proposed 0.2
Dibenzo(a,h)-anthracene	μg/L	.24	.79	ND	<MDL	1.8	21	Σ PAHs .044	Proposed 0.3
Dibenzofuran	μg/L	.086	.29	ND	<MDL	3.5	21	NA	NA

Table 26A-5. Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
1,2-Dichlorobenzene	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
1,3-Dichlorobenzene	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
1,4-Dichlorobenzene	μg/L	.001	.004	.006	.001	1.00	.006	ND	NA	ND	ND	NA	ND
3,3'-Dichloro-benzidine	μg/L	.028	.130	.19	.023	1.11	.17	.010	.045	.067	.009	1.04	.063
Diethyl Phthalate	μg/L	1.8	6.0	9.5	.61	2.1	3.1	1.6	5.7	8.9	.50	2.0	2.7

Table 26B-5. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
1,2-Dichlorobenzene	μg/L	.120	.40	ND	<MDL	<MDL	21	Σ DCBs 25500	NA
1,3-Dichlorobenzene	μg/L	.127	.42	ND	<MDL	<MDL	21	Σ DCBs 25500	NA
1,4-Dichlorobenzene	μg/L	.123	.42	ND	<MDL	<MDL	21	900 or Σ DCBs25500	5.0
3,3'-Dichloro-benzidine	μg/L	1.00	3.3	ND	<MDL	<MDL	21	45	NA
Diethyl phthalate	μg/L	.090	.299	.054	<MDL	28	21	165000	NA

Table 26A-6. **Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.**

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Dimethyl Phthalate	μg/L	.040	.127	.20	.35	1.11	.18	.077	.20	.34	.063	1.17	.30
Di-n-butyl Phthalate	μg/L	1.35	.54	2.0	1.29	1.26	2.1	2.2	2.0	4.8	1.8	1.7	4.4
2,4-Dinitrotoluene	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
2,6-Dinitrotoluene	μg/L	ND	NA	ND	ND	NA	ND	.004	.019	.028	.004	1.02	.028
Di-n-octyl Phthalate	μg/L	.73	.62	1.5	.64	1.38	1.47	.75	.67	1.6	.66	1.39	1.5

Table 26B-6. **Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.**

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Dimethyl Phthalate	μg/L	.096	.32	ND	<MDL	.71	21	4100000	NA
Di-n-butyl Phthalate	μg/L	.090	.30	1.5	.44	6.9	21	17500	NA
2,4-Dinitrotoluene	μg/L	.87	2.9	ND	<MDL	<MDL	21	13	NA
2,6-Dinitrotoluene	μg/L	.88	2.9	ND	<MDL	<MDL	21	NA	NA
Di-n-octyl Phthalate	μg/L	.097	.32	.036	.087	2.3	21	NA	NA

Table 26A-7. Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.

Physical Analysis or Chemical Analyte Name	g/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Fluoranthene	μg/L	.16	.17	.37	.150	1.14	.36	.117	.123	.27	.111	1.11	.27
Fluorene	μg/L	.017	.033	.059	.016	1.03	.058	.031	.067	.117	.029	1.06	.111
Hexachlorobenzene	μg/L	ND	NA	ND	ND	NA	ND	.014	.063	.095	.013	1.06	.087
Hexachlorobutadiene	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Hexachlorocyclo-pentadiene	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
Hexachloroethane	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND

Table 26B-7. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Fluoranthene	μg/L	.092	.30	.020	<MDL	.59	21	75	NA
Fluorene	μg/L	.093	.31	ND	<MDL	.35	21	ΣPAHs.044	NA
Hexachlorobenzene	μg/L	.90	3.0	ND	<MDL	<MDL	21	.00105	Proposed 1
Hexachlorobutadiene	μg/L	.95	3.2	ND	<MDL	<MDL	21	70	NA
Hexachlorocyclo-pentadiene	μg/L	2.0	6.5	ND	<MDL	<MDL	21	290	Proposed 50
Hexachloroethane	μg/L	.20	.67	ND	<MDL	<MDL	21	12.5	NA

Table 26A-8. Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Indeno(1,2,3,4-cd)pyrene	μg/L	.18	.42	.72	.139	1.28	.57	.146	.36	.60	.112	1.25	.48
Isophorone	μg/L	.021	.034	.065	.020	1.03	.064	.007	.020	.032	.007	1.02	.031
2-Methylnaphthalene	μg/L	.33	1.40	2.1	.120	1.5	.96	.21	.84	1.29	.105	1.42	.73
Naphthalene	μg/L	.112	.26	1.8	.092	1.19	.37	.15	.53	.83	.095	1.31	.55
2-Nitroaniline	μg/L	.027	.125	.19	.022	1.10	.064	.002	.011	.016	.002	1.01	.016
3-Nitroaniline	μg/L	ND	NA	ND	ND	NA	ND	.004	.018	.027	.004	1.02	.027
4-Nitroaniline	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND

Table 26B-8. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Indeno(1,2,3,4-cd)pyrene	μg/L	.88	2.9	ND	<MDL	<MDL	21	NA	Proposed 0.4
Isophorone	μg/L	.148	.49	ND	<MDL	<MDL	21	750	NA
2-Methylnaphthalene	μg/L	.19	.62	ND	<MDL	6.4	21	NA	NA
Naphthalene	μg/L	.102	.34	.011	<MDL	2.3	21	NA	NA
2-Nitroaniline	μg/L	.93	3.1	ND	<MDL	<MDL	21	NA	NA
3-Nitroaniline	μg/L	.71	2.4	ND	<MDL	<MDL	21	NA	NA
4-Nitroaniline	μg/L	.99	3.3	ND	<MDL	<MDL	21	NA	NA

Table 26A-9. Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Nitrobenzene	μg/L	.070	.26	.41	.051	1.19	.31	.107	.16	.32	.097	1.14	.29
N-Nitrosodimethylamine	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
N-Nitrosodi-n-propylamine	μg/L	.004	.020	.029	.004	1.02	.029	ND	NA	ND	ND	NA	ND
N-Nitrosodiphenylamine	μg/L	.030	.092	.147	.027	1.08	.135	.038	.110	.18	.033	1.09	.16
Phenanthrene	μg/L	.29	.93	1.48	.17	1.43	.84	.070	.076	.17	.068	1.07	.16
Pyrene	μg/L	.31	.28	.67	.28	1.21	.63	.15	.138	.33	.145	1.12	.33

Table 26B-9. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Nitrobenzene	μg/L	.80	2.7	ND	<MDL	<LOQ	21	24	NA
N-Nitrosodi-methylamine	μg/L	.74	2.5	.18	<MDL	<MDL	21	36	NA
N-Nitrosodi-n-propylamine	μg/L	.40	1.32	ND	<MDL	<MDL	21	NA	NA
N-Nitrosodi-phenylamine	μg/L	.124	.41	ND	<MDL	.49	21	12.5	NA
Phenanthrene	μg/L	.096	.32	.010	<MDL	4.3	21	ΣPAHs.044	NA
Pyrene	μg/L	.103	.34	.021	<MDL	1.18	21	ΣPAHs.044	NA

Table 26A-10. Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\overline{X}$	σ	90%	$\overline{X}$	σ	90%	$\overline{X}$	σ	90%	$\overline{X}$	σ	90%
1,2,4-Trichlorobenzene	μg/L	ND	NA	ND	ND	NA	ND	.003	.012	.019	.003	1.01	.019
Benzoic Acid	μg/L	3.2	2.4	6.2	2.5	2.0	7.2	3.9	2.9	7.6	3.2	1.7	7.6
4-Chloro-3-methylphenol	μg/L	.019	.080	.123	.017	1.07	.110	ND	NA	ND	ND	NA	ND
2-Chlorophenol	μg/L	.012	.028	.048	.012	1.03	.047	.010	.032	.050	.009	1.03	.049
2,4-Dichlorophenol	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND

Table 26B-10. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\overline{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
1,2,4-Trichlorobenzene	μg/L	.21	.69	ND	<MDL	<MDL	21	NA	NA
Benzoic acid	μg/L	2.4	8.0	.36	<MDL	12.9	21	NA	NA
4-Chloro-3-methylphenol	μg/L	.41	1.37	ND	<MDL	<MDL	21	Σ Chloro-Phenols 5	NA
2-Chlorophenol	μg/L	.40	1.33	ND	<MDL	.134	21	Σ Chloro-Phenols 5	NA
2,4-Dichlorophenol	μg/L	.73	2.4	ND	<MDL	<MDL	21	Σ Chloro-Phenols 5	NA

Table 26A-11. Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
2,4-Dimethyl-phenol	μg/L	.136	.45	.72	.090	1.29	.51	.018	.066	.103	.016	1.06	.095
2,4-Dinitro-phenol	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
2-Methyl-4,6-dinitrophenol	μg/L	.047	.15	.24	.038	1.13	.21	ND	NA	ND	ND	NA	ND
2-Methylphenol	μg/L	.068	.26	.40	.049	1.19	.31	.018	.031	.058	.018	1.03	.058
4-Methylphenol	μg/L	.24	.62	1.03	.15	1.41	.79	.109	.17	.33	.097	1.16	.32
2-Nitrophenol	μg/L	.024	.062	.104	.023	1.06	.100	.005	.022	.032	.005	1.02	.031
4-Nitrophenol	μg/L	.33	1.39	2.1	.127	1.5	.97	ND	NA	ND	ND	NA	ND

Table 26B-11. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
2,4-Dimethyl-phenol	μg/L	.48	1.6	ND	<MDL	2.1	21	ΣPhenols150	NA
2,4-Dinitro-phenol	μg/L	2.0	6.6	ND	<MDL	<MDL	21	20 or ΣPhenols 150	NA
2-Methyl-4,6-dinitrophenol	μg/L	1.6	5.4	ND	<MDL	<MDL	21	1100 or Σ Phenol 150	NA
2-Methylphenol	μg/L	.53	1.8	ND	<MDL	1.12	21	ΣPhenols 150	NA
4-Methylphenol	μg/L	.59	2.0	ND	<MDL	2.1	21	ΣPhenols 150	NA
2-Nitrophenol	μg/L	.76	2.6	ND	<MDL	.21	21	ΣPhenols 150	NA
4-Nitrophenol	μg/L	3.0	9.9	ND	<MDL	6.4	21	ΣPhenols 150	NA

Table 26A-12. Evaluation of Semi-Volatile Organic Analytes Before and After Ozonation.

Physical Analysis or Chemical Analyte Name	μg/L or PPB	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
		Normal Distrib.			Geometric Distrib.			Normal Distrib.			Geometric Distrib.		
		$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Pentachlorophenol	μg/L	.074	.25	.40	.056	1.19	.31	.015	.069	.103	.013	1.06	.094
Phenol	μg/L	.20	.140	.38	.19	1.12	.37	.149	.143	.33	.141	1.13	.33
2,4,5-Trichlorophenol	μg/L	ND	NA	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND
2,4,6-Trichlorophenol	μg/L	.008	.029	.046	.008	1.03	.044	.015	.062	.094	.013	1.06	.087
Σ Phenols	μg/L	1.16	NA	5.6	.76	NA	3.8	.34	NA	1.1	.31	NA	1.06
Σ Chlor Phenols	μg/L	.113	NA	.62	.093	NA	.51	.045	NA	.25	.035	NA	.23
Σ PAHs	μg/L	1.9	NA	6.6	1.6	NA	5.4	1.6	NA	5.2	1.27	NA	4.4

Table 26B-12. Quality Assurance Statistical Evaluation and Selected Standards for Ozonation Analytes.

Physical Analysis or Analyte Name	μg/L or PPB	MDL 3σ	LOQ 10σ	Travel Blanks $\bar{X}$	Minimum Sample Value	Maximum Sample Value	Sample Number N Pairs	Ocean Plan Standard 5:1 Dilution	Drinking Water Standard
Pentachlorophenol	μg/L	1.9	6.2	ND	<MDL	<MDL	21	Σ ClPhenols 5	NA
Phenol	μg/L	.91	3.0	.029	<MDL	<MDL	21	ΣPhenols 150	NA
2,4,5-Trichlorophenol	μg/L	1.7	5.6	ND	<MDL	<MDL	21	Σ ChloroPhenols 5	NA
2,4,6-Trichlorophenol	μg/L	.70	2.3	ND	<MDL	<MDL	21	1.45 or ΣCl Phenols 5	NA
Σ Phenols	μg/L	NA	NA	.029	<MDL	15.0	21	ΣPhenols 150	NA
Σ ChlorPhenols	μg/L	NA	NA	ND	<MDL	1.9	21	Σ ClPhenols 5	NA
Σ PAH's	μg/L	NA	NA	.22	<MDL	17.	21	ΣPAHs.044	NA

OZONE DISINFECTION AND TREATMENT OF URBAN STORM DRAIN DRY-WEATHER FLOWS

A PILOT TREATMENT PLANT DEMONSTRATION PROJECT ON THE KENTER CANYON STORM DRAIN SYSTEM IN SANTA MONICA

TECHNICAL AND DATA APPENDICES

(Dissertation Format)

APPENDIX 1C

GLOSSARY

Base Flow: See Dry-weather Flow.

By-products: Incidental products (chemicals) that are formed during a process, such as water disinfection, many of which are undesirable, but difficult to prevent from being formed.

Chlordane: A technical (commercial) grade of chlorinated pesticide which contains many similar compounds that vary slightly in the number and placement of chlorines. Included in the mixture is heptachlor a pesticide that is sold in a more pure form. Chlordane was a popular and widely available pesticide for use in foundations for the control of ants and termites. Over the last 20 years it use has become more restricted and is now unavailable for use in the United States.

Chlorine: Chlorine gas has been widely used for destroying disease causing organisms and can be credited with preventing many human epidemics. Recent studies have shown that it also generates many hazardous by-products. In this report chlorine disinfection refers to treatment by chlorine gas, chloramines, chlorine dioxide and other similar treatment compounds.

<u>Coliform:</u> A group of bacteria that ferment lactose (milk sugar) and includes several genera in the <u>Enterobacteriaceae</u> family, such as <u>Arizona</u>, <u>Citrobacter</u>, <u>Enterobacter</u>, <u>Escherichia</u>, and <u>Klebsiella</u>. While some genera are found in animal intestines, many are also found free-living in soils and other media. For decades, total coliform organism counts have been used as an indicator of the effectiveness of disinfection of drinking water.

<u>Dilution:</u> See Initial Dilution.

<u>Disinfection:</u> A term originally used to describe methods used to remove or inactivate infectious or disease causing organisms, but also used to refer to the control of microscopic organisms in general.

<u>Dry-weather Flow:</u> The flow observed from storm drains during the dry season and several days after storms. While the relative source contributions varies significantly, the flow is assumed to be composed of infiltration (leaks into the storm drain from groundwater or septic systems), runoff from lawns and other residential sources (pools, car washing, etc.), NPDES permitted facilities, and illegal floor drains, maintenance activities, and sewer connections. Many other sources have been observed.

Enteric virus: As used here, see Human Enteric Virus.

Enterococcus bacteria: A subset of Streptococcus bacteria including S. fecallis, S. faecium, S. avium, S. bovis, S. equnius, and S. gallunarum, which have been isolated from the feces of mammals and birds.

Fecal Coliform: A subset of the Coliform bacteria group, characterized by the ability to ferment lactose at elevated temperatures ($> 39°C$). Escherichia coli and some strains of Klebsiella make up this group and the former is commonly found in mammalian and avian feces. While generally a beneficial constituent of the human intestinal tract, the presence of fecal coliform in water maybe an indicator of sewage contamination and the presence of pathogenic (disease-causing) organisms.

F-male Specific Coliphage: A virus that attacks and replicates exclusively in a specific (F-male) type of Coliform bacteria. Coliphage are indicative of fecal contamination and may be a good indicator of chlorine disinfection efficacy.

Geometric: As used here, this refers to a statistical method whereby the logarithmic value (base 10) is calculated and used to estimate the mean and standard deviation. This method, which is commonly applied in bacteriology and to a lesser degree in environmental analysis, acts to reduce the statistical effect of unusually high events (spills) on the overall mean and standard deviation.

Halogenated Compounds: Chemicals that contain Chlorine, Bromine, Fluorine or Iodine. Many are biologically hazardous.

Heptachlor: A chlorinated pesticide that is available in a relatively pure form and found in pesticide mixtures such as Chlordane.

Human Enteric Virus: Any virus found to replicate in humans and be present in the human digestive system. Many types are pathogenic (disease-causing) in humans.

Humic Acids: Colloidal organic material derived from decomposing plant and animal matter. It often induces a brown color when dispersed in water and can exert a significant disinfectant demand during disinfection. Humic and Fulvic matter are believed to be significant sources of mutagen precursors in chlorinated water.

Initial Dilution: is the process which results in the rapid and irreversible turbulent mixing of wastewater with ocean water around the point of discharge.

Mutagens: Chemicals and processes that cause a change or mutation in the genome (DNA) of an organism. Some mutagens are also carcinogens, causing mutations that disrupt normally cellular growth and result in the rapidly cellular proliferation generically referred to as a cancer.

NTU: National Turbidity Units. A standardized scale based on the ability of matter in water to scatter incident light at a ninety degree angle. Comparable to Formazin or Jackson Turbidity Units (FTU or JTU).

