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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-logs, 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 also are managed (GAO, 1990). Many point sources, such as publicly owned treatment works (POTWs), power plants, factories, and refineries, have identifiable contaminant sources, outfalls, 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 frequently are 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 also is 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 presently are 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 physically are 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 backyards 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 dwellings, 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 quantified separately. 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 studied extensively 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 mL, 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 one-third of the time. Local agencies previously had 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 viruses, 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 virus 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 disinfect the dry-weather flow. The first evaluation (JMM, 1987) proposed using ultraviolet (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 byproducts (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 correlated positively with microbial contamination. (The observed mean suspended solids concentration was five 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, then was 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 terminated immediately 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 recently has begun investigating its use as an alternative disinfectant that produces fewer halogenated byproducts (AWWA, 1985, 1991, and 1992). The CT values (concentration multiplied by time) of ozone generally are 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 then are flushed into the watershed drainage.

Since ozone decays rapidly, 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 normally is 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 often is used by large marine aquaria, such as the Sea Worlds, as their primary oxidant (IOA, 1992). Unlike chlorination byproducts, which often are mutagenic, ozonation DBPs generally are 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 often is 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).

De 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 then were 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 1980s, 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 startup, 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 the science of designing a wastewater ozone disinfection facility still is in its infancy.

While information exists endorsing the use of ozone for disinfection of secondary 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 primarily has 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 up to 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 (SLPM) with a 6-meter water head pressure. Ozone-containing 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.

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.

