Treatment of Trace Organic Compounds by Ozone–Biological Activated Carbon for Wastewater Reuse: The Lake Arrowhead Pilot Plant

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ABSTRACT: Organic and trace organic performance data for preozonation and biological activated carbon (BAC) filtration of the Lake Arrowhead, California, water reclamation pilot plant secondary effluent were analyzed to determine treatment efficiency of these processes in a potable water reuse project. Five types of organic analysis were performed: dissolved organic carbon (DOC), UV at 254 nm (UV-254), ultimate soluble biochemical oxygen demand ($SBOD_U$), base-neutral analysis (BNA), and specific aldehyde analyses.

Preozonation favored the breakdown of high-molecular-weight organic matter (>1000 daltons [Da]), measured as DOC, to biodegradable organic compounds, measured as an increase in $SBOD_U$. Also, a shift in mass concentration of BNAs from the higher scan index fraction (<1000 Da) to the lower scan index fraction was shown by gas chromatography–mass spectrometry profile analysis.

After preozonation, organic compounds were sorbed and biodegraded through the BAC filter. Steady state was reached for DOC and UV-254 absorbance after 50 to 100 days. Trace organic compounds started breaking through the column 200 days after BAC startup. Breakthrough was not uniform for BNAs. Apparent differences between the lower and higher molecular weight fractions of BNAs were shown, indicating a greater breakthrough rate for the higher scan index fractions. Finally, lists of tentatively identified BNA compounds were created, highlighting the change in chemical composition of the base-neutral fraction before and after each process. *Water Environ. Res.,* **72,** 388 (2000).

KEYWORDS: wastewater reuse, ozone, activated carbon, potable reuse, micropollutants, organic treatment, base neutral.

Introduction

Indirect potable reuse projects in Southern California during the past 10 years have become a factor to consider to satisfy the water demand associated with the region's growth and development. The 5-year drought period, which took place in the late 1980s, reinforced this trend and favored the development of new projects such as the Lake Arrowhead water reclamation pilot plant (LAWRPP). The objective of the LAWRPP was to produce, as a drought-proofing measure, high-quality water from secondary effluent to replenish Lake Arrowhead, which is the region's main potable water supply and recreational area.

To ensure public and environmental safety when reusing wastewater effluent, the state of California developed stringent rules and regulations, which have led to high-technology tertiary treatment processes. Water Factory 21 and the West Basin wastewater reclamation plant are the product of this policy. One concept that has emerged from this approach is multi-barrier treatment. To guarantee the removal of a given contaminant, several processes that target the same pollutant are placed in the same treatment chain. Therefore, if one process were to fail, the pollutant would still be reliably removed from the effluent by the second barrier.

The concept of multi-barrier treatment was used in 1991 for the design of the LAWRPP (Figure 1). This plant included denitrification, alum-coagulation–flocculation–sedimentation, sand filtration, primary oxidation with ozone, biological activated carbon (BAC) filtration, ultrafiltration (UF)–nanofiltration, reverse osmosis (RO), and final ozone disinfection (Madireddi et al., 1996). In this set of unit operations, bulk organics and trace organic compounds were primarily removed or transformed after sand filtration, preozonation, BAC filtration, UF, RO, and final ozonation.

Ozonation–BAC filtration is used not only to disinfect but also to control tastes and odors, eliminate water coloration, and remove unwanted trace organic compounds and dissolved organic carbon (DOC) that can react with chemical disinfectants and form disinfection byproducts or cause membrane fouling. This treatment process combines both ozonation and granular activated carbon (GAC) filtration. Primary ozonation disinfects and breaks down high-molecular weight organic compounds to more biologically degradable organic matter. Granular activated carbon removes matrix organic compounds from water by sorption. When operated as a biological filter, microorganisms colonize the GAC surface and metabolize organic matter so the GAC filter becomes a BAC filter.

This paper focuses on the fate of bulk organics and trace organics before and after preozonation and BAC filtration at the LAWRPP. Particular attention is paid to those compounds that are both extractable by dichloromethane (DCM) and analyzed by gas chromatography (GC). This organic fraction is typically identified as base-neutral acids (BNAs) and includes all semivolatile trace organic compounds. These compounds have been identified as potentially harmful and defined by government organizations such as U.S. Environmental Protection Agency as target or nontarget compounds. In the absence of adapted and required monitoring programs or strategies, little data are available today on BNA compounds in water reuse systems. The purpose of this paper is to address this issue using integrated chromatographic analysis (ICA).