O-xylene: (1,2-Dimethyl Benzene) is present in gasoline and may be used as a solvent, but is less hazardous than benzene.

Ozone: is a gas composed of three atoms of oxygen, while the oxygen humans breathe consists of only two atoms. Simplistically, ozone tends to "degrade" back to molecular oxygen, but the third oxygen atom may react with other compounds, especially organics with double bonded carbons. This process effectively attacks microbial membranes and kills the organism (bacteria).

PAH's or PNAH's: are Polynuclear Aromatic Hydrocarbons and are essentially compounds containing multiple (commonly 3-5) benzene rings (6-carbons forming a ring with each carbon bonded to a hydrogen and the adjacent carbons). Benzene and many of the PAH's have been identified as mutagens and are likely carcinogens. They are formed during combustion processes and have been associated with soot and particulates from diesel engines among other sources. The list of compounds included in "Total PAH's" varies among regulators and analysts and care should be taken in making comparisons among different sources.

Pathogen: An organism (normally microscopic) that cause diseases in other organisms (generally vertebrates and commonly humans).

Polio and Polio virus: The common name and causative agent of the disease Poliomyelitis which is characterized by inflammation of brain stem and spine and results in loss of muscle control or death. During this study noninfectious or vaccine type polio virus were used to investigate disinfection efficiency.

TOC or Total Organic Carbon: refers to an analytical chemical method to detect carbon atoms from sources that were of biologic (living) sources. This would include carbon from oil and hydrocarbon fuels such as gasoline

Total Coliform: See Coliform.

Water Reclamation: The treatment, transportation, and use of wastewater for a direct beneficial or controlled use that would not otherwise occur. While not technically a wastewater, storm drain dry-weather flows can exhibit many of the same undesirable qualities.

Wet-Weather Flows: The relatively high flows from storm drains that occur during and after storms as water is conveyed away from areas in the upstream areas.

APPENDIX II

OZONE DISINFECTION OF URBAN STORM DRAIN WATER.

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OZONE DISINFECTION OF URBAN STORM DRAIN WATER

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Abstract

Concerns regarding bacteria in runoff entering Santa Monica Bay were validated by the isolation of human enteric virus in storm drain effluents. As an alternative to chlorination, ozonation was investigated for disinfection of dry-weather urban runoff. Ozone at 10-20 mg/L reduced coliform counts an average of 3.4 log, with 6 log maximal disinfection. Although varying contaminant concentrations complicate the analyses, total organic carbon predicted ozone demand and effluent coliform counts were correlated with ozone residuals.

Introduction

While the Federal Water Pollution Control Act (Clean Water Act) has significantly improved water quality by controlling point sources of pollution, further advances will require that non-point sources are also managed (GAO 1990). Many point sources, such as public owned treatment works (POTWs), power plants, factories, and refineries, have identifiable contaminant sources, out falls, and relatively predictable pollutant streams and flow rates, which are amenable to monitoring and management under the National Pollutant Discharge Elimination System (NPDES) permit program. In contrast, non-point emissions, such as agriculture and urban runoff, are primarily composed of low-volume or transient inputs from diffuse sources, which are difficult to predict or regulate, and are frequently innocuous to the downstream environment. When the discharge from a storm drain is observed to be polluted, the spill may have occurred days earlier, and miles away, in an area with low dry-weather flows, but where subsequent activities have flushed the contaminant downstream. The cumulative flow from non-point sources is also erratic, often being negligible during dry-weather, then suddenly swelling due to the contributions from storms, drainage, irrigation, fire fighting, water main breaks, or illegal activities. Although best management practices are presently the primary emphasis of the non-point source pollution control program, some areas are considering mass emission or discharge limitations that could require the construction of innovative treatment facilities.

The 1072 km^2 Santa Monica Bay watershed, which includes parts of Los Angeles and other cities, is drained by over 75 storm drains ranging from suburban river beds to open concrete lined channels, although most are enclosed conduits of various sizes (SMBRP 1993). Unlike the combined sewer systems that are prevalent in many parts of the country, the local storm drain and sewer systems are physically separate and theoretically sewage should never be present in the storm drains. In practice, illicit connections, transients, sewer line breaks, and infiltration all intrude into the storm drain system and are potential sources of biological, physical, and chemical contaminants. During the winter season, when the beaches are uncrowded, these contaminated flows are diluted in storm runoff and the exposure risk is limited. However, during the dry season (May to October), the contamination mixes only with the base flow of permitted discharges, landscape drainage, pool maintenance and other nuisance water. This dry-weather urban runoff, released during the busy summer season, constitutes a persistent flow of contamination into the surf, exposing recreational bathers to a significant health risk. While incidents of chemical contamination have occurred, dilution, and the limited human ingestion exposure, minimizes the potential public health threat from toxicity. In contrast, just a few pathogenic organisms can initiate an infection and cause serious, even fatal, illnesses, especially in children and the immuno-compromised.

During the last decade, the popular recreational beaches of the Santa Monica Bay, have experienced a decline in visitors from 79 to 48 million person-days, despite an increase in population and tourism (SMBRP 1993). While changing leisure patterns and crowding contributed to this decline, many attribute the drop to concerns regarding water pollution. In a local survey (SMBRP 1992), while the beach was second only to peoples' own backyard as the preferred place for recreation, 41% indicated that they would not swim in the bay and 60% of those indicated water pollution was the primary reason. These apprehensions were substantiated by the discovery of human pathogens (Coxsackie B virus) in the three Santa Monica Bay storm drains examined during a recent study (Gold et al. 1992).

The Pico Blvd.-Kenter Canyon-CalTrans storm drain system is an assemblage of drains throughout a 36 km^2 basin within the cities of Santa Monica and Los Angeles. Land use within the watershed is 48% single- and 21% multi-family dwelling, 19% open (mountain canyons and parks), 6% commercial, 3% public (schools and civic facilities), and 3% other urban categories (Stenstrom and Strecker, 1992). Paved areas comprise a significant fraction of each land use, except open areas, but were not separately quantified. The CalTrans relief drain is a 3.3 meter concrete pipe and the Kenter Canyon drain is a 3.3 x 3.7 meter arched brick structure, which was constructed prior to 1940 with the mouth designed to be in the surf zone off Santa Monica State Beach. Since then, sand accretion has distanced the mouth from the ocean and resulted in debris accumulation and ponding on this public beach, providing an attractive nuisance to both wildlife and children.

The Pico-Kenter storm drain has been extensively studied and while chemical contamination appears to be insignificant and comparable to other drains in the area (SCAG 1988), bacterial contamination is relatively high. Gold et al. (1990) found that enterococcus, fecal, and total coliform counts, at ankle depth in the surf zone adjacent to the storm drain, always exceeded the California Ocean Plan Standards (SWRCB 1990) of 24, 200, and 1000 organisms per 100 mls respectively. At ankle depth 23 meters away from the drain, the standards were exceeded 100%, 43% and 86% of the time respectively, and even at 137 meters the standards were exceeded at least a third of the time. Local agencies had previously discounted similar results as being attributable to seabirds and other wildlife that frequent the beach ponds at the mouth of the drain. However, each of the three studies by Gold et al. (1990, 1991, 1992), which were collected during dry-weather and included a viral pathogen survey, succeeded in isolating various human virus, including Coxsackie, Echo, and attenuated Polio, from the effluent. The frequency of detection and dispersed occurrence of these enteric virus, which are indicative of sewage contaminated waters, indicate that the urban storm drain runoff must be recognized as a potential public health threat to beach users. This concern is exacerbated by reports that much of the health threat may be associated with non-enteric organisms (O'Shea and Field 1992).

While a sanitary sewer main break may have contributed to the results of the 1991 study, many unidentified alternative sources of human virus remain. Roaches and flies may passively transfer each of the three identified viruses types (Harwood and

James 1979) from a sewer or fecal mass to the drains. Migrant workers and the homeless are both mobile and recalcitrant sources that have been known to camp along the larger channels and use them for washing and other sanitary needs. The continued decline of the mature infrastructure assures that sewer breaks or blockages will occur and infiltrate into the storm drain system. In summary, even if a sanitary survey eliminated all illegal and illicit connections, there exists significant potential for continued, if sporadic, microbial contamination.

Concerns for public safety and the environmental impact of storm drain effluents, led the City of Santa Monica to investigate construction of a facility to disinfection the dry-weather flow. The first evaluation (JMM 1987) proposed using ultra-violet (UV) light or chlorine disinfection. However, the community was not receptive to the possible consequences of chlorination, which include: 1) Cylinder storage; 2) Dechlorination prior to ocean release; and 3) The formation of toxic and carcinogenic halogenated disinfection by-products (DBPs). Concerns regarding the use of chlorine have expanded to where some advocate its abandonment (Hileman 1993). The use of UV light was predicated on low suspended solids and turbidity concentrations, while both contaminants are present in the effluent and positively correlated with microbial contamination. (The observed mean suspended solids were 5 times that required for adequate UV disinfection, although a screen twice as fine as the proposed unit was used.) Ozone, which was not among the proposed alternatives, was then suggested as an alternative. Unlike other oxidants, ozone is generated just prior to use, so that hazardous material need not be transported to, or stored at, the site. If a failure occurs, ozone is easily detected by olfactory or instrumental methods, that are below health threatening concentrations, and its generation can be immediately terminated by either automated or manual procedures.

While the europeans have a century of experience in the ozonation of water (AWWA 1991), the American water industry has recently begun investigating its use as an alternative disinfectant that produces fewer halogenated by-products (AWWA 1985, 1991, and 1992). The CT values (dose multiplied by time) of ozone are generally an order of magnitude lower than those of chlorine, chlorine dioxide, or chloramines (Morris 1975) and it is effective against virus, bacteria, amoeba, and encysted protozoans such as Giardia (Hoff 1987) and Cryptosporidium (Korich et al. 1990). The disinfection of these protozoans is particularly challenging since they are relatively resistant to most oxidants and are zoonoses of both wild and domestic animals. Infected animal and human carriers shed large numbers of hardy cysts with their feces, which are then flushed into the watershed drainage.

Since ozone rapidly decays, its major disadvantage is the lack of residual bacteriostasis in potable water, requiring the addition of persistent disinfectants, such as chlorine or chloramines, to prevent microbial regrowth in the distribution system. Since runoff is normally directed to an adjacent bay or river, residual disinfection is undesirable, making the primary disincentive to ozone treatment in drinking water, an attribute for disinfecting storm drain water. In fact, ozone is often used by large marine aquaria, such as the Sea Worlds, as their primary oxidant (IOA 1992). Unlike chlorination by-products, which are often mutagenic, ozonation DBPs are generally more oxygenated and less toxicologically potent (Tate 1991). (The bromate issue remains unresolved, see Means and Krasner 1993). Ozonation often forms additional assimilable organic carbon (AOC) and is often followed by biologically active filtration (BAF) which supports the growth of heterotrophic organisms (AWWA 1991) that are acclimated to these aldehydes, ketones, alcohols and carboxylic acids (van der Kooij 1987).

Meritens first tested ozone for disinfecting polluted water in 1886 (AWWA 1991), but its extensive use in treating wastewater began with the U.S Army around 1955. Comprehensive studies were then conducted by the Los Angeles County Sanitation Districts and the United States Environmental Protection Agency in the 1970s (White 1992). The EPA studies included investigations into high-rate disinfection of combined sewer overflows (CSOs) (Maher 1974). Although intuitively analogous to storm drain runoff, the effluent quality in these studies was more reminiscent of sewage. To summarize and paraphrase the review by White, ozone was effective as a disinfectant in tertiary treatment, but was more expensive than chlorination and residuals could not be monitored effectively. During the late 1980's, improvements in the automated monitoring of gas and liquid phase ozone concentrations have proven capable of tracking ozone demand and responding to the influent water matrix

(Gordon et al. 1988). Of 45 ozone utilizing American wastewater facilities, started between 1975 and 1989, 13 have closed for technical or economic reasons, while the status of 11 is either unknown, or in start up, leaving less than half in operation (Robson and Rice 1991). Even though most of the operational treatment plants are second generation facilities that learned from the mistakes of earlier treatment works, it is apparent that science of designing a wastewater ozone disinfection facility is still in its infancy.

While information exists, endorsing the use of ozone for disinfection of secondarily treated wastewater, there is no literature support for its dedicated use in treating storm drain water that has not been mixed with sewage. This finding was not surprising, since urban runoff is a non-point pollution source and has primarily been treated by modified management practices and passive structures, such as detention basins, debris dams, silt filters, and diffusers. While ozone has been used to treat both potable and wastewater, storm drain effluent shares more characteristics with the latter, where implementation is more recent and less assured. These observations led the City of Santa Monica to develop a pilot demonstration plant to test the efficacy of ozone in disinfecting the unfiltered dry-weather flow or nuisance urban runoff from the Pico-Kenter Storm Drain. The Santa Monica Bay Restoration Project and United States Environmental Protection Agency provided additional support to expand the scope of the study to include characterizing many of the chemical and physical properties of the water and their temporal variability (Greene 1992).

This study characterizes the: 1) Pertinent physical and microbial attributes of the urban runoff water; 2) Results of the disinfection investigations; and 3) Associations between some potential operational and process control parameters and influent and effluent water characteristics.

Methodology

PILOT PLANT DESIGN

The pilot plant process and equipment schematic layout is shown in Figure 1. All surfaces exposed to ozone were constructed of stainless steel, borosilicate glass, polyvinyl chloride (PVC), or teflon. An oil-less compressor (Dayton Speedaire® 3Z852) with filter supplied air, while compressed oxygen was purchased from Liquid Air Corporation and used to double both the influent gas ozone production and applied dose. The submersible pump (Goulds #3885) was secured in a plastic housing, with a 1.5 mm aluminum mesh screen, and lowered into the storm drain upstream of a v-notch weir. The screened water was pumped upto a 400 liter holding tank, through a second pump (Ace-50), an RMC-145 rotameter (4-31 LPM) and into the top of the contactor tower. The 6 meter, by 10 cm diameter, stainless steel tower and dual Ozotec® ozone generator were supplied by the Hankin Ozone Company. The gas rotameters were calibrated to deliver 1.9-8.6 standard liters per minute or SLPM with a 6 meter water head pressure. Ozonated gas passed through the rotameter and into the bottom of the contactor tower through a cylindrical ceramic diffuser. A side stream from the generator passed through a 3-way valve to the PCI HC® ozone monitor. An Orbisphere dissolved residual ozone probe was installed near the effluent sampling port. The treated effluent was discharged to the drain downstream of the temporary weir.

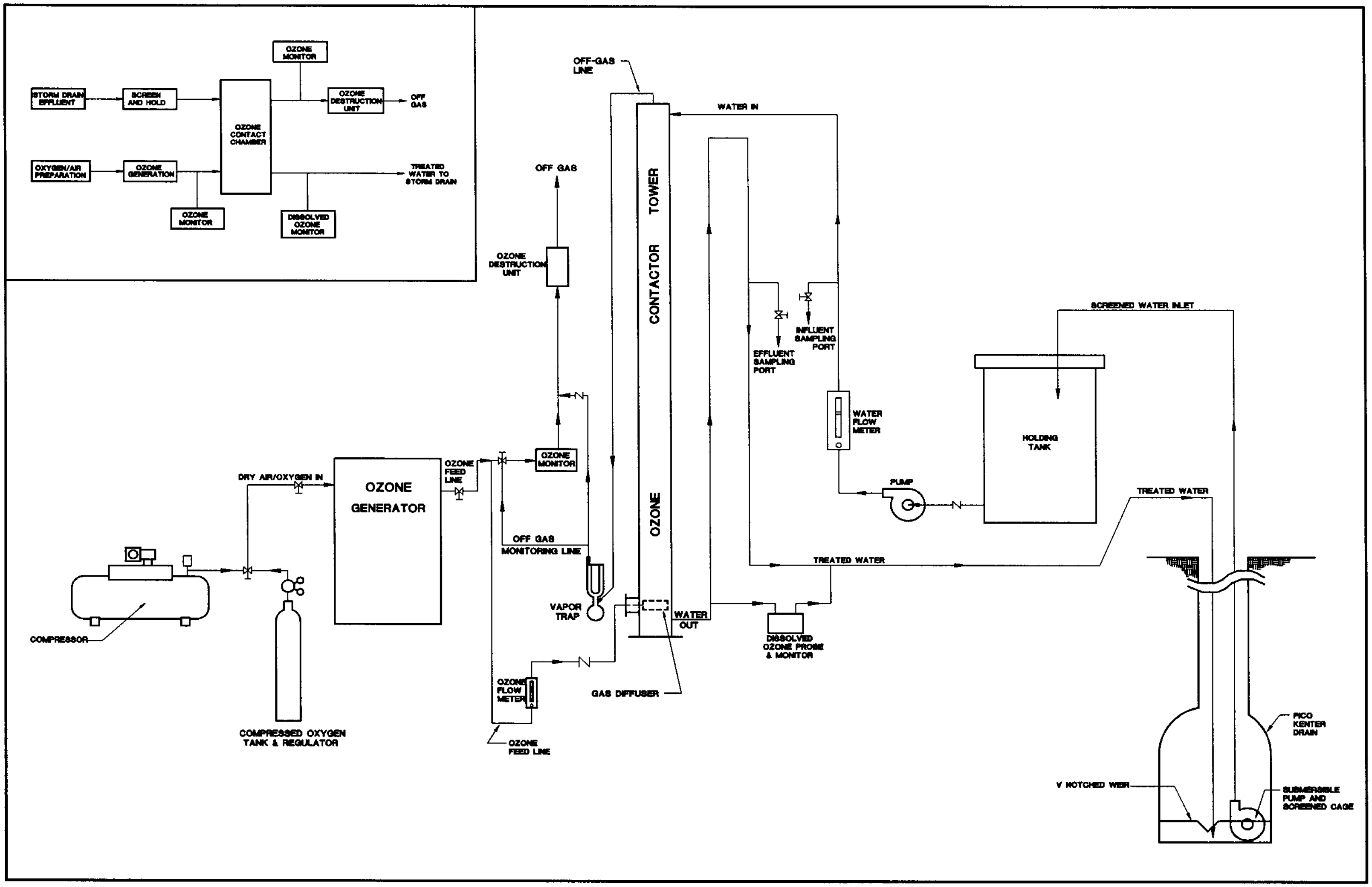

Figure 10. Ozone Pilot Plant Process Diagram and Equipment Schematic.