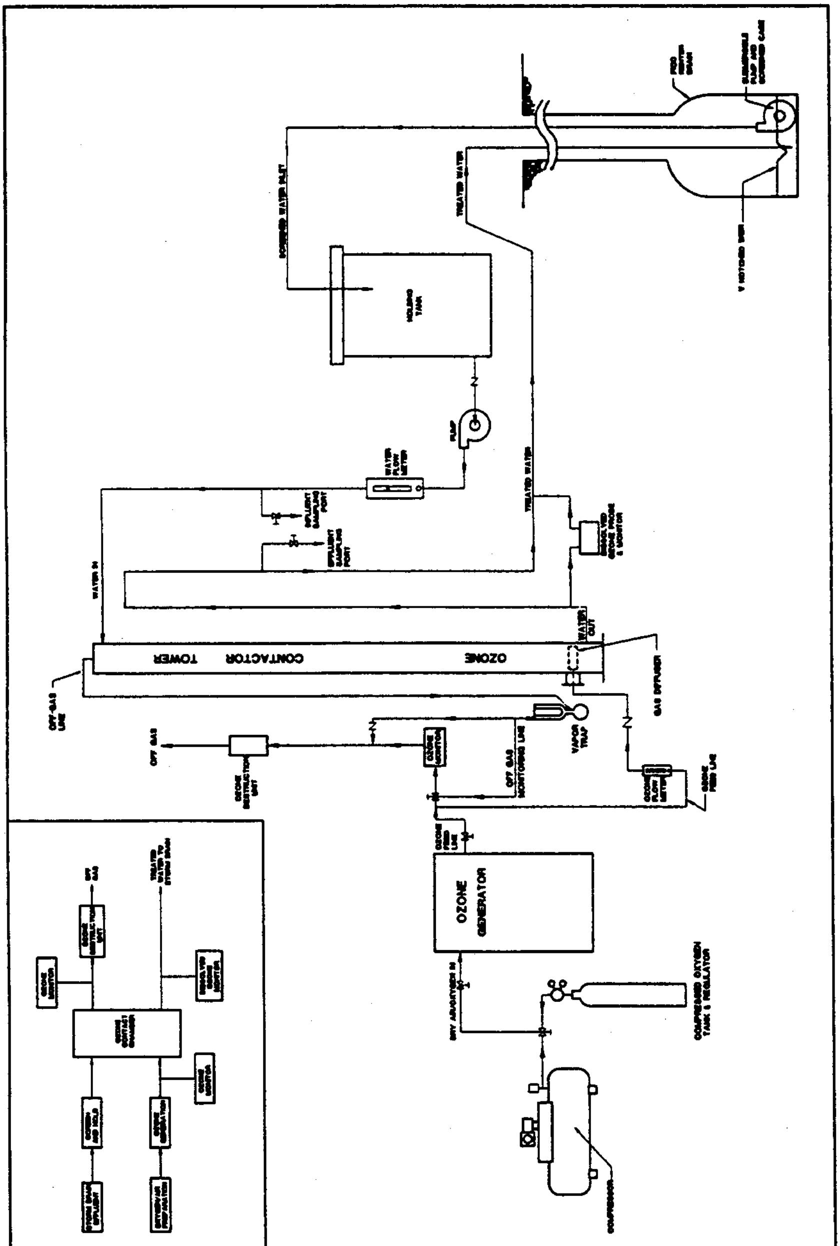

Figure 1. Ozone pilot plant process diagram and equipment schematic.

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 generally was 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 either at 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, flow meters and ozone monitors previously described. Water and gas flow rates always were 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 Imhoff 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 then were serially diluted and plated, following the EPA Interim Procedures for Conducting the Ames Mutagenicity Test (EPA, 1983b), using strains TA98 and TA100 with and without S9 activation. The total and fecal coliform analyses were conducted using the minimal media ortho-nitrophenyl-beta-D-galactopyranoside4-methyl umbelliferyl-beta-D-glucuronide method, also referred to as the minimal media O-MUG or MMO-MUG method 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 was 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 phosphorus. 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.