Materials and Methods

Lake Arrowhead Water Reclamation Pilot Plant. Primary ozone oxidation was achieved in five polyvinyl chloride (PVC) columns in series (0.3 m diameter and 6 m height). The top of each

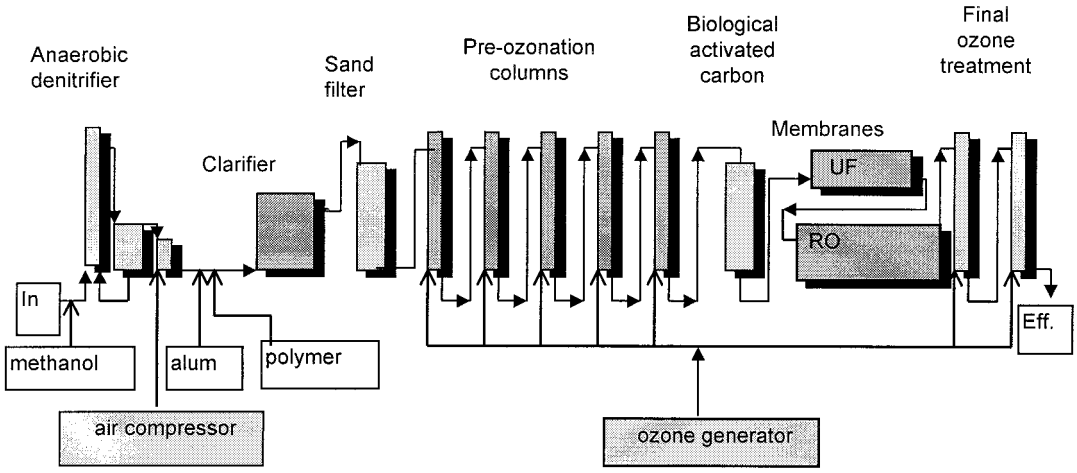

Figure 1—Schematic of the LAWRPP (In.: influent; Effl.: effluent water; UF.: ultrafilter; RO.: reverse osmosis).

column was sealed to prevent light or any foreign body from entering. The ozone columns were operated in a countercurrent mode (water flow was downward, while ozone injected at the bottom of each column flowed upward). Ozone was produced with an ozone generator fed with liquid oxygen at constant flow. The inlet gas phase concentrations ranged from 0.5 to 1% of ozone by weight. The retention time in the columns ranged from 20 to 40 minutes depending on the feed flow. The ozone dose was set at 15 ± 5 mg/L. The ozonated effluent was discharged in a 200-L tank (not shown in Figure 1).

The BAC downflow pressurized filter (4 m height, 0.8 m diameter, and sealed on top) was loaded on April 12, 1995, with 1.2 m of Filtrasorb F-400 (Calgon Corporation, Pittsburgh, Pennsylvania). A 1.2-m head space was ensured after 100% bed expansion during backwash. The column was backwashed every 8 hours. The flow to the filter was maintained at 20 L/min. The filter feed was saturated with dissolved oxygen from the ozone columns, providing adequate dissolved oxygen concentration in the column for biological growth with oxygen residual after GAC filtration. The empty bed contact time of the GAC column was 15 minutes. The startup date of the GAC column is used as the reference point for time in this study.

Five types of organic analysis were performed: DOC, UV at 254 nm (UV-254), ultimate soluble biochemical oxygen demand ($SBOD_U$), BNA, and specific aldehyde analyses. The UV-254, $SBOD_U$, and DOC analyses were used to monitor the overall treatment efficiency of both processes. Specific base-neutral analysis was performed to understand the effect of each process on the potentially hazardous trace organic fraction. The analysis of both specific and nonspecific parameters contributes to a broad understanding of the treatment process.

Nonspecific Organic Parameters. Dissolved organic carbon and UV-254 were analyzed according to *Standard Methods* (APHA et al., 1995). The $SBOD_U$ was analyzed using the method developed by Khan et al. (1996). Dissolved organic carbon measurements were made on a Dohrman DC-80 carbon analyzer, and UV-254 absorption measurements were made on a 5652 Hewlett Packard diode array spectrophotometer. Measurements were made on grab samples collected before and after each process; before analysis, grab samples were stored in amber vials with Teflon-lined caps, without head space.