The tower off-gas passed through a water vapor trap, a check valve, and the remaining ozone was reverted to oxygen using manganese dioxide (Carulite® 200 Carus Corp.). The vapor trap was a Dewar type condenser filled with a dry-ice/butanol mixture. After the trap, a "T" led to the three-way valve on the ozone gas monitor. During each sample run, this valve was switched between influent and off-gas lines, the flow rate adjusted, and the ozone concentrations recorded. Both ozone feed- and off-gas concentrations were measured twice per sample run. If foam was noted in the vapor trap, holding tank or influent sampling port, sampling was suspended and the tower drained. When foam was present, the tower pressurized, reducing the effective volume, shortening the contact time, and obstructing ozone dosage and CT calculations.

SAMPLING

The sampling design followed the EPA Project Quality Assurance Plan. Operation began in November 1989 and continued until December 1990, but was sporadic during May, June, and July, when a ruptured sanitary sewer contaminated the runoff water. The daily operating schedule began with provision of compressed gas and warming of the ozone generation and monitoring systems. After the flow of water and gas were initiated, the system was monitored and allowed to stabilize for 15 minutes prior to sample collection. Since the runoff is subject to slugs of contaminants, a preozonation sample was taken just prior to the contactor tower, then, following a retention time delay, a post-ozonation comparison sample was collected. One to three sample runs, each composed of a pre- and post-ozonation pair, were prepared during a day of plant operation. The feed gas contained up to 4.5% by weight ozone, and the absorbed dose was calculated by subtracting the off-gas concentration from the measured value and multiplying by the density corrected gas flow rate divided, by the water flow rate. Although dosages of up to 40 mg/L of ozone were absorbed, operation was generally in the 5 to 20 mg/L range with effluent dissolved ozone residuals of up to 10 mg/L. The reacted ozone was estimated by subtracting the residual concentration from the absorbed dose. The ozone generator, flow meters, and monitors were maintained as per manufacturers recommendations.

ANALYTICAL METHODS

Most of the analyses were conducted at either the pilot plant site or at the Laboratory of Biomedical and Environmental Sciences (LBES) at the University of California at Los Angeles (UCLA). The methodologies used during this study were approved by the EPA in 1989. Among the process controlling components were the various valves, flowmeters and ozone monitors previously described. Water and gas flow rates were always verified prior to, during, and following each sampling run. Monitors were repaired when indicated by ambiguous performance, and samples taken on the same day, but prior to the failure, were discarded and retaken after repairs or maintenance activities were completed and normal performance restored.

Physical analyses included temperature, pH, conductance, turbidity, settleable solids, suspended solids, dissolved solids and total solids. The samples for pH, temperature, conductivity, settleable solids and turbidity analyses, were collected in one liter polycarbonate graduated cylinders and, with the exception of settleable solids, analyzed during the run. Conductance measurements were initiated in January, using an ICM model 71250 portable, temperature correcting, conductivity meter and conformed to EPA Method 120.1 (EPA 1983A). The measurement of pH was initiated using a pocket meter, but by January analyses were made with a portable ICM model 41250 unit, to conform with EPA method 150.1 (EPA 1983A). Commercial buffer solutions were used to calibrate the units before each sample. Temperature was measured using a standard laboratory thermometer that was checked weekly against a precision thermometer and conformed to EPA method 170.1 (EPA 1983), except that the thermometer was not mercury filled. Settleable solids were determined, using polycarbonate Immhoff cones, as per EPA method 160.5, but when material settled on the walls of the cone a rapid rotation of the cone was used to dislodge the matter for inclusion in the measurement.

Turbidity measurements began in early 1990 using a Monitek model 21PE Nephelometer and following EPA method 180.1. The unit was calibrated just prior to each use. When any sample exceeded 100 NTU, the sample pair were diluted to the desired working range and measured on the same scale. Effluent samples were observed to form gas bubbles on the wall of the cuvette, probably due to the aggregation of microbubbles. Although the bubbles could be "bumped" free, it is unknown if the reduction in turbidity was due to the removal of bubbles or settling of suspended material. The analyses for total (total residue, Method 160.3), dissolved (filterable residue, method 160.1) and suspended (non-filterable residue, method 160.2) solids followed EPA methodology except that the volume used in the latter analysis varied between 50-1000 ml based on passage through the filter, rather than anticipated residue weight. Samples were dried overnight in a standard laboratory oven. Total organic carbon (EPA method 415.2) analyses were performed using a Dohrman DC-180 and the recommendations of the manufacturer. Fifteen samples containing high dissolved solids concentrations gave erroneous results due to chloride interferences and were excluded from the data base.

Mutagenicity assays were prepared by resin extraction of influent and effluent waters, followed by extraction and concentration in hexane and acetone. The extracts were then serially diluted and plated, following the EPA Interim Procedures for Conducting the Ames Mutagenicity Test (EPA 1983B), using strains TA 98 and TA100 with and without S9 activation. The total and fecal coliform analyses were conducted using the Minimal Media Ortho-nitrophenyl-beta-D-galactopyranoside 4-Methyl Umbelliferyl-beta-D-Glucuronide method, also referred to as the Minimal Media O-MUG or MMO-

MUG in the EPA ruling on its use (EPA, 1989). The Colilert® test uses the same statistical methods as the Multiple Tube Fermentation (MTF) method, and results in an estimate of the Most Probable Number (MPN) of total and fecal coliform organisms per volume of sample. The virus spiking study was conducted by staff of the Los Angeles County Sanitation Districts on June 5, 1990, using a modification of Standard Method 9510-B (APHA 1989). Attenuated, vaccine strain, type 1 poliovirus were added to about 320 liters of water pumped from the storm drain into the surface holding tank. The tank was mixed for about 5 minutes prior to being pumped into the pilot plant. Influent samples were taken at the beginning and termination of each run. Effluent samples were collected after 80, 160, and 240 liters of seeded water had been treated. Samples were assayed on Buffalo Green Monkey Kidney cells using the plaque forming unit technique (EPA 1984).

Results

Most of the runoff water resembled the unfiltered effluent from an activated-sludge sewage treatment plant (Metcalf and Eddy 1979), except that it is lower in nutrients such as nitrogen and to a lesser extent phosphorous. The most characteristic feature of the nuisance runoff from the Pico-Kenter storm drain is its variability. On several occasions, a trash carrying wave front could be heard upstream of the pilot plant site and the flow was observed to increase from an estimated 500 to as much as 10,000 LPM. These fronts resuspend settled matter and significantly reduced the influent quality. This is shown graphically in Figure 2, which depicts the variability in suspended solids concentration. With the exception of temperature and pH, similar plots could be prepared for most of the analytes.

The pilot plant operational parameters and runoff analytes are statistically summarized in Table 1. Environmental and bacterial data distributions are often skewed and appropriately analyzed using a logarithmic (geometric) distribution (APHA 1989). Both the arithmetic and geometric distributions were scrutinized for normality using D'Agostino's test (Zar 1974). Those parameters meeting the criteria are shaded, while the distribution data given in bold type more closely approximated normality than the data given in normal type.

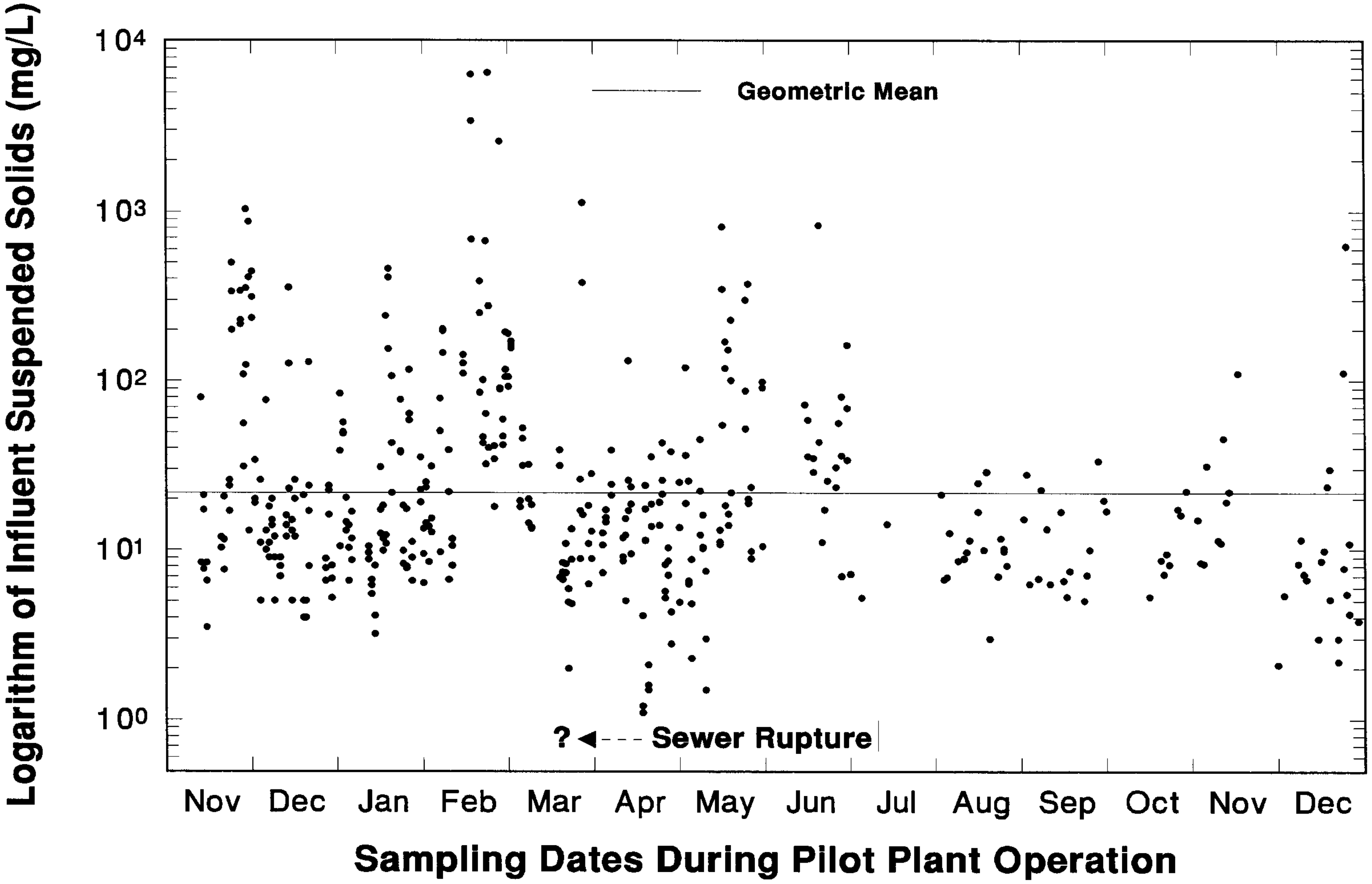

Figure 11. **Scatter Plot of Pilot Plant Influent Water Suspended Solids Concentrations in mg/L.** (note 4 orders of magnitude variability).

Table 27. Descriptive Statistics for Pilot Plant Operational Parameters and Urban Runoff Analytes[1].

Pilot Plant Process Parameter or Analyte (with units)	Sample Number n Pairs	Minimum Sample Value	Maximum Sample Value	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
				Normal Distribution			Geometric Distribution			Normal Distribution			Geometric Distribution		
				$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Water Flow Rate (LPM)	438	4.0	31.0	**3.1**	**1.11**	**4.5**	2.9	1.48	4.8	-------	-------	------	-------	-------	------
Gas Flow Rate (SLPM)	438	1.9	8.6	12.9	3.4	17	12.3	1.35	18	-------	------	------	-------	-------	------
Influent Ozone (Wt.%)	387	.34	5.1	**2.7**	**1.09**	**4.1**	2.4	1.7	4.7	-------	-------	-------	-------	-------	------
Off-gas Ozone (Wt.%)	387	0.0	2.2	------	-------	-------	-------	-------	-------	.61	.53	1.29	.54	1.35	1.27
Absorbed Ozone (mg/L)	414	3.6	38	-------	-------	-------	-------	-------	-------	13.0	4.9	19	12.1	1.48	20
Ozone Residual (mg/L)	414	0.0	7.8	-------	-------	-------	-------	-------	-------	1.47	1.6	3.5	1.05	1.8	3.4
Reacted Ozone (mg/L)	387	1.02	37.6	-------	-------	-------	-------	-------	-------	11.4	4.9	18	10.4	1.6	19
Temperature (°C)	430	14.0	24.4	18.5	1.7	20.7	18.2	1.10	20.5	18.8	1.8	21.1	18.6	1.10	21.0
pH	401	7.1	9.6	**8.1**	**.29**	**8.5**	8.1	1.04	8.5	**7.8**	**.32**	**8.2**	7.8	1.04	8.2
Conductivity (μmho/cm)	332	470	36000	1310	2200	4100	**1070**	**1.5**	**1900**	1300	2100	4000	**1070**	**1.5**	**1900**
Turbidity (NTU)	349	2.3	5800	83.	370	550	**22**	**3.5**	**110**	71	250	390	**21**	**3.5**	**106**
Settleable Solids (mg/L)	438	<.20	78	.52	5.3	7.3	**<.20**	**6.6**	**2.1**	.52	5.0	6.9	**<.20**	**6.6**	**2.2**
Suspended Solids (mg/L)	434	0.6	6500	103.	500	740	**22**	**4.0**	**129**	97	440	660	**19**	**4.2**	**122**
Dissolved Solids (mg/L)	435	190	30000	870	1600	3000	**690**	**1.6**	**1250**	900	1700	3100	**710**	**1.7**	**1500**
Total Solids (mg/L)	435	280	31000	1010	1800	3300	**780**	**1.7**	**1500**	1010	1800	3300	**780**	**1.7**	**1500**
Total Organic Carbon TOC (mg/L)	425	2.2	124	19	16	40	**15**	**1.9**	**35**	19	15	38	**16**	**1.8**	**34**
Total Coliforms x10^3 (MPN)	438	<.002	54000	1490	3400	5900	520	4500	3600	7.6	4.4	13.2	.16	160	5.6
Fecal Coliforms x10^3 (MPN)	436	<.002	7900	160	670	1020	**19**	**7.8**	**260**	.52	4.2	5.9	**.007**	**7.2**	**.088**
Enterococcus sp.x10^3 (MPN)	47	<.002	1700	190	310	590	**69**	**4.8**	**510**	**.25**	1.04	1.6	**.030**	**5.9**	**.29**

[1] Shaded data was normally distributed (D'Agostino's test). The bold type data, more closely approximates a normal distribution than regular type.

In summary, the data sets for water flow, gas flow, feed gas ozone concentration, water temperature and pH, did not require logarithmic transformation to fit (gas flow and temperature) or approach a normal distribution. The remaining analytes required transformation to approximate (or in the case of total coliforms, fit) a normal distribution. The logarithmic transformation of the effluent water process parameters were all normally distributed.

Even after transformation, few analytes were normally distributed, leading us to use nonparametric statistics to determine which were affected by ozonation. Based on the Mann-Whitney ranking test (Zar 1974) and null hypothesis that pre- and post-ozonation samples came from the same population, rejection of the premise ($P<5\%$) would lead us to conclude that ozone affected the parameter. Influent/effluent sample sets for conductivity, dissolved solids, and total solids, were indistinguishable ($P>40\%$) leading to acceptance of the null hypothesis and indicating that, as expected, ozone had little affect on inorganic contaminants. Settleable solids were also unaffected by treatment, probably because the high values were associated with inorganic clays and most of the others were near zero. For suspended solids and TOC, which are organic and potentially more reactive with ozone, the null hypothesis could not be rejected ($P<17\%$). The probability that turbidity was affected during treatment, was intermediate ($P<30\%$) between the inorganic and organic analytes. The effect of ozonation on bacterial counts, pH, and water temperature was highly significant ($P<0.5\%$), although the increase in temperature was due to the compression of air for ozone generation. The increase in temperature was negligible when oxygen cylinders were used instead of the air compressor. The pH of the water decreased toward neutrality during the treatment and well ozonated effluent water was generally one-half pH unit lower than the influent urban runoff.