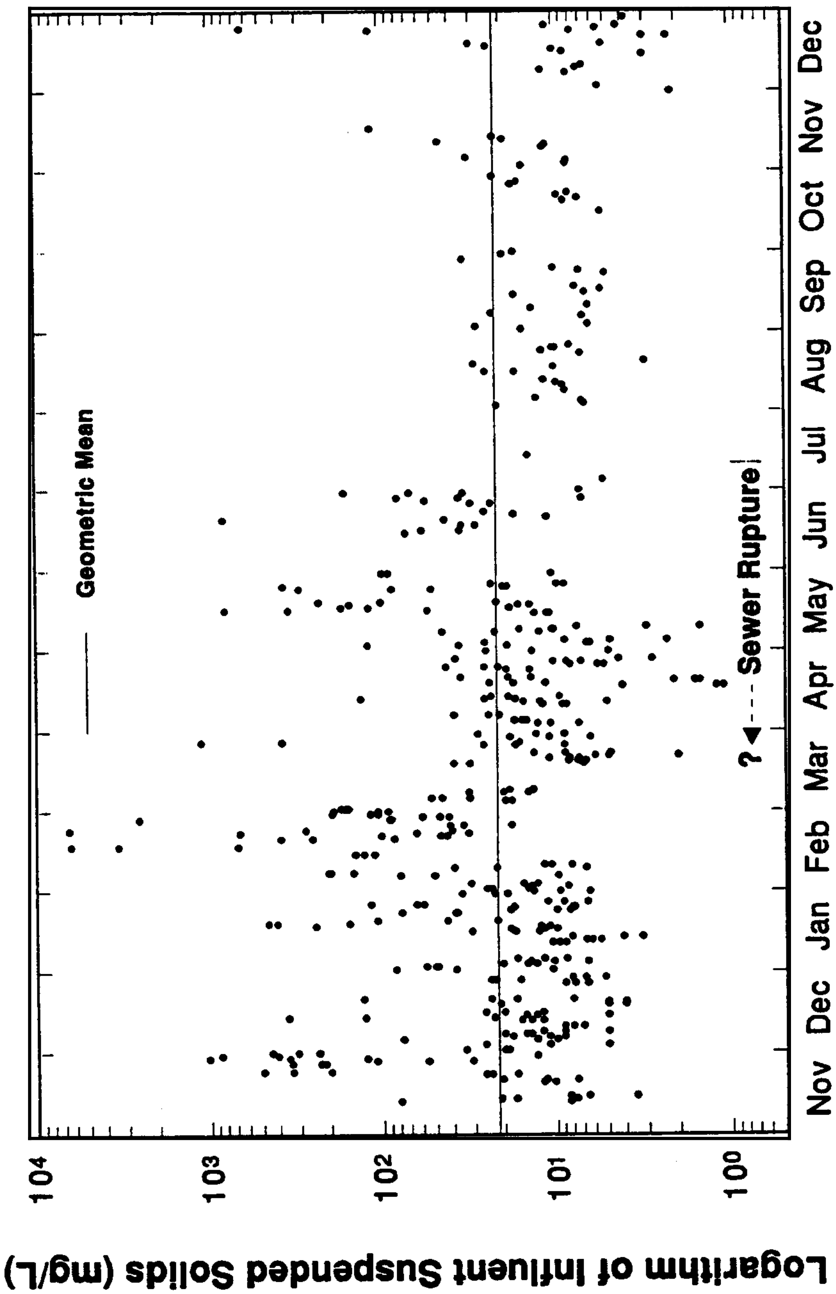

Figure 2. Scatter plot of pilot plant influent water suspended solids concentration in mg/L (Note four orders of magnitude variability).

The pilot plant operational parameters and runoff analytes are summarized statistically in Table 1. Environmental and bacterial data distributions often are 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. 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 distributed normally, 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 also were 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-logs. However, the estimate of the mean kill still was 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 to the rupturing sewer line, absorbed ozone doses of 15 to 20 mg/L were able to reduce viral

TABLE 1. 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 Concentration (Wt.%)	387	.34	5.1	2.7	1.09	4.1	2.4	1.7	4.7	....	....	....	....	....	....
Off-gas Ozone Concentration (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	8.6	2.1	.52	5.0	6.9	<.20	8.6	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 x10³ (MPN)	438	<.002	54000	1490	3400	5900	520	4500	3600	7.6	4.4	13.2	.16	160	5.8
Fecal Coliforms x10³ (MPN)	436	<.002	7900	160	670	1020	19	7.8	260	.52	4.2	5.9	.007	7.2	.088
Enterococcus species x10³ (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 distribution data in bold type more closely approximates a normal distribution than that given in regular type.