Base-Neutral Analysis. Five- and 10-gallon grab samples (approximately 19 and 38 L) were extracted with DCM less than 2 hours after sampling with a continuous liquid–liquid extractor (CLLE) (Baker et al., 1987). The occurrence of emulsions at the DCM–water interface for both sand filter and preozonation effluent required modifications of the original CLLE extraction protocol developed for surface waters. The addition of sodium sulfate and phosphoric acid (pH = 3) and the increase of the extraction flow rate from 2 to 3 L/h had a positive effect on minimizing the emulsions at the DCM–water interface. Sodium sulfate was added at 100, 75, and 50 mg/L for the sand filter, preozonation, and BAC filtration effluents, respectively. This is the first time this apparatus was used to extract large wastewater volumes. Extraction efficiency data, shown in Table 1, were consistent between extractions and sampling points despite the addition of different sodium sulfate concentrations. The overall estimated average extraction efficiency was 45%.

For quality assurance and quality control purposes, surrogate standards were systematically injected in the sample before ex-

Table 1—Recovery data for the modified protocol for the CLLE.[a]

Surrogate standards[b]	Recovery, %			
	Sand[c]	Ozone[c]	Carbon[c]	Overall[d]
4-Terphenyl-D14	6 (4)[e]	11 (1.5)	9.8 (4)	9 (4)
Phenol-D6	20 (5)	26 (12)	15 (10)	20 (10)
2-Fluorophenol	23 (3)	29 (16)	19 (11)	24 (11)
2-Fluoro, 1,1′-biphenyl	39 (18)	44 (14)	48 (16)	44 (15)
Nitrobenzene-D5	64 (14)	59 (26)	53 (29)	59 (22)
2,4,6-Tribromophenol	90 (59)	109 (69)	101 (56)	100 (56)

[a] Four samples were used for each effluent, giving an overall 12 samples used.
[b] Sodium sulfate was added at 100, 75, and 50 mg/L to the sand filter, ozonation, and BAC effluents, respectively.
[c] $n = 4$.
[d] $n = 12$.
[e] Numbers in parentheses represent standard deviations.

traction (Table 1). After extraction, the samples were dried on a sodium sulfate column, concentrated to 1 mL by Kuderna Danish evaporation, and analyzed on a Finingan 4000 automated gas chromatography–mass spectrometer (GC–MS). The GC column used was a DB-5MS, 30 m × 0.25 mm. The temperature program was 4 minutes at 30 °C, 6 °C/min ramp to 300 °C, and 30-minute hold. For analytical purposes, six internal standards (IS) were injected in the sample before GC/MS analysis at 40 μg/L (1,4-dichlorobenzene-D4, perylene-D12, phenanthrene-D10, naphthalene-D8, chrysene-D12, and acenaphthene-D10). Analysis was performed for both target and nontarget compounds. Nontarget compounds were tentatively identified based on a mass spectra library search and mass spectra evaluation, and target compounds were confirmed and quantified.

Base-Neutral Analysis Interpretation. Integrated chromatographic analysis was performed on the original chromatograms obtained after GC–MS analysis. Therefore, all chromatograms were normalized based on the average GC–MS scan index numbers of the six IS (Table 1). This first step allows direct comparison of chromatograms. Because ICA integrates all components of the chromatogram, it can provide useful information in fewer than 4 hours after sampling. This method was preferred over the more conventional trace organic analysis strategies based on peak identification and peak quantification typically used for drinking water samples because they were viewed as too selective, leading to the loss of information.

An average elution scan index number for each IS was calculated based on 45 chromatograms. These values were used as arbitrary references for the reconstruction of each chromatogram. The average scan index numbers for the IS were 837, 1133, 1584, 1946, 2640, and 2983 for 1,4-dichlorobenzene-D4, perylene-D12, phenanthrene-D10, naphthalene-D8, chrysene-D12, and acenaphthene-D10, respectively. The scan index number of each peak was calculated based on these values (Levine, 1999).