While the influence of the ozone treatment on the physical analytes was limited, the change in microbial parameters was highly significant. As illustrated in Figures 3 through 5, the pilot plant ozonation treatment effectively reduced the mean geometric bacteria count 3.4 log, indicating that about 99.96% of the organisms were killed or inactivated. During the latter half of the study, when the use of oxygen as a feed gas greatly increased the proportion of runs where ozone dose exceeded demand, disinfection often approached 6 log. However, the estimate of the mean kill was still constrained by the 2 organisms per 100 ml limit of quantification (note Figure 4) and organic contamination from a ruptured sanitary sewer that was increasing discernable from samples 248 until 362 when the source was repaired.

On June 5, 1990 three sample runs were conducted to test the ozonation disinfection efficacy against attenuated polio virus which were mixed into the influent holding tank. Although turbidities of almost 100 NTU were encountered, probably due of the rupturing sewer line, absorbed ozone doses of 15 to 20 mg/L were able to reduce viral counts 3.5 log.

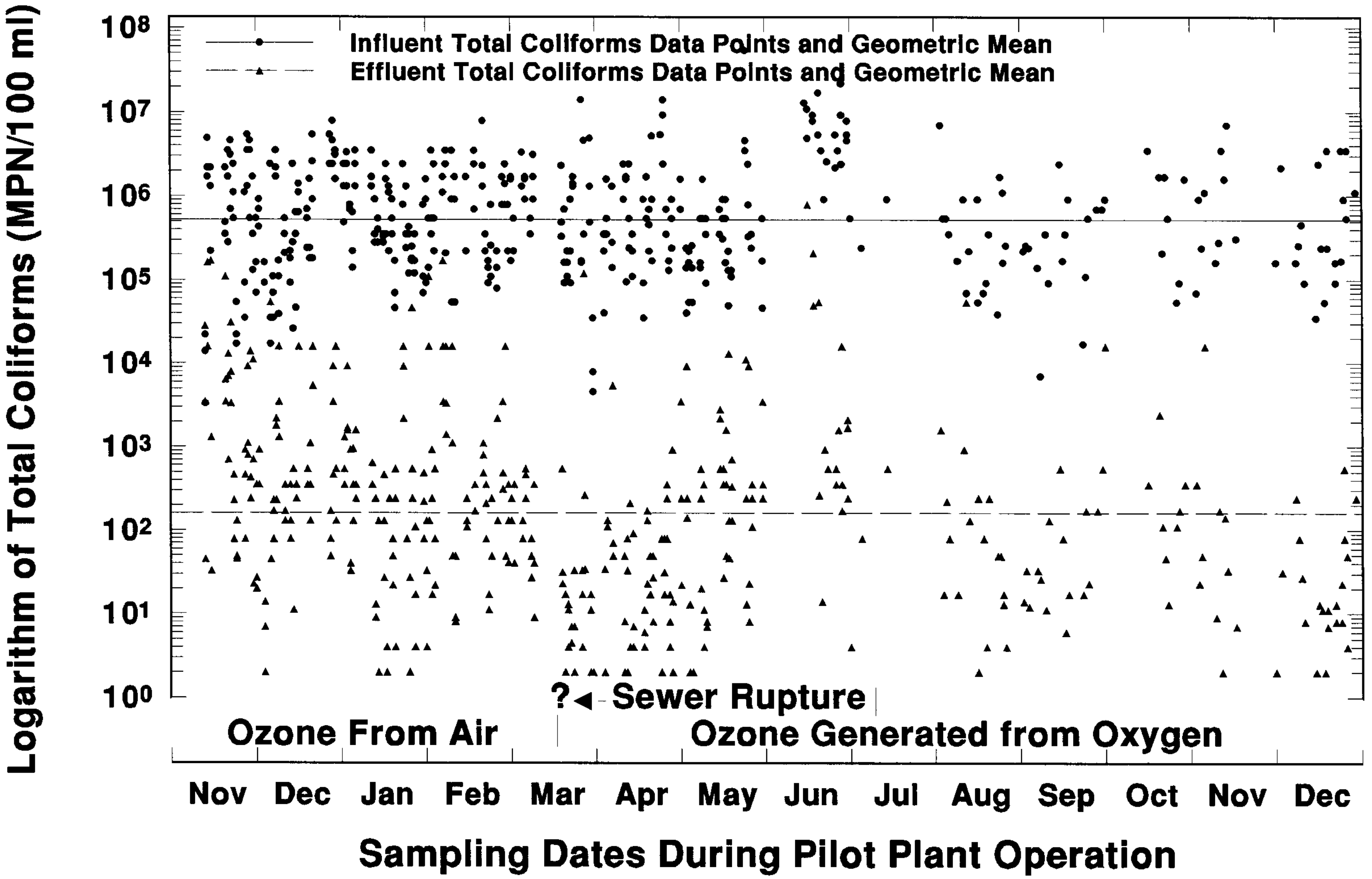

Figure 12. Scatter Plot of Total Coliform Organism Counts (MPN/100 ml) for Raw and Ozonated Pico-Kenter Storm Drain Runoff Water.

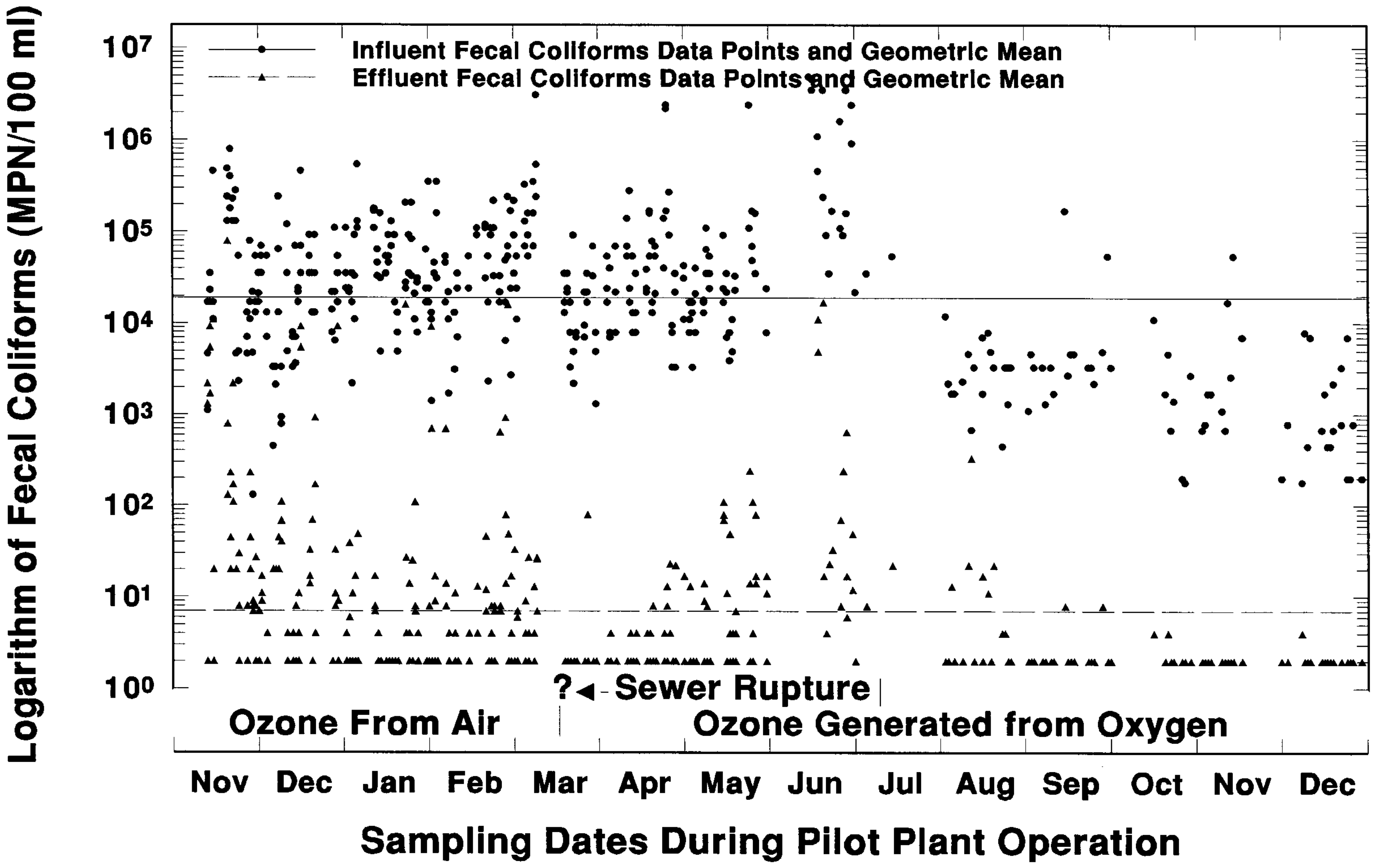

Figure 13. Scatter Plot of Fecal Coliform Organism Counts (MPN/100 ml) for Raw and Ozonated Pico-Kenter Storm Drain Runoff Water.

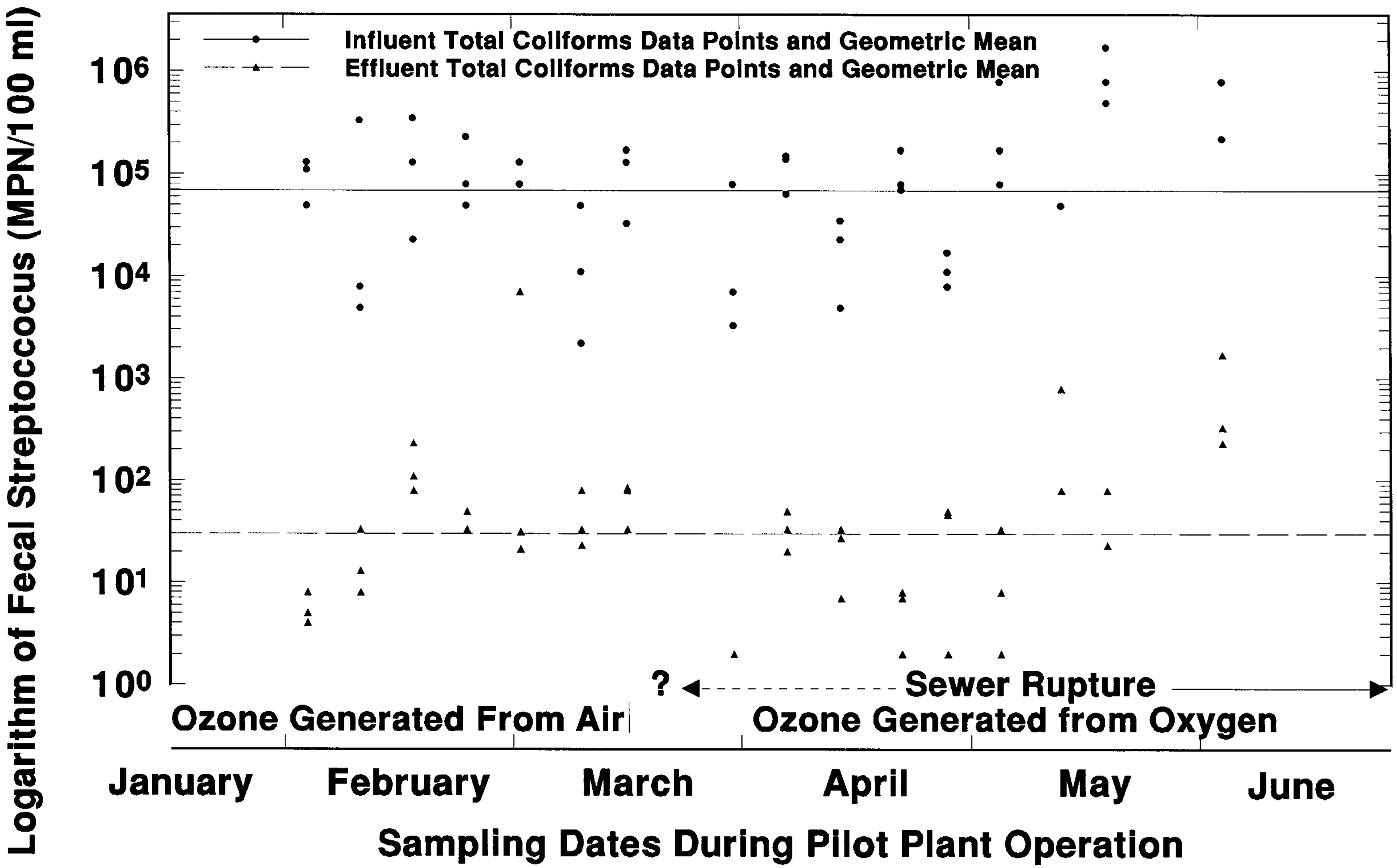

Figure 14. Scatter Plot of Fecal Streptococcus (Enterococcus) Organism Counts (MPN/100 ml) for Raw and Ozonated Pico-Kenter Storm Drain Runoff Water.

During these runs, bacterial kills were unusually low, at an average of about 2.5 log and the total organic carbon content of the effluent was notably higher than in the influent, probably because of the viral suspension media. The increase in TOC concentration is likely to have contributed to the reduced bacterial disinfection efficacy.

During 5 runs, mutagenicity assays were conducted. Although ozonation reduced the mutagenicity 7-24%, the change was not statistically significant. Since this study was undertaken to ensure that ozonation did not increase mutagenicity, these analyses were not more thoroughly investigated.

Discussion

During this disinfection study, counts for enterococcus, total and fecal coliform bacteria fell an average of 3.4 log, indicating that 99.96% of the indicator organisms were killed, and establishing the effectiveness of ozone in treating storm drain runoff. Although analogous levels of disinfection should be exhibited against most pathogens, including protozoan cysts, it is probably coincidental that the identical rate of inactivation was observed against type I attenuated polio virus. The efficacy of an enhanced treatment facility can probably be optimized to achieve more than five log disinfection since: 1) Many of these runs were conducted using suboptimal conditions, including low ozone dosages;

2) A sewage spill degraded the water during much of the study; 3) The lower limit of bacterial enumerations was 2 organisms per 100 ml and lower estimates were rounded up to that value; and 4) Additional intermediate processes, such as sedimentation and filtering, should increase the treatability of the water and reduce particulate-bound contaminants, such as pathogens. In order to optimize disinfection, the parameters controlling treatment must be identified and their impact on the runoff water matrix patterned and calibrated. The identification step can be accomplished through correlation statistics and the results subsequently used in model development and calibration.

CORRELATIONS

A correlation matrix was prepared relating the process parameters monitored during this study. Excluding associations between bacterial enumerations, effluent total coliform counts were positively correlated with effluent pH, suspended solids, effluent turbidity, and TOC concentrations, but the negative correlation with ozone residuals was most significant. The relationship between indicator bacteria numbers and suspended solids, turbidity, and TOC, is intuitively evident since these parameters are indicative of organic matter that shields microbes from disinfection. The relation between effluent pH and bacterial numbers, may be an artifact of the narrow range of pH values observed and the tendency for highly ozonated water to decrease ½ pH unit. Figure 6 shows a linear regression of the log of effluent total coliform count as a function of the log of effluent water ozone residuals. The coefficient of determination ($r^2 = 0.41$) indicates that 41% of the variability in coliform count was explained by residuals and the F distribution found virtually no chance that the correlation was random. The incorporation of other parameters, such as suspended solids, TOC, or turbidity, in a multiple linear regression reduced the correlation. Although 6 samples containing extreme concentrations of solids were excluded as outliers from Figure 6, most (26) of the missing samples were collected prior to the installation of the ozone residual monitor. Correlations using the change in bacterial counts (N/N_0, or log N/N_0), rather than effluent numbers, were of lower significance.