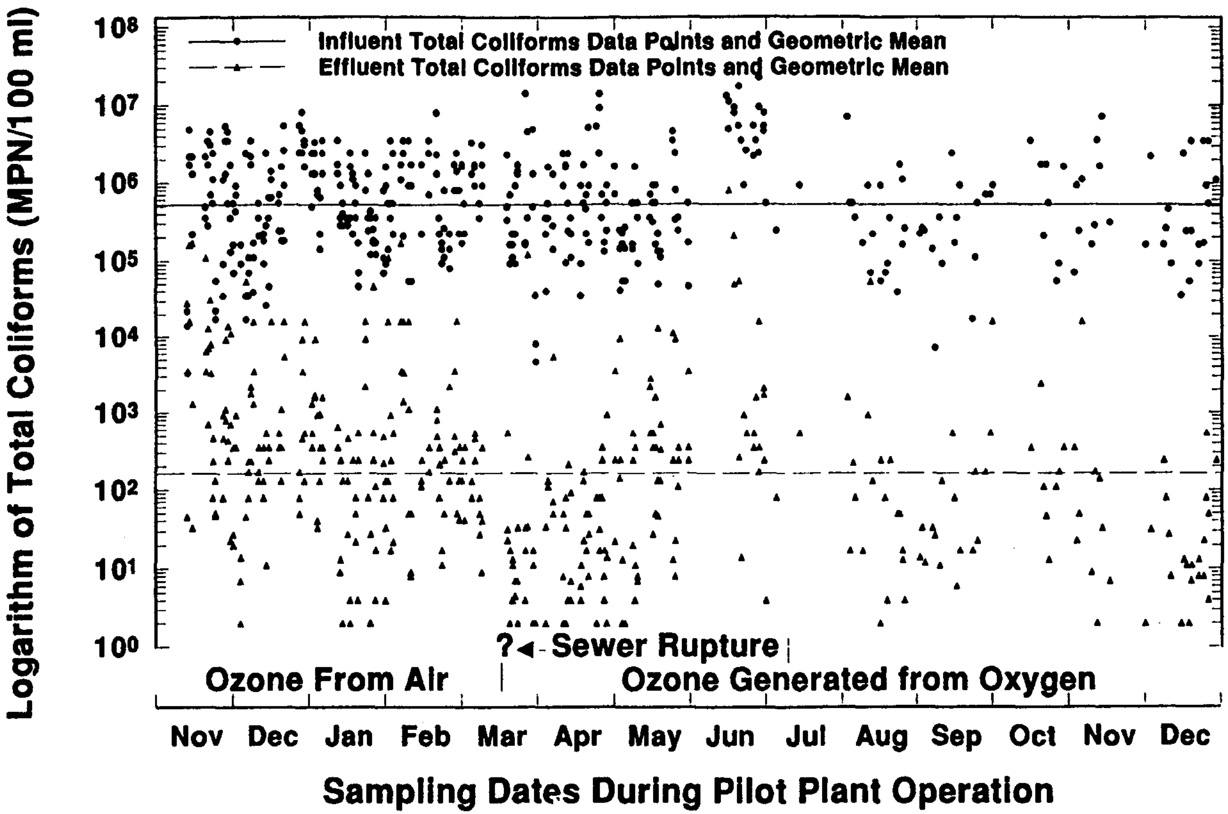

Figure 3. Scatter plot of total coliform organism (MPN/100 mL) comparing raw and ozonated Pico-Ketner storm drain runoff water.