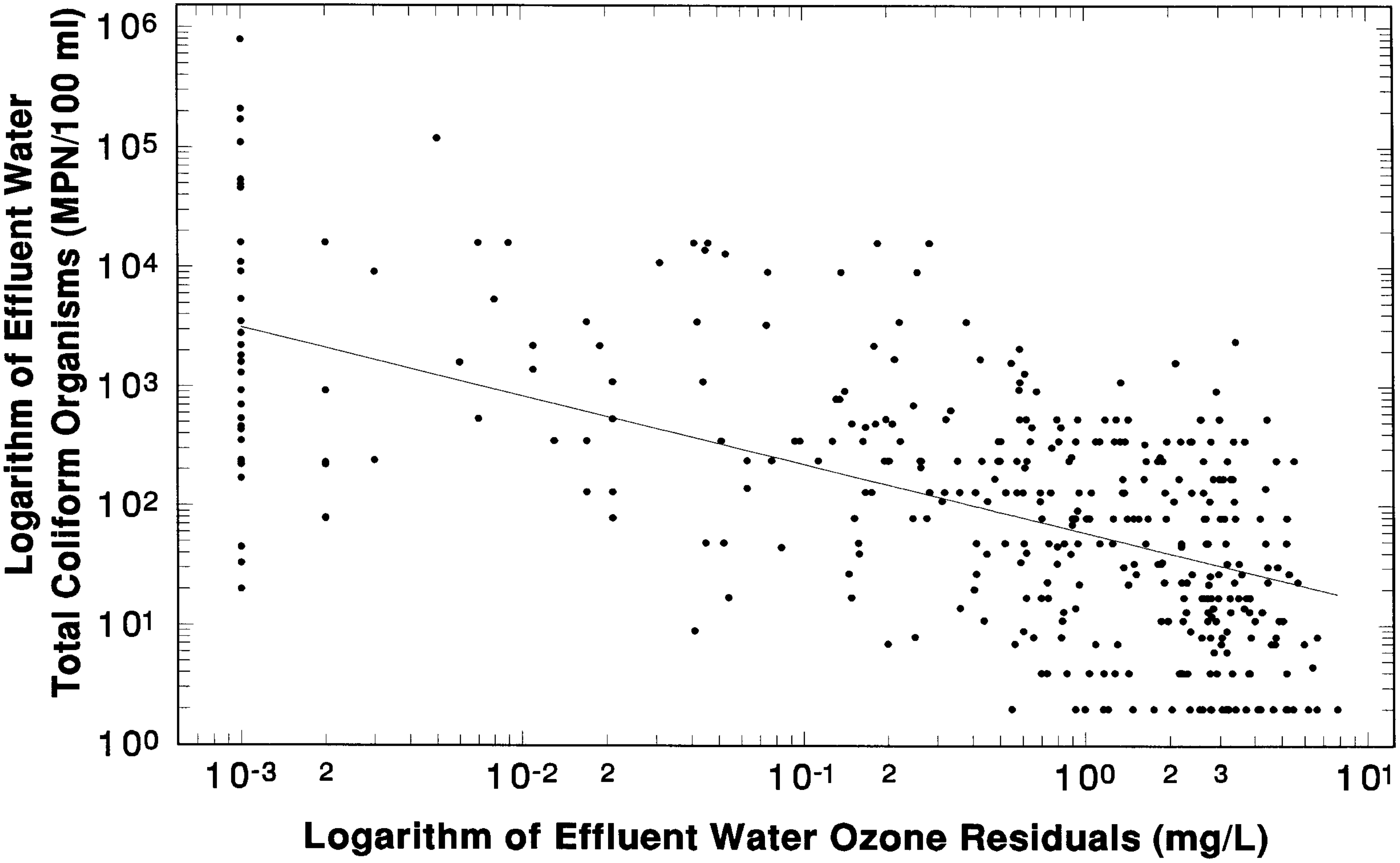

Figure 15. **Linear Regression Showing Dependence of Effluent Total Coliform Count on Ozone Residual.** Log $TC_e = (1.784 \pm 0.045) - (0.622 \pm 0.037)$ Log O_{3r}; $n = 406$, $r = -0.64$, $r^2 = 0.41$, $F << 0.01$.

Given the variability of the storm water matrix and changes in pilot plant operation, the dependence of effluent coliform counts on ozone residual is meaningful, but evaluated relatively late in the treatment process. The residual develops after the ozone demand of the water has been satisfied and the prediction of the demand is a more pivotal parameter in anticipating the ozone dosage required to achieve a given level of disinfection. Ozone demand is an evaluation of the organic and inorganic compounds that are oxidized during ozonation, or consume ozone and its reactive by-products. It is the oxidation and free-radical reactions that primarily contribute to disinfection, while the consumptive, or terminating, reactions reduce its efficacy. The best surrogate for the immediate (during treatment) demand is the reacted ozone (O_{3d}) which was calculated by subtracting the residual from the absorbed ozone concentration. The reacted ozone was correlated with TOC, influent total coliform count, temperature and effluent pH. Since enumerating bacteria is labor intensive and requires at least 24 hours, its predictive value is limited when the count is variable. The other parameters were subjected to sequential multiple linear regression to characterize their value in predicting ozone demand.

The most significant correlation ($r = 0.58$) was between the logarithm of reacted ozone and the logarithm of TOC as shown in Figure 7. Including effluent pH, in a multiple linear regression, increased the correlation to 0.69 although, as previously stated, the connection with pH maybe artifactual.

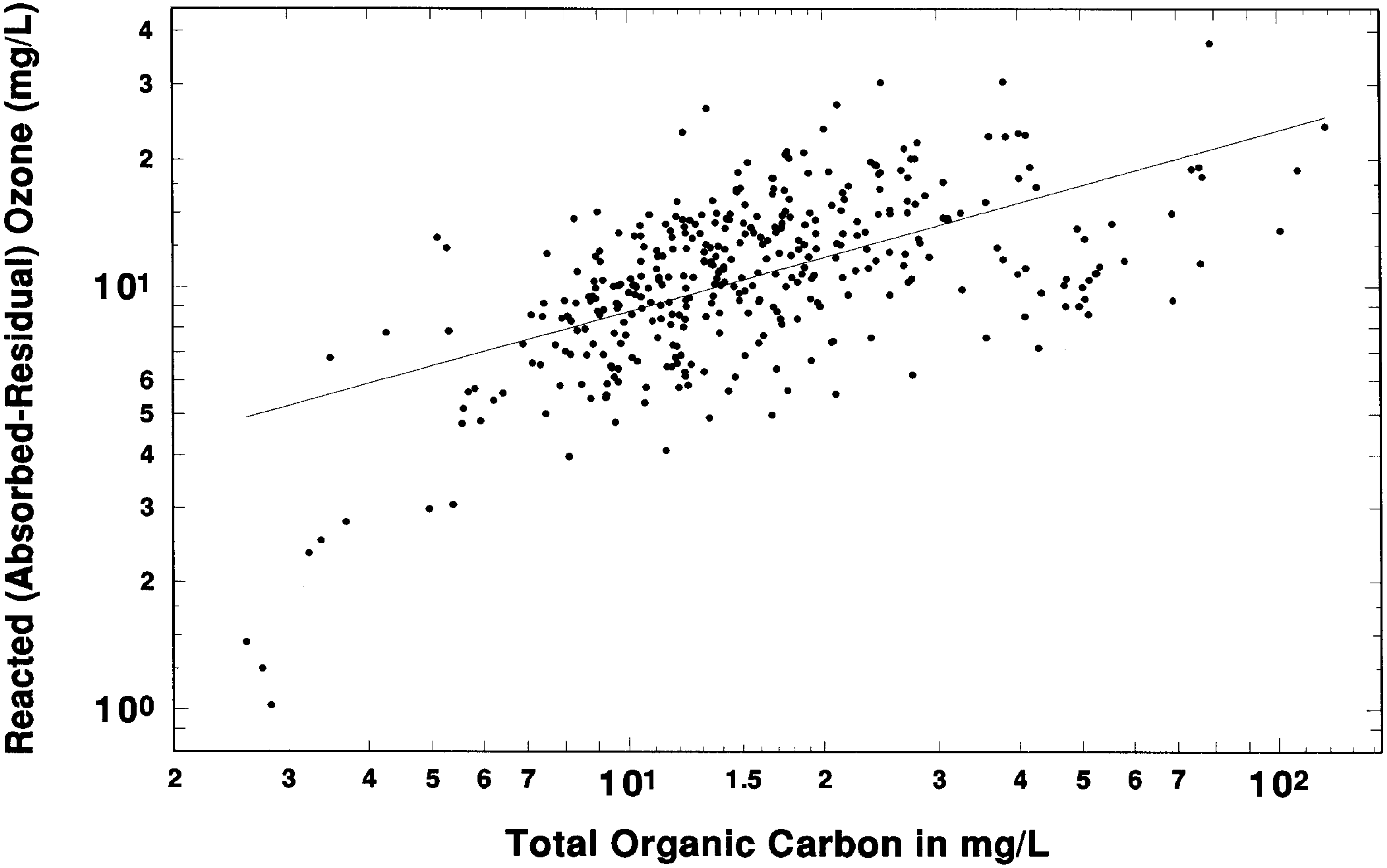

Figure 16. Linear Regression of the Dependence of Reacted Ozone on Total Organic Carbon Concentrations. Log O_{3d} = (0.514 $\pm$ 0.038) + (0.427 $\pm$ 0.031) Log (TOC); n = 375, r = 0.58, r^2 = 0.34, F < < 0.01.

The multiple regression of reacted ozone against both TOC and temperature resulted in a correlation coefficient of 0.63, while TOC, pH, and temperature gave a correlation of 0.71. The coefficient of determination (r^2) is the percentage of the variation in the dependent variable explained by the independent variable(s), and these regressions resolved from 34-50% of the variation in reacted ozone. For these comparisons the F or Fisher distribution approached zero indicating that the correlation was not random. Given the variability of the runoff water, TOC appeared to explain a significant amount of the variation in ozone demand, nonetheless, other models were investigated for analogous relationships.

MODELING

The most general disinfection model is the classic Chick-Watson version (Haas and Karra 1984) which describes the process as a first-order chemical reaction of the form:

$$\log (N_T / N_0) = - k\, C\, T \qquad [1]$$

where: N_0 is the number of organisms per volume at time 0
N_T is the number of organisms per volume at time T
k is the pseudo first order reaction rate constant
C is the residual concentration (mg/L) of the disinfectant
T is the time (min) that the reactions has been occurring

Finch et al. (1992) found that this model inadequately explained ozone deactivation of giardia cysts, but indicated that disinfection could be achieved based on ozone residual, ozone demand, and a contact time of at least 5 minutes. They also indicated that pH, temperature, and contact time affected ozone decomposition and reaction kinetics in a complex manner. Although this study found that residuals were related to disinfection, as shown in Figure 6, the classic model did not appear to describe the observed results, especially when the reaction time term was included.

In an attempt to estimate ozone consumption, Yurteri and Gurol (1988) developed the following formula using synthetic water with the pH set from 6.8-9.0, the TOC set from 0.3-5.3 mg/L, and the alkalinity ranging between 10 and 500 mg/L as $CaCO_3$:

$$\log w = 0.66\ pH + 0.61 \log TOC - 0.42 \log (alk./10) - 3.98 \qquad [2]$$

where: w is the ozone utilization rate per hour
pH is the influent pH units
TOC is the Total Organic Carbon in mg/L
alk. is the alkalinity measured in mg/L as $CaCO_3$

The model was evaluated using diluted digester effluent, stream, and tap water. The TOC ranged from 1.7-7.3 mg/L and alkalinities varied between 15-90 mg/L. The pH of the digester effluent was 6.0 and the predicted rate constant (w) poorly matched the measured value. The pH of the other test waters were from 6.8 and 7.3 and the measured ozone utilization approximated the predicted value. None of the tested pH, TOC, or alkalinity, values affected the constant by more than 10% and it is difficult to anticipate how this model would respond to the variability observed with storm drain effluents.

White (1992) reviewed a study by Venosa et al. (1979) which investigated ozone disinfection of secondarily treated sewage. As with this study, they were attempting to predict effluent coliform counts by monitoring various parameters. For filtered effluent the following equations were developed:

$$\log TC = 3.95 + 0.030\ TCOD + 0.50\ NO_2^{-}\text{-}N - 3.05 \log T \tag{3}$$
$$\log FC = 3.34 + 0.029\ TCOD + 0.48\ NO_2^{-}\text{-}N - 3.40 \log T \tag{4}$$

where:

TC	is the total coliform organisms/100 ml of ozonated effluent
FC	is the fecal coliform organisms/100 ml of ozonated effluent
$TCOD$	is the total chemical oxygen demand of the secondary effluent (mg/L)
$NO_2^{-}\text{-}N$	is the nitrite nitrogen concentration of the secondary effluent (mg/L)
T	is the absorbed ozone dose (mg/L)

The following equations relate to unfiltered sewage effluent:

$$\log TC = 0.96 \log TC_0 - 0.89 + 0.012 TCOD + 0.60 NO_2^{-}\text{-}N + 0.013 TSS - 4.024 \log T - 0.57 R^{1/2} \tag{5}$$
$$\log FC = 4.06 + 0.020 TCOD + 0.37 NO_2^{-}\text{-}N + 0.012 TSS - 3.94 \log T - 0.59 R^{1/2} \tag{6}$$

where the additional terms are:

TC_0	is the number of total coliforms per 100 ml of secondary effluent
TSS	is the concentration of suspended solids in the secondary effluent(mg/L)
R	is the ozone residual in the ozonated effluent (mg/L)

While the present investigation did not quantify the chemical oxygen demand or nitrite concentration, storm drain water is normally well oxygenated and the contribution of the nitrite term should be small. The oxidation of organic carbon (TOC) is ordinarily the most significant contributor to the TCOD. If both TOC and TCOD are suitable for automated monitoring, the latter might be the more appropriate parameter since it would include any sulfite and nitrite, that might be present. Although the influent total coliform count in equation [5] is impractical to use for process control, equation [6] for fecal coliform distributed the influence of this term among other related parameters such as the slope of TCOD and the constant. The suspended solids in sewage are mostly organic and exert a significant ozone demand; however, during the present study, high concentrations of inorganic clay-like material exerted little demand and suggest exclusion of this term. In summary, the last four equations estimate effluent bacterial counts based on: 1) A constant that appears to be correlated with influent bacterial counts; 2) Several ozone demanding substances terms; and 3) The absorbed ozone dose. The unfiltered sewage equations, also include the square root of ozone residual, which may be required when pathogens are contained within particles and not readily vulnerable to disinfection.

The regression equations developed in Figures 6 and 7 can be combined to form equations similar to those developed by Venosa. However, both regressions equations stand alone and, since ozonation is often a multistage process (Rice 1987), they might be independently applied.

The regression in Figure 6 was developed to enumerate the effluent total coliform count and was presented as follows:

$$\text{Log } TC_e = 1.784 - 0.622 \text{ Log } (O_{3r}) \qquad [7]$$

where: TC_e is the total coliform count per 100 ml of effluent water
O_{3r} is the ozone residual in the effluent water in mg/L

The California Ocean Plan (SWRCB 1990) and reclaimed water restricted irrigation (EPA 1992) standards of 1,000 and 23 organisms per 100 ml respectively, are pertinent objectives that equation [7] might be applied to. Their corresponding residual values are .011 and 4.8 mg/L respectively.

The regression in Figure 7, predicts the ozone demand based on the reacted ozone, which was defined as the concentration of ozone absorbed by the water minus any residual. The simplified equation is:

$$\text{Log } O_{3d} = 0.514 + 0.427 \text{ Log TOC} \qquad [8]$$

where: O_{3d} is the estimated reacted ozone or demand in mg/L
TOC is the influent water total organic carbon in mg/L

Assuming a typical TOC concentration of 20 mg/L, the estimated ozone demand is 11.7 mg/L.

The absorbed ozone dose equals the ozone demand plus the ozone residual which can be expressed as:

$$O_{3a} = O_{3d} + O_{3r} = 10^{\log O_{3d}} + 10^{\log O_{3r}} \qquad [9]$$

where: O_{3a} is the predicted absorbed ozone dose in mg/L

Solving equation [7] for the log O_{3r} and substituting it and [8] into [9] we get the following:

$$O_{3a} = 10^{(2.868 - 1.608 \log TCe)} + 10^{(0.514 + 0.428 \log TOC)} \qquad [10]$$

which simplifies to:

$$O_{3a} = 740\ TC_e^{-1.6} + 3.3\ TOC^{0.43} \qquad [11]$$

This equation ignores the ozone delivered to the contacting chamber that is not absorbed and escapes as off-gas. When the effluent total coliform count goal is a set value, the equation simplifies to a constant and an ozone demanding substances term, similar to those developed by Venosa, but using TOC or TCOD which are amenable to recently developed automated process technologies. Incorporation of additional pretreatments, such as coagulation or filtration, into the treatment process would require that this formula, and the regressions on which it was based, be modified. However, these improvements should result in lower applied ozone dosages and a higher quality effluent.

APPLICATIONS

In order to effectively utilize a treatment process, it is critical to understand, control, and monitor the parameters that affect operation. Although the dry-weather effluent from the Pico-Kenter storm drain is generally comparable to secondarily treated wastewater, the quality rapidly degrades in response to either an increase in contaminants or flow, which resuspends settled solids. This variability is evident from Figure 2 and the 90th percentile values in Table 1. A facility designed to disinfect the mean or base flow, which is low in suspended solids, would probably be challenged to adequately treat an extended, order of magnitude increase in both flow and suspended solids. While detention basins could be used to contain these high flows, the runoff is often sustained for hours due to construction site dewatering, fire fighting, potable or sewage main breaks and pool drainage, requiring that extensive structures are constructed. Given the cost and limited availability of property in urban areas, economics favor the inclusion of solutions that conserve area and minimally impact adjacent properties.

One of these alternatives is to make the treatment facility more responsive to rapidly changing conditions through the use of supervisory control and data acquisition (SCADA) systems. The primary limitation to automating a facility is accurate and dependable monitors for the process parameters of interest. Unfortunately, the primary pollutants of concern in the dry-weather storm drain effluent are pathogens, which are difficult to analyze for and the results are delayed until long after the effluent has left the treatment facility. However, based on the findings in this study, a prototype ozonation treatment facility can be envisioned which estimates ozone demand based on effluent bacterial goals and contaminant concentrations. Following pretreatment to reduce the concentration of suspended solids, organic carbon and other ozone demanding substances, monitors for COD or TOC can be used to estimate the ozone demand. The disinfection efficacy can then be verified by monitoring ozone residuals before releasing the effluent to the local receiving waters or potentially reclaiming it for use in irrigation projects. Filter wash water, and any heavily contaminated effluents, would be directed to a traditional wastewater treatment facility. When high volume wet weather flows are encountered, ozone could still be injected into the effluent and used to achieve a modest level of disinfection.

Conclusions

With the initiation of national stormwater and urban runoff pollution control programs, many metropolitan areas are beginning to grapple with the challenge of reducing the contamination associated with storm drain effluents. The results from this pilot plant study show that ozone was extremely effective at disinfecting dry-weather urban runoff, reducing microbial contamination by an average of 3.4 log, and achieving 6 log under optimized conditions. Ozonation also benefitted the environment by oxidizing non-biodegradable organic compounds to forms that are microbially assimilable, while disinfecting without production of a persistent residual. This study also characterized the variability in runoff water contaminant concentrations and derived formulas to assist in predicting the ozone demand of the influent water and total coliform count of the ozonated effluent. While further evaluations of alternative disinfectants such as UV light should be undertaken, ozonation has the potential to significantly reduce the release of contamination and the exposure of recreational bathers to pathogenic virus that have been found in unfiltered storm drain effluents throughout the Santa Monica Bay. In comparison to chlorine disinfectants, ozone is an environmentally and socially acceptable alternative that forms few halogenated or mutagenic by-products and does not require the storage of large volumes of hazardous materials or use of large contact chambers.

Acknowledgements

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Key Words

Ozone; Disinfection; Urban Runoff; Storm Drain; Stormwater; Stormwater Runoff; Pilot Plant; Total Coliforms; Fecal Coliform; Fecal Streptococcus; Enterococcus; Indicator Bacteria; Human Enteric Pathogens; Polio Virus; Public Health; Reclaimed Water.

Résumé

Les inquiétudes concernant l'écoulement de bactéries dans la baie de Santa Monica ont été confirmées quand le virus entérique humain fut découvert dans les évacuations d'eaux pluviales. L'ozonation des eaux urbaines par temps sec fut étudiée comme alternative à la désinfection par le chlore. 10 à 20 mg/L d'ozone a réduit d'une moyenne de 3.4 log le taux de coliformes, la désinfection maximale ayant été obtenue pour 6 log. Les concentrations variables de divers contaminants ont compliqué les analyses, mais elle n'ont pas empêché de montrer que la teneur totale en carbone organique prévue par la consommation d'ozone et le taux du coliformes présents dans les canalisations étaient en lien avec les résidus d'ozone.

Zusammenfassung

Die Bedeutung von Mikroorganismen im Regenwasserabfluß in die Bucht von Santa Monica wurde mittels Isolation von enterischen Humanviren in den Abwasserströmen bewertet. Als Alternative zur Desinfektion durch Chlorierung wurde die Ozonierung der Regenwasserabflußströme nach Trockenwetterperioden untersucht. Coliforme Stämme konnten bei Ozonkonzentrationen von 10 bis 20 mg/L um 3.4 Zehnerpotenzen im Mittel und bis zu maximal 6 Zehnerpotenzen reduziert werden. Obwohl schwankende Schadstoffkonzentrationen die Analyse erschwert haben, konnte der Ozonbedarf anhand des enthaltenen Gesamtkohlenstoffs vorausgesagt werden. Außerdem konnte die Anzahl coliformer Stämme im Abfluß mit den Ozonrestkonzentrationen korreliert werden.

APPENDIX III

DESIGN CONSIDERATIONS IN DISINFECTION URBAN RUNOFF WATER WITH OZONE.

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DESIGN CONSIDERATIONS IN DISINFECTING URBAN RUNOFF WATER WITH OZONE

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ABSTRACT: Because of concerns about pathogens and contaminants in storm drain water, many advocate stringent mass emission controls, in addition to the Best Management Practices (BMPs) mandated under the NPDES storm water program. If implemented, these strategies may require the construction of urban runoff treatment facilities similar to the pilot dry-weather runoff ozonation plant evaluated in this study. The average ozone dose of 12 mg/L was effective in reducing geometric mean bacteria and virus counts 3.4 log (99.96%) and higher doses achieved 6 log (99.9999%) disinfection. Many organic pollutants also appeared to be oxidized during treatment. Runoff contaminant concentrations varied by 2 to 4 orders of magnitude and appeared to be associated with settled solids that re-suspend with increasing flows, requiring that a full scale facility be responsive to changing conditions of water quality and flow. Based on the results and experience acquired during operation of the pilot plant, this paper describes a hypothetical urban runoff treatment facility and characterizes the individual treatment and control processes. The proposed design is provided as a foundation for further discussion and refinement.

KEYWORDS: Stormwater; Treatment; Ozone; Disinfection; Pathogens; Urban Runoff; Process Control.

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INTRODUCTION

Although the Federal Water Pollution Control Act has improved water quality by controlling point sources of pollution, many non-point sources will require management if we are to achieve the goals of the Clean Water Act (GAO 1990). Unlike point sources, which are amenable to management under the National Pollutant Discharge Elimination System (NPDES), non-point sources, such as agricultural and urban runoff, have intermittent or irregular flows, small or diffuse sources, and are difficult to regulate. In urban areas, storm drains collect and convey this non-point contamination and consolidate it into a point discharge. Because most storm drain connections are poorly documented, locating the source of polluted runoff is often difficult and may be complicated by low spots which allow the contaminants to accumulate until some otherwise innocuous activity flushes them from the drain. The spatial and temporal complexity of the system allows these non-point sources to remain unidentified and unabated.

The Santa Monica Bay watershed contains over 75 storm drains, ranging from suburban river beds to concrete lined channels, although most are enclosed conduits of various sizes (SMBRP 1993a). The regional storm and wastewater systems are separate and although sewage should be absent from the drains, landscape irrigation and drainage, pool maintenance, cooling tower blow-down, and other releases, constitute a persistent flow of dry-weather runoff. This nuisance water can contain heavy metals, polycyclic aromatic hydrocarbons (PAHs), phthalates, pesticides

(Greene 1992), polychlorinated biphenyls (PCBs) (Suffet et al. 1993), dibenzo-dioxins and furans (Fisher et al in review). These contaminants, which may result from the deposition of aerial particulates and isolated dumping, are normally at trace (ng/L) or low (μg/L) levels in the water phase, but adsorb onto suspended solids and sediments, where the concentration may be four-orders of magnitude greater (Greene 1992). Pathogen surveys found human enteric virus (Coxsackie B, Echo, and Polio) in three Santa Monica Bay drains (Gold et al. 1992), although others (O'Shea and Field 1992) argue that the nonenteric bacteria and virus embody the greater health threat. Even if sanitary surveys eliminated illicit and illegal connections, recalcitrant sources, such as transients and viral transfer by coprophilic insects (Harwood and James 1979), will continue to require that runoff be recognized as a potential public health threat.

The Pico-Kenter watershed is a 36 km^2 basin, within the cities of Santa Monica and Los Angeles, that discharges onto Santa Monica State Beach through two 3.4 m diameter conduits. Excluding roadways, land use in the watershed is 48% single- and 21% multi-family dwellings, 19% canyons and parks, 6% commercial, 3% schools and civic facilities, and 3% other groups (Stenstrom and Strecker 1993). Chemical contamination is comparable to other drains in the area, while bacterial counts are high (SCAG 1988). Gold et al. (1990) found that enterococcus, fecal, and total coliform counts, at ankle depth in the surf near the drains, always exceeded the California Ocean Plan Standards of 24, 200, and 1000 organisms per 100 mls respectively (SWRCB 1990). At the same depth, these standards were also exceeded

100%, 43% and 86% of the time at 23 m and one third of the time at 137 m down-beach of the discharge.

The stormwater NPDES program primarily controls pollutant emissions through Best Management Practices (BMPs) that prevent contaminants from entering the storm drain system. These include actions, such as street sweeping and catch basin cleaning, and structures, like silt filters, diffusers, grassy swales, detention basins, and debris dams, that reduce erosion, settle suspended solids, trap pollutants, and facilitate biodegradation. Although cities like Santa Monica have implemented many action BMPs, it is nearly impossible to add grassy swales and detention basins to densely populated urbanized areas. These structures may even be counter productive due to the release of fertilizers, pesticides, and botanical refuse. Regulators have begun promoting mass emissions polices to control pollution without designating mandatory treatment processes (SMBRP 1993b), while others advocate that storm drain effluents meet Ocean Plan Objectives (SWRCB 1990), which are often stricter than potable water standards.

Concerns regarding public safety and the environmental impact of storm drain effluents, led the City of Santa Monica to investigate construction of a facility to disinfection the dry-weather flow. The first evaluation (JMM 1987) proposed using chlorine or ultra-violet (UV) light; however, the community was not receptive to the consequences of chlorination, which include: 1) hazardous material storage and transport; 2) dechlorination prior to ocean release; and 3) the formation of carcinogenic disinfection by-products (DBPs). UV light disinfection requires low suspended solids, and the first design suggested inclusion of a 3 mm mechanical screen to reduce these solids below 20 mg/L. During this pilot study, a 1.5 mm screen produced an average suspended solids concentration 5 times this level and elevated flows were observed to re-suspend previously settled solids, resulting in reduced efficacy during periods of peak demand. During the dry summer beach season, when the potential public health exposure is greatest, the runoff is temporarily being pumped to the Hyperion treatment facility, where it receives costly sewage treatment using storm water infiltration and inflow capacity.

WATER TREATMENT WITH OZONE

Ozone has proven invaluable in a myriad of treatment processes including disinfection, oxidation, flocculation, removal of turbidity, tastes, odors and color, and preventing halogenated DBP formation (Rice 1987). Ozone is generated on demand, from air or oxygen, and leaks are detectable at concentrations that allow corrective actions to be taken before health threatening levels are exceeded. Ozone is an effective disinfectant against bacteria, virus, algae, encysted giardia (Hoff 1987) and cryptosporidium (Korich et al. 1990), at CT values (dose multiplied by time) far below those of chlorine oxidants (Finch et al. 1992). The encysted zoonotic protozoans are particularly resistant to oxidation and can be shed from wild and domestic animals throughout the watershed. Ozone has also been used to oxidize pesticides (Reynolds et al. 1989), hydrocarbons (Fronk 1987), toxics like TCE and PCE (Glaze and Kang 1988), cyanide, iron, manganese, sulfide, and nitrite (AWWA 1991), but for most facilities, these applications, are secondary, or incidental, to its primary utilization as a disinfectant.

One disadvantage to ozonating potable water is the lack of residual bacteriostasis, so that persistent disinfectants must be added to prevent distribution system regrowth. However, runoff normally enters bays and rivers where disinfection, and DBPs are undesirable, and the rapid residual decay by dilution and chemical reactions is an attribute. Although fish chronic exposure LC_{50} values range from 10 to 400 μg/L (AWWA 1991), ozone, followed by biologically active filtration

(BAF) to control assimilable organic carbon (AOC), is often used in closed system mariculture (Kobayashi et al. 1993) and marine aquaria like Sea World (IOA 1992). While many chlorine DBPs are mutagenic, most ozonation DBPs, such as ketones, aldehydes, alcohols, and carboxylic acids (van der Kooij 1987), are oxygenated and less hazardous (Tate 1991). Although ozonating water with high bromide levels can form bromate and brominated organics (Means and Krasner 1993), their formation can be controlled by varying disinfection conditions.

Meritens first ozonated polluted water in 1886 (AWWA 1991), but the U.S. Army began extensively testing it use on wastewater in 1955. Additional studies on waste water ozonation were conducted by the Los Angeles County Sanitation Districts and United States Environmental Protection Agency (USEPA) in the 1970s (White 1992). Applications included flocculation, oxidation, flotation, increasing assimilable organic carbon (AOC), and sludge stabilization. During this period, the USEPA also evaluated ozone disinfection of combined sewer overflows (CSOs) (Maher 1974). To paraphrase White, ozone was effective as a tertiary disinfectant, but was expensive and difficult to monitor. Recent improvements in monitoring gas and liquid phase ozone concentrations have alleviated this criticism (Gordon et al. 1988). Robson and Rice (1991) reviewed the operation of the 45 ozone-using American wastewater facilities constructed from 1975 to 1989. While 11 were either in start up or their status unknown, 13 had closed for technical or economic reasons, indicating that the design of these facilities is still problematic.

In comparison to potable and wastewater, the use of ozone on dry-weather urban runoff is virtually undocumented, leading Santa Monica City to conduct a pilot study on the efficacy of ozone in disinfecting the Pico-Kenter Storm Drain nuisance, or base, flow. The Santa Monica Bay Restoration Project (SMBRP) and USEPA also provided support to specifically characterize many of the chemical and physical properties of the water and their temporal variability.

This investigation found that ozone was effective in disinfecting attenuated polio virus, coliform and enterococcus bacteria, with a geometric mean kill of 3.4 log (99.96%) and optimized performance approaching 6 log (Greene 1992). The temporal variability of dissolved conventional and priority pollutants, and organic priority pollutants in sediments, were also documented. Pollutants in the water column were generally near (lead, chromium, arsenic, selenium, PAHs) or far below drinking water standards. High concentrations of chlordane, o-xylene and mixed heavy metals were observed as isolated events. Ozone effectively oxidized many organics when they were present at high concentrations, but was inefficient at background (sub μg/L) concentrations relative to total organic carbon (TOC in tens of mg/L). Subsequent studies (Greene and Stenstrom 1994) have correlated effluent bacterial counts with dissolved ozone residuals, while ozone demand was related to TOC or chemical oxygen demand (COD).

Process parameters and conventional pollutant concentrations observed during the study, are summarized in Table 1. Environmental data often have logarithmic, or geometric, distributions and require transformation to assume a normal distribution. Shaded data fit the normal distribution, based on D'Agostino's test (Zar 1974), while bold-type data approximated a normal distribution better than standard-type data. Temperature and gas flow were normally distributed, while influent percent ozone, pH and water flow, approached a normal distribution. The other analytes and parameters required transformation to approximate, or in the case of coliform and effluent process parameters fit, the normal curve. The contrast between normal and geometric means for bacterial counts, turbidity and suspended solids, emphasize the concentration variability and influence of extreme values on a distribution.

Table 28. Descriptive Statistics for Pilot Plant Operational Parameters and Urban Runoff Analytes[1].

Pilot Plant Process Parameter or Analyte (with units)	Sample Number n Pairs	Minimum Sample Value	Maximum Sample Value	Ozone Pilot Plant Influent Water						Ozone Pilot Plant Effluent Water					
				Normal Distribution			Geometric Distribution			Normal Distribution			Geometric Distribution		
				$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%	$\bar{X}$	σ	90%
Water Flow Rate (LPM)	438	4.0	31.0	**3.1**	**1.11**	**4.5**	2.9	1.48	4.8	-------	-------	------	-------	-------	------
Gas Flow Rate (SLPM)	438	1.9	8.6	12.9	3.4	17	12.3	1.35	18	-------	------	------	-------	-------	------
Influent Ozone (Wt.%)	387	.34	5.1	**2.7**	**1.09**	**4.1**	2.4	1.7	4.7	-------	-------	-------	-------	-------	------
Off-gas Ozone (Wt.%)	387	0.0	2.2	------	-------	-------	-------	-------	-------	.61	.53	1.29	.54	1.35	1.27
Absorbed Ozone (mg/L)	414	3.6	38	-------	-------	-------	-------	-------	-------	13.0	4.9	19	12.1	1.48	20
Ozone Residual (mg/L)	414	0.0	7.8	-------	-------	-------	-------	-------	-------	1.47	1.6	3.5	1.05	1.8	3.4
Reacted Ozone (mg/L)	387	1.02	37.6	-------	-------	-------	-------	-------	-------	11.4	4.9	18	10.4	1.6	19
Temperature (°C)	430	14.0	24.4	18.5	1.7	20.7	18.2	1.10	20.5	18.8	1.8	21.1	18.6	1.10	21.0
pH	401	7.1	9.6	**8.1**	**.29**	**8.5**	8.1	1.04	8.5	**7.8**	**.32**	**8.2**	7.8	1.04	8.2
Conductivity (μmho/cm)	332	470	36000	1310	2200	4100	**1070**	**1.5**	**1900**	1300	2100	4000	**1070**	**1.5**	**1900**
Turbidity (NTU)	349	2.3	5800	83.	370	550	**22**	**3.5**	**110**	71	250	390	**21**	**3.5**	**106**
Settleable Solids (mg/L)	438	<.20	78	.52	5.3	7.3	**<.20**	**6.6**	**2.1**	.52	5.0	6.9	**<.20**	**6.6**	**2.2**
Suspended Solids (mg/L)	434	0.6	6500	103.	500	740	**22**	**4.0**	**129**	97	440	660	**19**	**4.2**	**122**
Dissolved Solids (mg/L)	435	190	30000	870	1600	3000	**690**	**1.6**	**1250**	900	1700	3100	**710**	**1.7**	**1500**
Total Solids (mg/L)	435	280	31000	1010	1800	3300	**780**	**1.7**	**1500**	1010	1800	3300	**780**	**1.7**	**1500**
Total Organic Carbon TOC (mg/L)	425	2.2	124	19	16	40	**15**	**1.9**	**35**	19	15	38	**16**	**1.8**	**34**
Total Coliforms x10^3 (MPN)	438	<.002	54000	1490	3400	5900	520	4500	3600	7.6	4.4	13.2	.16	160	5.6
Fecal Coliforms x10^3 (MPN)	436	<.002	7900	160	670	1020	**19**	**7.8**	**260**	.52	4.2	5.9	**.007**	**7.2**	**.088**
Enterococcus sp.x10^3 (MPN)	47	<.002	1700	190	310	590	**69**	**4.8**	**510**	**.25**	1.04	1.6	**.030**	**5.9**	**.29**

[1] Shaded data was normally distributed (D'Agostino's test). The bold type data, more closely approximates a normal distribution than regular type.