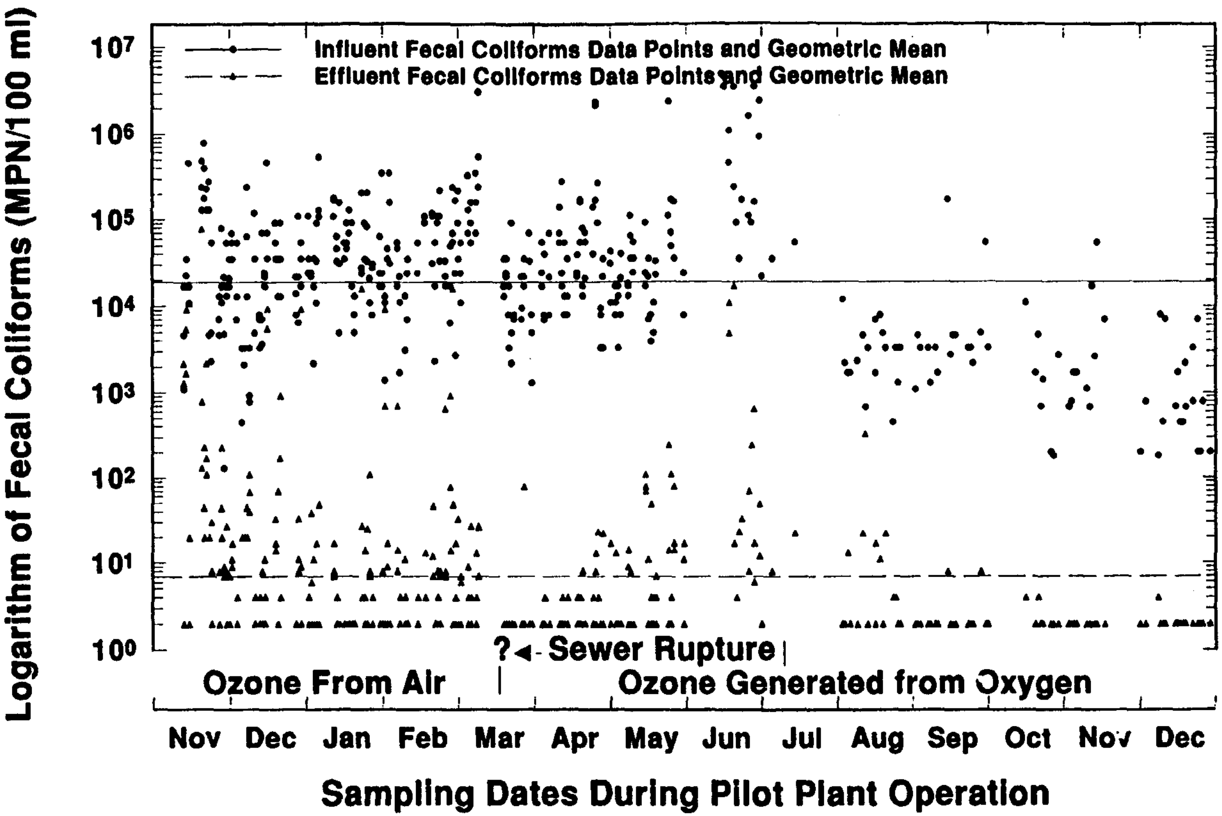

Figure 4. Scatter plot of fecal coliform organisms (MPN/100 mL) for raw and ozonated Pico-Ketner storm drain runoff water.