OBJECTIVES

While information on treating potable and wastewater abounds, investigations into the remediation of non-CSO urban runoff are relatively recent and the paucity of published literature restricts the potential responses to any forthcoming regulations. This study describes processes and control systems applicable to a small dry-weather urban runoff treatment facility. Treatment processes include, trash control and straining, preozonation and foam control, biologically active filtration, predisinfection monitoring and chemical adjustment, disinfection, auxiliary treatments, effluent stream disposition, and ozone preparation. The control strategies consist of preliminary operations, predisinfection and disinfection monitoring, effluent discharge, and peak and design flow estimation. This hypothetical "straw man" design is a foundation for discussion, based on the operation of a pilot plant in an urbanized area and the results from several thousand physical and chemical analyzes. The pilot study evaluated ozonation of unfiltered runoff without comparison to chlorine-based or UV disinfection. Runoff treatment should be considered after fully implemented standard BMPs are unable to achieve local environmental objectives.

HYPOTHETICAL TREATMENT PROCESS

Urban runoff is intermediate in quality between potable and wastewater and similar to a secondary effluent, that is low in nitrogen, phosphorous, and microbial contaminants. The quality abruptly declines when increased flows re-suspend settled solids and their adsorbed contaminants. The initial treatment processes function in controlling this concurrent increase in flow and contamination. After mediating these excursions, the water quality is characterized, an adequate disinfectant dose delivered, disinfection verified, and the effluent discharged.

Trash Control and Straining

Collecting the urban runoff, in a junction box that can incorporate a trash rack and wet well, and pumping it to the facility are the initial treatment processes shown in Figure 1. Trenches or inflatable dams, perpendicular to the storm drain, can divert the runoff into alcove-like boxes or existing pump stations can be converted. The basal flow from several drains can be collected in a single intercepting conduit and conveyed to a central treatment facility. Maintenance, such as pre-storm dam extraction, trench, conduit, and wet well debris removal, is significant and should be anticipated. Whichever option is chosen, it should be located after the last influent connection, generally near the receiving water, to maximize the runoff treated.

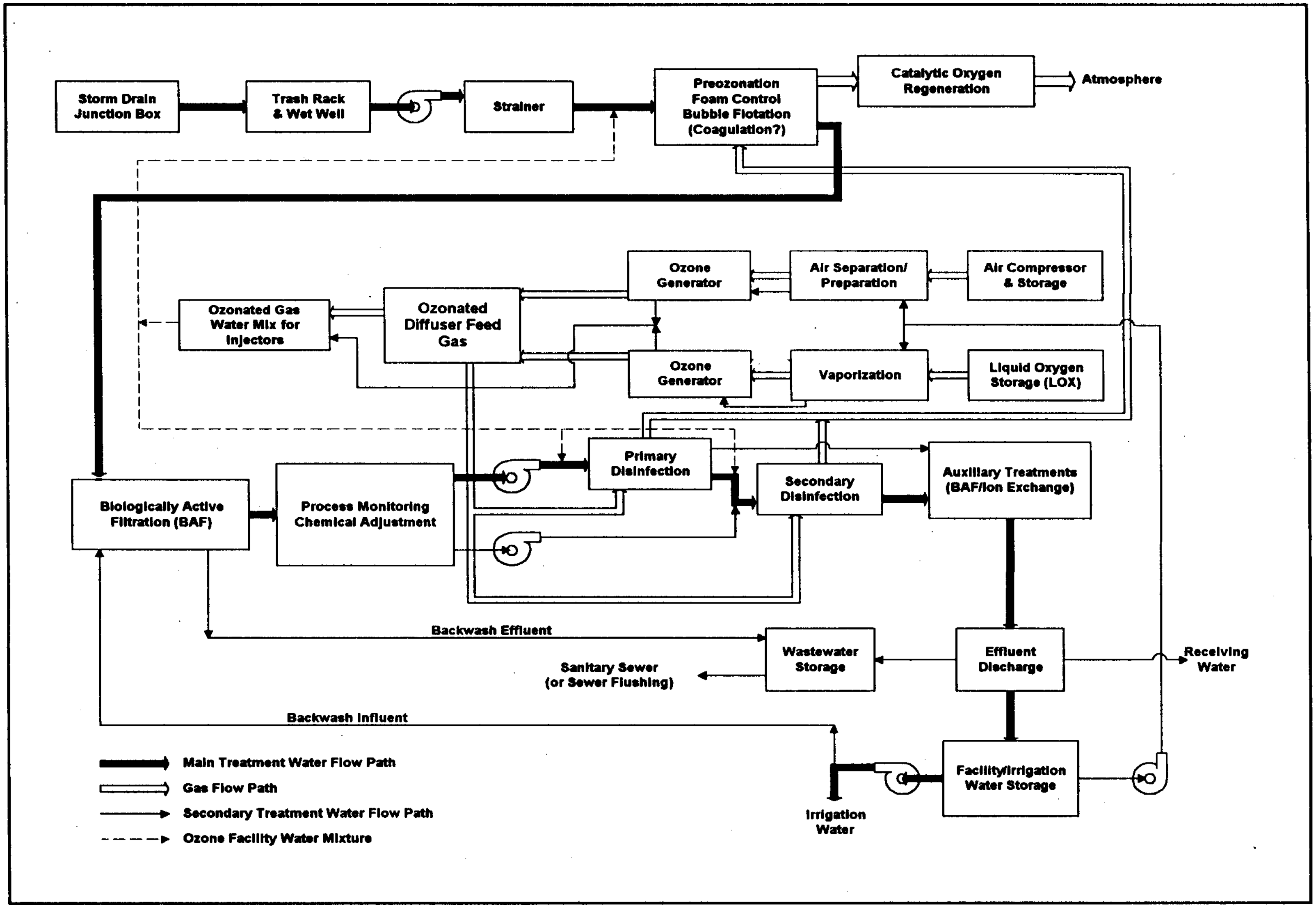

Figure 17. Schematic of Proposed Dry-weather Urban Runoff Treatment Process Flow Configuration.

Because of aesthetic and wildlife impacts, trash is among the most objectionable pollutants. Fortunately, storm runoff is amenable to trash removal, using racks or screens, and consideration should be given to removing trash from flows that exceed the peak flow capacity of the plant. Runoff carries plastic bags, bottles, cans, and other debris, which clog stationary grates, so that a mechanical design, with intermittent operation based on differential water height, is preferred. Depending on installation and hydrology, the rack can traverse the main channel or be located in a parallel channel or alcove to minimize the obstruction from rocks and metal objects which travel in the mainstream. The storage and disposal of solid wastes should also be anticipated. Pumps, located adjacent to the trash rack, deliver the water to the facility. Low flow values during the pilot study were often half of the mean estimate, making single speed units vulnerable to over-cycling, and suggesting that variable speed pumps would be more appropriate.

While screens remove debris larger than a few cm., suspended solids in the pressurized stream can be removed by strainers that catch particles to around 0.2 mm. Automatic strainers perform a backwash cycle whenever clogging causes the differential head pressure to exceed a preset level. These units conserve water by periodically backwashing during normal conditions, then operating continuously when water quality deteriorates. The backwash contains sediments and suspended solids and can be discharged to the sanitary sewer for conventional treatment.

Preozonation and Foam Control

Foams and organic matter interfere with ozonation, decrease disinfection, and increase DBP formation. One-fourth of the pilot facility tests were impacted by their presence. These substances maybe eliminated by combining preozonation with air floatation. This technology was utilized on the influent to the Moule (France) potable water plant which contains TOC in excess of 10 mg/L and algae number in the tens of thousands per ml (AWWA 1991). Flotation was chosen, over sedimentation, because of the low concentration and buoyancy of the organic matter, including microorganisms, in the runoff. Foams disrupt contact chamber hydraulics by displacing the water column, reducing retention times and impeding transfer at the gas/liquid interface. While anti-foaming agents improve flows, they are expensive, potentially toxic, increase ozone demand, inhibit disinfection, and may impact gas transfer. Preozonation improves filtration, by increasing particle removal (Wilczak et al. 1992), forming AOC, improving filter ripening, decreasing turbidity, and initiating disinfection (AWWA 1991).

After straining, the water flows downward through the preozonation chamber and passes countercurrent through diffused ozone containing off-gas from the disinfection process. This consumes the remaining ozone, while any foam rises into the upper chamber where it is scraped or sprayed into a sludge discharge trough. After the diffusers, an ozonated facility water side-stream is injected with the mainstream into the coagulation chamber, producing fine bubbles that carry foam and floc upward to the sludge trough. The off-gas is de-misted and enters a thermal catalytic oxygen regenerator, that removes any remaining ozone. Although the coagulating ozone dose is difficult to predict (AWWA 1991), Sontheimer (1988) recommended a 2:1 TOC to ozone does, as a compromise between AOC formation and excessive organic oxidation.

The effectiveness of including coagulant addition and flocculation in the proposed treatment train has not be determined. Addition prior to preozonation would result in floc dispersal prior to air floatation. If added after preozonation, aggregation could be delayed until after bubble entrapment, air flotation, and skimming occur. Flocculating with coagulants and ozone is erratic, often counterproductive (Edwards et al. 1994), and requires space that may be unavailable in urbanized areas. Furthermore, the variable water quality complicates estimation of the coagulant dosage. Until on-line instrumentation for determining coagulant addition becomes available, it would be difficult to include this processes in the treatment train.

Biologically Active Filtration

With the deletion of sedimentation, filtration becomes one of the most critical processes in the proposed treatment strategy and should be constructed as duplicate units that allow either isolated or parallel operation. Using a multimedia filter with a thick layer of coal or granulated activated carbon (GAC), would encourage development of biologically active carbon (BAC) and biologically active filtration

(BAF). Although preozonation precedes BAF, the low disinfectant dose, and delay during flotation, assure that most of the residual is consumed prior to filtration. In potable applications, the benefits of layering BAC over conventional filters include, reduced effluent AOC, absorption of toxic and organic contaminants, and longer filter run times (AWWA 1991). Although excessive facility water backwashing and compressed gas media agitation could eliminate predators, flow rates to 20 m/h (8.2 GPM/ft^2) have little impact on microbial growth (AWWA 1991). Operating the paired filters on alternating loading/depletion cycles, would also encourage the biomass to utilize both adsorbed AOC and refractory contaminants, such as PAHs.

Predisinfection Monitoring and Chemical Adjustment

Following filtration, parameters such as TOC or COD should be monitored to estimate ozone demand and disinfectant dosage (Greene and Stenstrom 1994). Sensors for pH, turbidity, and conductivity could determine the effluent discharge path, since many values from the pilot study (Table 1) were indicative of contamination that is unacceptable for environmental release.

Any chemical adjustments required for disinfection should be undertaken immediately after process monitoring. Unfortunately, the effectiveness of most chemical treatments on urban runoff is untested. The combination of hydrogen peroxide and ozone often reduces chemical contamination by accelerating hydroxyl radical formation and oxidation, but it rarely improves disinfection and may decrease

AOC formation (Volk et al. 1993). Given the variable concentration and susceptibility of organic contaminants, it would be difficult to anticipate the optimal peroxide dose; however, 50% of the ozone dose, by weigh, is typical. When bromide bearing waters are ozonated, bromate, which has unclear carcinogenicity and health effects (Pontius 1993), can form. This reaction can be controlled by acidifying the water to a pH of less than 7.0 with sulfuric acid. During the pilot study, the effluent pH ranged from 7.0 to 9.0 and remained within Ocean Plan Standards, making adjustment unnecessary. This decision should be reassessed based on runoff characteristics and developing information.

Disinfection

The primary methods of ozonating water were reviewed by the Metropolitan Water District of Southern California (1988) and the American Water Works Association (1991) and included: 1) Bubble diffusers; 2) Turbine mixers; 3) Venturi-type Injectors; 4) Packed columns; 5) Spray chambers; 6) Deep U-tubes; 7) Sweeping porus plate diffusers; and 8) Submerged static radial turbine contactors. Submerged static turbines are similar to side-stream injectors, but discharge vertically and have higher maintenance costs. Sweeping porus plate and deep U-tube technologies require consistent, rather than variable flow rates. Spray chambers inefficiently transfer ozone to the liquid phase and have high pumping costs. While packed columns mimic plug flow reactors, the packing reduces the hydraulic retention time, builds up scale, and increases head loss. Turbines resemble stirred reactors, require regular maintenance, and constant energy and gas inputs, regardless of runoff flow rates.

Normally the gas in ozone generating systems is pressurized, complimenting diffusion and injector systems. Most fine bubble diffusion chambers are 6 m deep, and pumping maybe required to overcome head pressure. Although diffuser pores clog if gas flows are intermittent, disinfection is a process that should rarely be interrupted. Bubble channeling is also a concern, but can be minimized by careful contactor design. The main disadvantages of Venturi injectors with static mixers, is head loss and limited turndown capabilities. This can be ameliorated using constant flow pumps to pressurize a side-stream through the venturi injector, then returning the ozonated flow into the more variable mainstream. Although the transfer coefficients (K_La) of injectors may exceed that of diffusers (Long Beach Water Department 1990), both exceed 95% transfer efficiency and, with off-gas recycling to the preozonation chamber, waste little ozone.

In their review of wastewater ozonation facilities, Robson and Rice (1991) suggested that at least two 5 m countercurrent disinfection stages should be utilized, with a contact time greater than 15 minutes. Based on these recommendations and the pilot study, the hypothetical facility would incorporate two towers, with two chambers each. Two variable speed pumps should linearly increase flow through the towers to maintain disinfection efficacy. Normally, the runoff should move serially through the four chambers to achieve reclamation standards, but, during high flows, the towers operate in parallel to maximize disinfection prior to discharge.

Under dry-weather conditions, facility water, that had previously cooled the ozone generators, is ozonated with a venturi injector, mixed with the main stream, and pumped into the first chamber of the first tower. At the apex, the water descends into the second chamber, countercurrent to a diffused ozone stream, then progresses to the second tower for similar treatment at lower ozone dosages. When flows approach half of peak capacity, disinfection switches to parallel operation and the second pump begins discharging through an ozonating venturi injector, sized to the maximum output, and into the second tower. The output from the first pump passes through a similar injector, but the feed gas line remains closed until the ozone demand exceeds that which can be supplied with the facility water side stream. The tower off-gas is repressurized and recirculated to the preozonation chamber.

The ozone dosage required for disinfection is dependent on water quality, disinfection goals, and to a lesser extent operational conditions such as contact time and flow. In potable applications, the dosage is generally between 1 and 5 mg/L (AWWA 1991). For wastewater applications with a discharge goal of 70 total coliforms per 100 ml, filtered secondary effluent requires 15 to 20 mg/L ozone, while demand was halved in nitrified effluent (Robson and Rice 1991). These dosages doubled when the discharge goal was the reclamation standard of 2.2 coliforms per 100 ml. For urban runoff screened through a 1.5 mm mesh and containing 20 mg/L of TOC, the calculated disinfectant dose needed to achieve the California Ocean Plan Standard of 1,000 coliform organisms per 100 ml, was 12 mg/L, while the landscape irrigation standard of 23 coliforms per 100 ml required 16.5 mg/L of ozone (Greene and Stenstrom 1994).

Auxiliary Treatments

Auxiliary treatments include processes that could be used to polish the effluent in order to achieve specific regulatory or effluent goals, but are not required for disinfection. The list of potential alternatives is extensive and dependent on the site, flow and runoff characteristics.

In the study leading to this investigation (Greene 1992), the mean concentration of lead, zinc, chromium, and copper exceeded California Ocean Plan objectives, and the highest values were associated with highly conductive runoff. Water with this characteristic could be treated with columns containing a solid phase resin with a metal chelating weak anionic group which preferentially binds heavy metal salts, while liberating the alkaline earth elements. Dilute sulfuric acid is used to elute the metals from the saturated resin, which is then regenerated using a sodium carbonate solution. The heavy metals, eluant, and regenerant can then be recycled or neutralized and discharged. Ozone may react with the resins and should not enter columns.

Another auxiliary treatment would be the inclusion of a BAC filter to remove residual organic contaminants and the AOC that is formed during ozonation. Although nonpathogenic microorganisms will be present in the effluent, it should remain suitable for ocean discharge.

Effluent Stream Disposition

The envisioned treatment facility has three possible effluent streams. One leads to the receiving water, where runoff had previously discharged and stormwaters still flow. The second carries filter backwash and recalcitrant runoff to the sanitary sewer for conventional wastewater treatment. The third, highest quality, effluent stream could be reclaimed for facility demands, such as backwashing, generator cooling, side-stream ozone injection, and landscape irrigation.

In California, the primary receiving water is the Pacific Ocean and although standards have not been set for runoff, previous storm drain studies (Greene 1992, Suffet et al. 1993) have compared effluent quality to the California Ocean Plan objectives (SWRQB 1990) and national potable water standards. While the proposed treatment should reduce the concentration of most contaminants to below potable water standards, the Ocean Plan objectives for copper, PAHs, and PCBs are far more restrictive and maybe impossible to meet using traditional technologies.