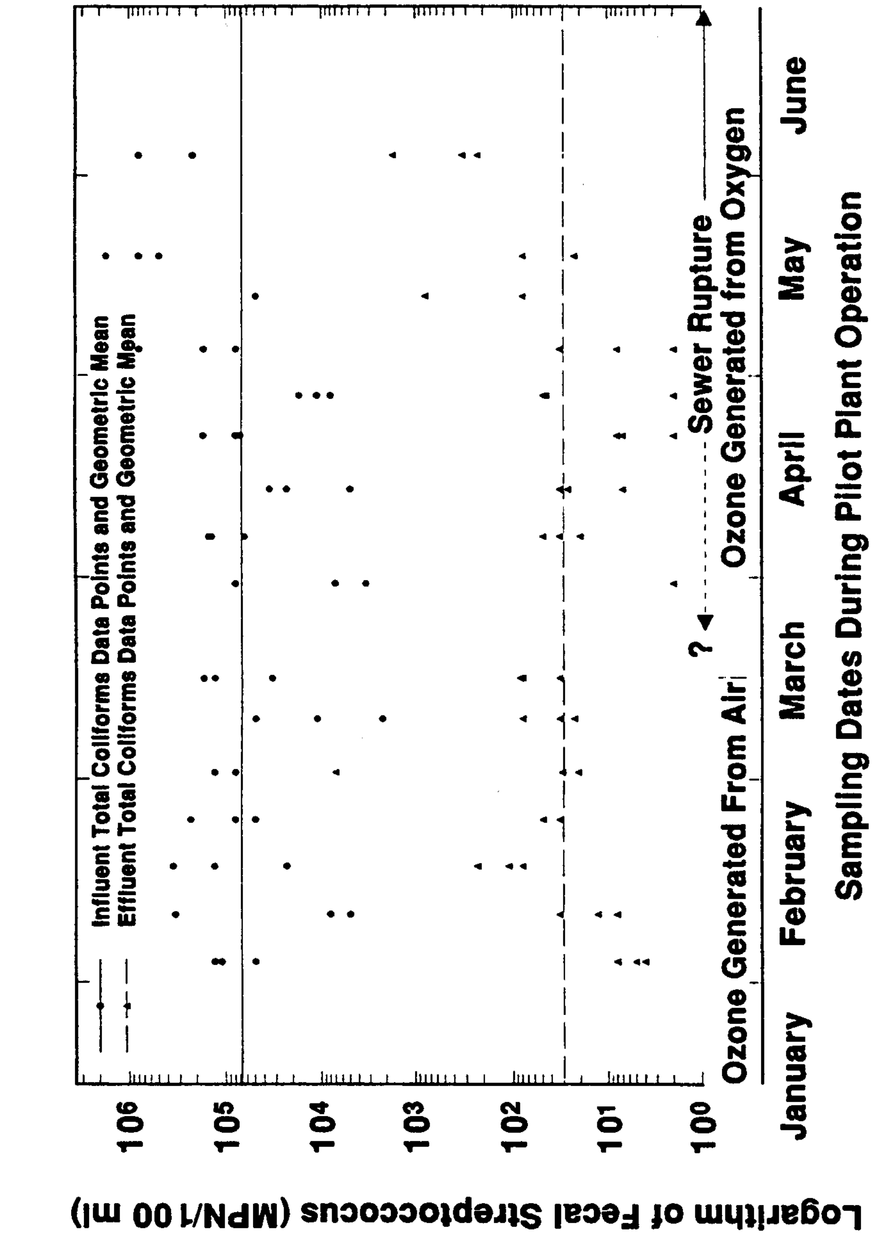

Figure 5. Scatter plot of fecal streptococcus (enterococcus) organisms (MPN/100 mL) for raw and ozonated Pico-Ketner drain runoff water.

counts 3.5-logs. During these runs, bacterial kills were unusually low, at an average of about 2.5-logs 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 five 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-logs, 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 probably can be optimized to achieve more than 5-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

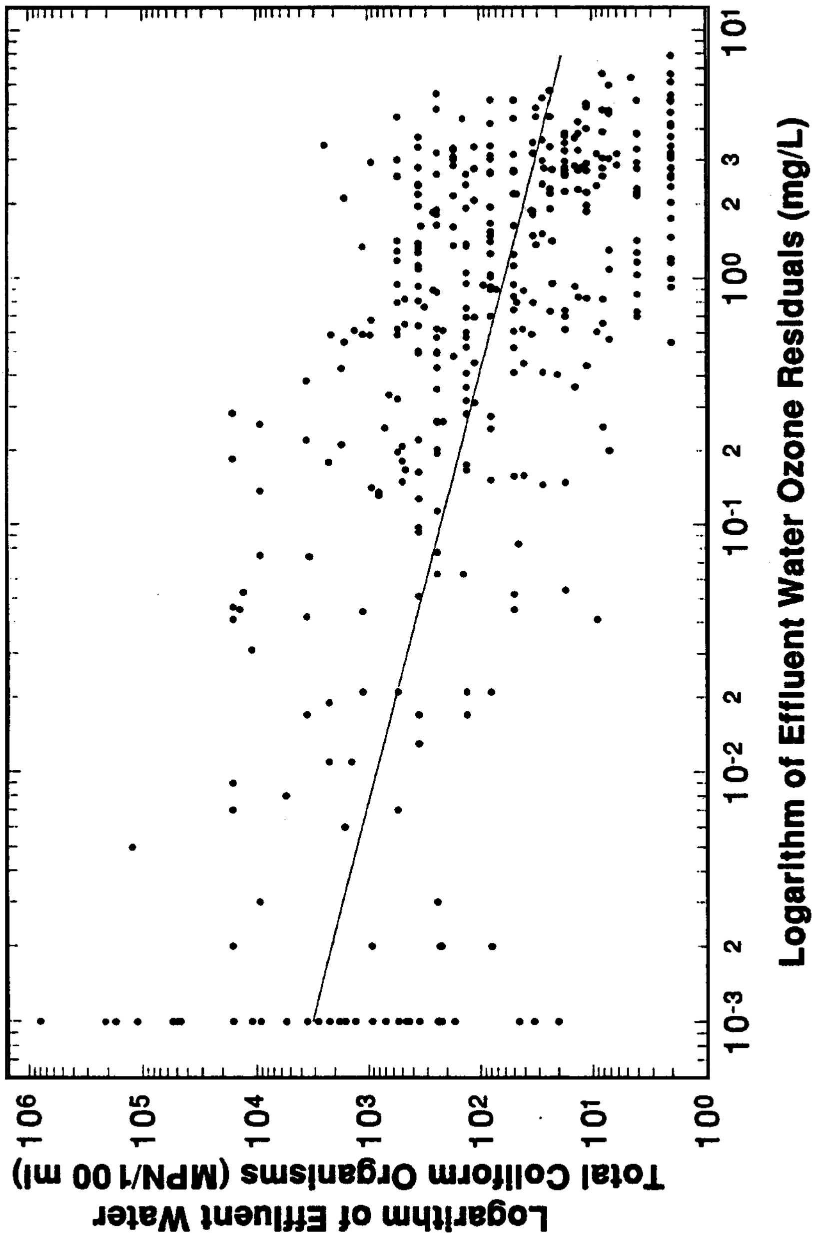

Figure 6. Linear regression plot showing dependence of effluent total coliform counts on effluent ozone residuals. Log TC_e = (1.784 ± 0.045) - (0.622 ± 0.037) Log O_{3r}; n = 406, r = -0.64, r^2 = 0.41, F << 0.01.

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 six 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.

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 byproducts. It is the oxidation and free radical reactions that contribute primarily 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 stated previously, the connection with pH maybe artifactual. 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:

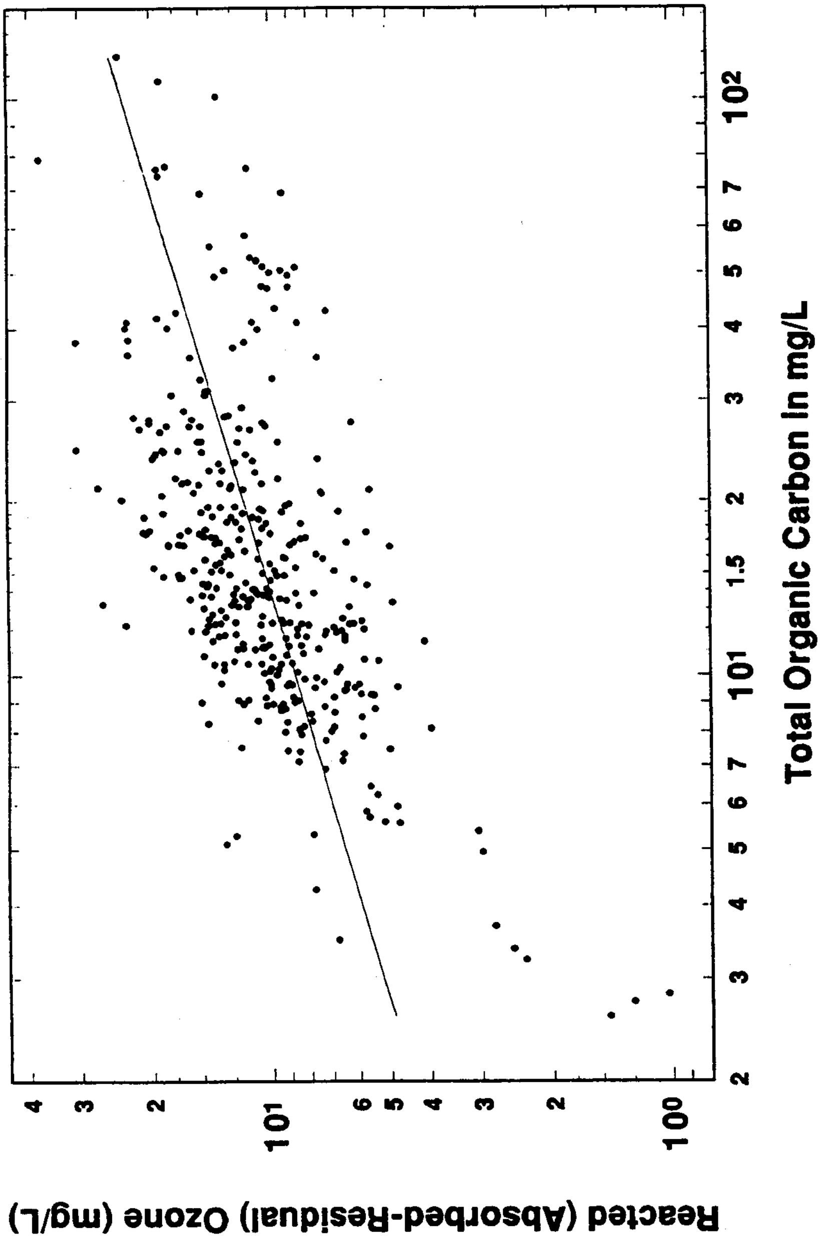

Figure 7. Linear regression plot showing the dependence of reacted ozone on total organic carbon (TOC) concentration. Log O_{3d} = (0.514 ± 0.038) + (0.427 ± 0.031) Log (TOC); n = 375, r = 0.58, r^2 = 0.34, F << 0.01.

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

where:

N_0 = number of organisms per volume at time 0
N_T = number of organisms per volume at time T
k = pseudo first order reaction rate constant
C = residual concentration (mg/L) of the disinfectant
T = time (min) that the reaction 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 to 9.0, the TOC set from 0.3 to 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 = ozone utilization rate per hour
pH = influent pH units
TOC = Total Organic Carbon in mg/L
alk = alkalinity measured in mg/L as $CaCO_3$

The model was evaluated using treated wastewater effluent, river, and tap water. The TOC ranged from 1.7 to 7.3 mg/L and alkalinities varied between 15 and 90 mg/L. The pH of the diluted effluent was 6.0, and the predicted rate constant (w) poorly matched the measured value. The pH values of the other test waters were from 6.8 to 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 secondary 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:

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

where:

TC = total coliform organisms/100 mL of ozonated effluent
FC = fecal coliform organisms/100 mL of ozonated effluent
TCOD = total chemical oxygen demand of the secondary effluent (mg/L)
NO_2^--N = nitrite nitrogen concentration of the secondary effluent (mg/L)
T = absorbed ozone dose (mg/L)

The following equations relate to unfiltered sewage effluent:

$$\log TC = 0.96 \log TC_0 - 0.89 + 0.012\ TCOD + 0.60\ NO_2^- \text{-N} + 0.013\ TSS - 4.024 \log T - 0.57\ R^{1/2} \quad [5]$$

$$\log FC = 4.06 + 0.020\ TCOD + 0.37\ NO_2^- \text{-N} + 0.012\ TSS - 3.94 \log T - 0.59\ R^{1/2} \quad [6]$$

where the additional terms are:

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

While the present investigation did not quantify the chemical oxygen demand or nitrite ion concentration, storm drain water normally is well oxygenated and the contribution of the nitrite term should be small. The oxidation of organic carbon (TOC) ordinarily is 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 ions 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 are 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 regression equations stand alone and, since ozonation often is a multistage process (Rice, 1987), they might be applied independently.

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

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

where:

TC_e = total coliform count per 100 mL of effluent water
O_{3r} = 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 to which equation [7] might be applied. Their corresponding residual values are 0.011 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} = estimated reacted ozone or demand in mg/L
TOC = 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 obtain 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 upon 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 utilize a treatment process effectively, it is critical to understand, control, and monitor the parameters that affect operation. Although the dry-weather effluent from the Pico-Kenter storm drain generally is comparable to secondary 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, probably would be challenged to treat adequately 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 often is 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 then can 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 still could be injected into the effluent and used to achieve a modest level of disinfection.

Summary

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-logs, and achieving 6-logs 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 reduce significantly the release of contamination and the exposure of recreational bathers to pathogenic viruses 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 byproducts 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 Study; Total Coliforms; Fecal Coliform; Fecal Streptococcus; Enterococcus; Indicator Bacteria; Human Enteric Pathogens; Polio Virus; Public Health; Reclaimed Water.

Résumé

Les inquiétudes concernant le rejet 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