Discharges to the sanitary sewer primarily consist of suspended solids backwashed from the strainer and filters, but could include moderately contaminated runoff that is unsuitable for environmental release. Exceptionally contaminated runoff could be retained in wastewater storage tanks, until appropriate disposal or decontamination can be arranged. In areas such as the Los Angeles basin, the small increase in wastewater volume ($\approx 0.25\%$) should have negligible impact on secondary treatment facilities.

The highest quality effluent could be reused for filter backwashing, air compressor and generator cooling, and liquid oxygen (LOX) vaporization. After cooling the generators, ozone could be injected into this facility water and the side-stream mixed into the main flow at the preozonation and disinfection steps. As the technology matures, investigations into effluent reuse should be made and the standards modified to permit ozonation (EPA 1992).

Ozone Preparation

Ozone is typically prepared from air or oxygen and the technology is well documented (AWWA 1991 and MWD 1988). Ozone production from oxygen is double that of air, but the expense of separating oxygen from air is substantial and may outweigh the benefits, especially for a small installation. Although LOX procurement is prohibitive for large facilities, urban facilities should evaluate the cost against the operational expense of air compression, preparation, cooling, and noise suppression. Using facility water to first vaporize the LOX, then cool the ozone generators, should also lower maintenance costs, while increasing ozone generation efficiency and gas to water phase ozone transfer. A hybrid system designed to operate on air, with LOX backup during periods of peak demand is also conceivable.

TREATMENT CONTROL STRATEGY

Unlike traditional treatment works, an urban runoff facility must be responsive to rapidly changing conditions of flow and contamination. Although Table 1 portrays the variability of the runoff, it cannot connote the rapidity with which the contaminant concentrations change. During the pilot study, dry-weather flows increased 50 fold over two minutes. Concurrent with these wave fronts, is an equally dramatic increase in suspended solids and trash that are entrained into the flow and the demand for ozone, and other additives. The effluent quality will also vary requiring that alternative effluent discharge streams are available. Fortunately, these parameters can be collected using sensors and on-line monitoring equipment and controlled with a SCADA (supervisory control and data acquisition) system. Figure 2 diagrams the major process control steps for the hypothetical treatment facility, which are described in the following paragraphs.

Preliminary Operations

Trash racks are rarely automated, however, in storm drain applications, the bars may remain unobstructed for days under typical conditions, then clog repeatedly due to trash-carrying storm runoff. The water height in the junction box and wet well could be compared using two ultrasonic water height sensors. When they differ by some preset value, the rack would initiate operation and run for some preset time.

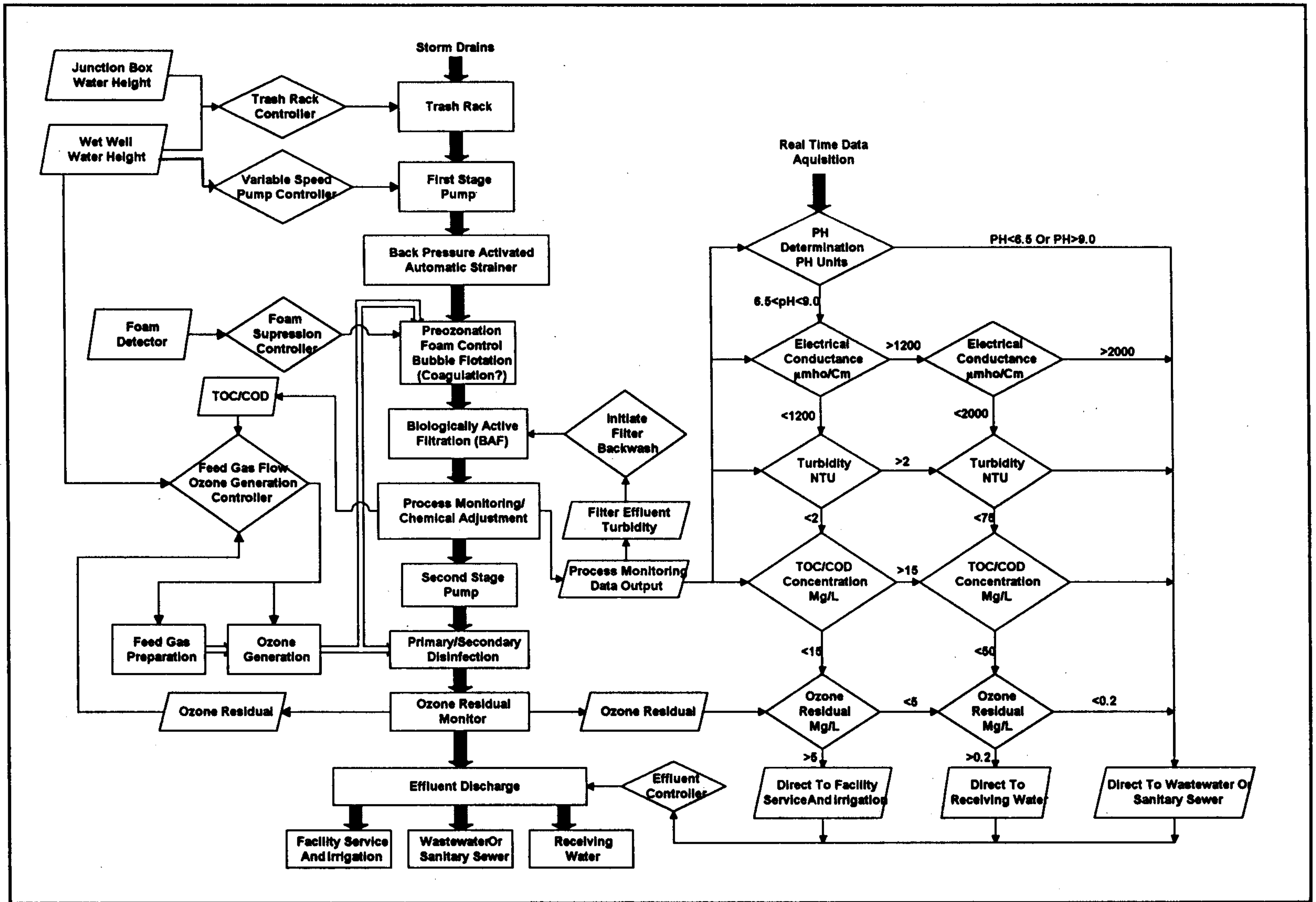

Figure 18. Schematic of Proposed Dry-weather Urban Runoff Treatment Process Control Strategy.

The wet well height sensor could also be calibrated to control the output from the variable speed pump(s) that deliver the runoff into the facility through the automated strainer. Among the available strainers are models that initiate backwashing based on differential pressure across the strainer. Since this process has little impact on other operations, there is no impetus to relocate control to the SCADA system. During air flotation, excessive foam formation can be detected using photo path sensors that spray facility water, or foam suppression agents, and divert the foam into the sludge troughs.

Predisinfection Process Monitoring

The only control operation during biologically active filtration should be directing flow between the paired units. BAF should remove most of the settleable and suspended solids from the runoff water and simplify the analysis of physical and chemical characteristics. Parameters to be monitored include turbidity, total organic carbon (or chemical oxygen demand), pH, and conductivity. Most of these will be used to determine the appropriate discharge path, but turbidity and TOC are critical in monitoring filter performance and ozone disinfection dose.

Along with head loss, turbidity and particle counting, are important means of regulating filter performance. Available in-line turbidimeters efficiently operate below the 2.0 NTU standard for water reuse applications in California (EPA 1992). Values exceeding this set point, would trigger a backwashing cycle and cause the strainer effluent to be directed to the parallel filter unit. A dual purpose, high output pump should deliver reclaimed facility water for either irrigation or backwash of the BAF. The backwash and pre-ripened effluent would be discharged to the sewer until low turbidities indicate that filter is ready for service.

Previous studies have correlated the organic carbon concentration of urban runoff (Greene and Stenstrom 1994), or the chemical oxygen demand of secondary sewage effluent (Venosa et al. 1979), with ozone demand. Process monitoring instruments would conduct these analyses on the filter effluent and the SCADA system would integrate this data with runoff and feed-gas flows, ozone residuals, and generator output to determine an effective ozone dose, then accordingly adjust feed gas and ozone generator output.

If acid, peroxide, or other chemical additive is required, the feed rates would probably be based on measurements conducted during predisinfection monitoring, while mixing could occur during pumping and ozone disinfection. The predisinfection variable speed pumps would be controlled in a analogous manner to, and with input from, the first stage pumps.

Disinfection Monitoring

Since previous runoff disinfection studies have demonstrated that ozone residuals are correlated with effluent coliform counts (Greene and Stenstrom 1994), dissolved ozone residuals are the primary parameter monitored during disinfection. The World Health Organization (WHO) recommends that potable water maintain a 0.4 mg/L residual for 4 minutes to achieve disinfection (AWWA 1991). The Surface Water Treatment Rule (EPA 1989) specifies a similar series of "C·T" values where C is the available disinfectant concentration and T is the exposure time in minutes. Disinfection is envisioned to occur in two towers, each consisting of a co- and counter-current chamber with runoff normally moving serially through the four chambers. An ozone residual sensor should be placed at the effluent of each chamber, since two measurements are needed to estimate the residual disinfectant concentration (C) and exposure duration (T).

The ozone dose entering the first chamber should be in slight excess of that estimated to meet demand and achieve a set residual. If the first sensor verifies the residual, subsequent chambers would receive modest doses of ozone to maintain it. If it is low, ozone delivery to the second chamber would be increased and the residual verified prior to passage into the second tower. Similar constraints should govern passage through chambers three and four. Under these conditions, failure of one sensor should not constrain operations. During high flows, the towers switch to parallel operation, with the first chamber of each tower being the primary disinfection contactor, while the second chamber would add additional ozone as required to achieve a residual. Once the residual is present, the effluent is ready for discharge.

Analysis of the off-gas ozone concentration has been used as an indicator of disinfection on the assumption that moderate concentrations of ozone indicate that demand has been satisfied and a residual is present. These observations may also indicative of plugged diffusers increased bubble size, and low transfer efficiency. Since the off-gas is recycled for preozonation, knowing the ozone concentration may warrant installation of this low-maintenance early-warning device.

Effluent Discharge

A paradigm shift in the design of this facility, is accepting that runoff quality and quantity are subject to excursions beyond the capabilities of the plant and that attempting to control these events is costly and results in unwarranted levels of treatment and idle resources. Instead, the treatment is adjusted for runoff quality and quantity and the effluent is discharges so that the potential health or environmental consequences are minimized. These discharge paths are: 1) The wastewater disposal system; 2) the local stormwater receiving water; and 3) The facility and irrigation reclamation system. The decision matrix, dominating the right half of Figure 2, characterizes the parameters, and representative set point values, used in determining the discharge path. In the matrix, movements to the right are indicative of decreasing water quality.

The California Ocean Plan requires that effluents remain between 6.0 and 9.0 pH units. In the pilot study, effluent pH was consistently between 7.1 and 8.9, although influent values reached 9.6, but dropped one to one half unit during ozonation. Runoff with a pH between 6.5 and 9.0 should be suitable for facility use and ocean release, while values outside of this range, result in the runoff being discharged to the wastewater system. Sensors can be used to measure pre- and post-disinfection pH, facilitating treatment and insuring effluent water quality goals.

Electrical conductivity is a measure of dissolved solids and salts, which if similar to those in the ocean, can be safely released. It is also indicative of objectionable heavy metal salts that are strictly regulated and until more robust means of estimating low concentrations of metal contamination are developed, runoff that is highly conductive should be treated as wastewater. Irrigation water with high dissolved solids can interfere with soil permeability and plant growth and should not be reclaimed, particularly when sodium exceeds calcium and magnesium, as in runoff water (EPA 1992). The conductivity of facility and reclamation water should be below 1,200 μmho/cm (1.2 ds/m), while runoff above 2,000 μmho/cm (2 ds/m) should enter the sewer. These suggested setpoints are based on previous results (Greene 1992) which are both site specific and related to local conditions, upstream permitted discharges, and regulatory goals.

California requires that reclaimed water contain a turbidity of less than 2 NTU, which is a convenient maximum value for runoff to be considered for reuse at the treatment facility or for irrigation. Likewise, the California Ocean Plan requires discharges to be below 75 NTU suggesting that effluent with a turbidity above 75 NTU be release to the sanitary system. Values between these extremes would generally be suitable for discharge to the environment. Ozone can disinfect very turbid water, especially when the suspended material is inorganic (Greene 1992). However, even runoff with suspended organics can effectively be disinfected by ozonation, an attribute that should be considered when comparing ozone and UV disinfection.

Although unregulated, total organic carbon can be continuously monitored to gauge water quality. While TOC concentrations reached 124 mg/L during the pilot study, the geometric mean was 15 mg/L. Flotation and filtration should significantly reduce these values, lowering ozone demand and improving disinfection. In Figure 2, the 15 mg/L breakpoint between facility and receiving water discharge is proposed on the basis of pilot plant operations. Levels of TOC above 50 mg/L are indicative of contamination or filter failure and unpredictable disinfection, requiring that the effluent be released to the sewer for conventional wastewater treatment.

The final input in determining the discharge path, is the dissolved ozone residual, which previous studies have shown to be correlated with effluent coliform counts (Greene and Stenstrom 1994). To meet the California irrigation standard of less than 23 coliforms per 100 ml. should require a 5 mg/L residual based on the pilot study which ozonated unfiltered urban runoff. This reference value should probably be much lower in the proposed facility because in the previous study: 1) Screening (1.5 mm) did not remove particles that shielded bacteria from disinfection; 2) Contact times were short (2-4 minutes) and residuals developed late in the treatment step; and 3) The residual was monitored at a single point and no "CT" values could be developed. Effluent with a residual above 0.2 mg/L should be significantly disinfected and dischargeable to the receiving water. Lower residuals values would generally indicate that ozone consuming contaminants are present and the discharge should receive wastewater treatment.

Measuring the parameters prior to disinfection, allows heavily contaminated runoff to by-pass disinfection and be discharged directly to the sanitary sewer, while runoff destined for receiving water discharge may be less thoroughly disinfected while achieving local objectives.

Peak and Design Flow Estimation

The coincident increase in flows and pollutant mass emissions, drives the sizing of the proposed facility. In some watersheds, a plant sized to treat storm flows would dwarf many sewage plants, while one designed for the mean dry-weather flow would be incapacitated by the extremes, that re-suspend contaminated sediments. An appropriate compromise sizes the facility for low flows, which may be half of the mean base runoff, but also events that are several times the mean, which if uncontrolled would flush contaminants into the environment. The decision should be based on several weeks of continuous dry-weather flow recording and the peak flow set at 4-10 times the mean. Although this figure should be adjusted for local conditions and is somewhat arbitrary, it should feasible to operate the facility within this range and the excess capacity is available for treating the first flush of materials that can antecede some storms.

CONCLUSIONS

Urban runoff, conveyed by storm drains, is a significant source of contamination to our nations waters and many groups advocate implementing emission standards. Pollution control specialists must begin to develop and evaluate alternatives, so that a practical dialogue can be developed and cost-effective strategies instituted. In urban areas, construction of large detention basins or wetlands is costly and often politically unacceptable, but education programs and policy adjustments will not eliminate most runoff contaminants. For dry-weather storm drain flows that exceed a thousand m^3 per day, the proposed runoff treatment facility should eliminate the health concerns of summer beach users, reduce environmental contamination, and provide reclaimed water. Although this study is based on a pilot evaluation of ozone disinfection of unfiltered runoff, further studies comparing UV light and ozone disinfection of filtered runoff should be undertaken, but balancing the lower cost of UV disinfection with the flexibility and adjustable output of ozone generation. In comparison to previous urban runoff practices, which discharged without treatment, the proposed plant would significantly reduce pollutant emissions.

Previous runoff disinfection studies found that: 1) Influent water flow and quality varied significantly and changed rapidly; 2) Foaming substances frequently interfered with treatment; 3) Most contaminants were associated with sediments and re-suspended solids; 4) Ozone demand was correlated with TOC concentration; 5) Ozone was an effective disinfectant, even in runoff with inorganic suspended solids;

6) Effluent bacterial counts were correlated with ozone residual; and 7) Metals, polycyclic aromatic hydrocarbons (PAHs), phthalates, and other contaminants could limit effluent discharge options and support the imposition of mass emission controls.

The proposed urban runoff treatment facility addresses these challenges by: 1) Utilizing dependable sensors and a SCADA system to adjust output and treatment to changing levels of flow and contamination; 2) Screening, straining, and combining flotation with ozonation to coagulate and remove suspended solids and foaming substances, then using biologically active filtration to remove assimilable organic carbon; 3) Eliminating most suspended solids, particulates, sediments, and their adsorbed contaminants prior to disinfection; 4) Including predisinfection processes to remove organic matter and estimating ozone demand using TOC or COD; 5) Disinfecting with ozone an effective, non-persistent, environmentally sensitive, form of oxygen; 6) Monitoring and controlling disinfectant dosage with a demand responsive system; and 7) Providing auxiliary treatments, such as metal chelating resins, to supplement the pollutant control that occurs during predisinfection and ozonation. Finally, the multiple effluent discharge paths assures that contaminated runoff receives further treatment, while high quality water is reclaimed for beneficial uses such as filter backwashing and landscape irrigation.

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