Each compound has a specific scan index number that is a function of the compound's physicochemical properties. Molecular weight and boiling point characteristics are the two key parameters. Therefore, within a group of similar compounds, the first eluting constituent on a nonpolar GC column is that with the lowest scan index number and typically with the lowest molecular weight or the highest volatility.

Data analysis was performed by comparing the influent and effluent of the same process for the same sampling date or by comparing the same sample point at different dates. Hence, direct chromatographic comparison provides an indication of the changes that occurred in the water matrix composition.

Semiquantitative analysis was performed by chromatographic fractionation. For each fraction total area count was performed. Peaks representing surrogates, internal standards, and phthalates are not accounted for either because they were added to the sample for quality assurance purposes or because they were found in the blanks and were considered experimental artifacts. Beyond scan index number 2640, a small number of peaks with large area counts were detected. Because of the high risk of error associated with this area, only qualitative data interpretation was performed. Finally, lists of tentatively identified compounds were created, highlighting the change in the chemical composition of the base-neutral fraction, and average estimated concentration values were calculated based on naphthalene-D8 surface area.

Aldehydes. Aldehyde samples were derivatized with *O*-(2,3,4,5,6,-pentafluorobenzyl)-hydroxylamine and analyzed using GC coupled with an electron capture detector (APHA et al., 1995). Formaldehyde, acetaldehyde, glyoxal, and butanal data before and after each process are presented in the following section.

Results

Lake Arrowhead Wastewater Reclamation Pilot Plant Treatment Efficiency. Figure 2 is a temporal presentation of both DOC and UV-254 data after sand filtration, ozonation, and BAC filtration. Systematic data analysis of both UV-254 and DOC began approximately 50 days after BAC filter startup. The UV-254 absorbance values ranged between 0.1 and 0.3 cm^{-1}, 0.05 and 0.2 cm^{-1}, and 0.01 and 0.12 cm^{-1} for the respective processes. Dissolved organic carbon values ranged between 5 and 15 mg/L for both sand and ozone effluents and 1 and 10 mg/L after BAC filtration. Both UV-254 and DOC data approach near random distribution around the average value highlighting the variability associated with the water matrix.

After BAC treatment, DOC and UV removal varies as a function of time. Despite the lack of data before the 50th day, a breakthrough curve can be presumed for both parameters (see dashed line). After breakthrough, the distribution of the data points around the average value shows that the BAC filter is close to a steady-state situation for these parameters. Data also show that the BAC filter behaves as a buffer and tends to level out the high variability found after sand filtration and ozonation.

Figure 3 is a spatial representation of average $SBOD_U$, DOC, and UV data gathered after the BAC filter reached steady state (Khan et al., 1996). The UV data indicate a decrease in concentration of the UV-sorbing compounds after ozonation and BAC filtration. Absorbance drops from 0.13 to 0.065 cm^{-1} between the sand and BAC effluent, and DOC concentration remains constant at 7.5 mg/L across the ozone columns. After BAC treatment, the DOC concentration drops to 5.75 mg/L. The $SBOD_U$ concentration increases from 6 to 8.2 mg/L after ozonation, then decreases to 4 mg/L after BAC treatment.

Base-Neutral Compounds Figure 4 groups three computer-reconstructed chromatograms from 125 days after BAC startup. Each chromatogram represents the estimated concentration for the extracted compounds as a function of its calculated scan index number. A direct comparison of the three chromatograms indicates that after ozonation a shift in mass and in the number of peaks in favor of the earlier eluting compounds occurred. After BAC filtration, the overall number of peaks and base-neutral concentration decreased to values that are below the limit of quantitation but above the detection limit of the method.

Figure 5 shows the percent mass remaining after ozonation of the different scan index fractions as a function of time. The total mass of the earlier eluting compounds increases by a factor of 2 to 4. On the other hand, the later eluting compounds undergo a decrease in mass that varies between 25 and 75% if day 280 is excluded. With the exclusion or inclusion of day 280, the shift in mass toward the earlier eluting compounds is confirmed for all samples.

Figure 6 shows three computer-reconstructed chromatograms of BAC effluent samples taken 125, 200, and 220 days after the startup of the BAC filter. The trend indicated by these chromatograms is an increase in concentration and in the number of peaks. For example, peak A, tentatively identified as cholestanol, gradually increased on each successive chromatogram. This break-

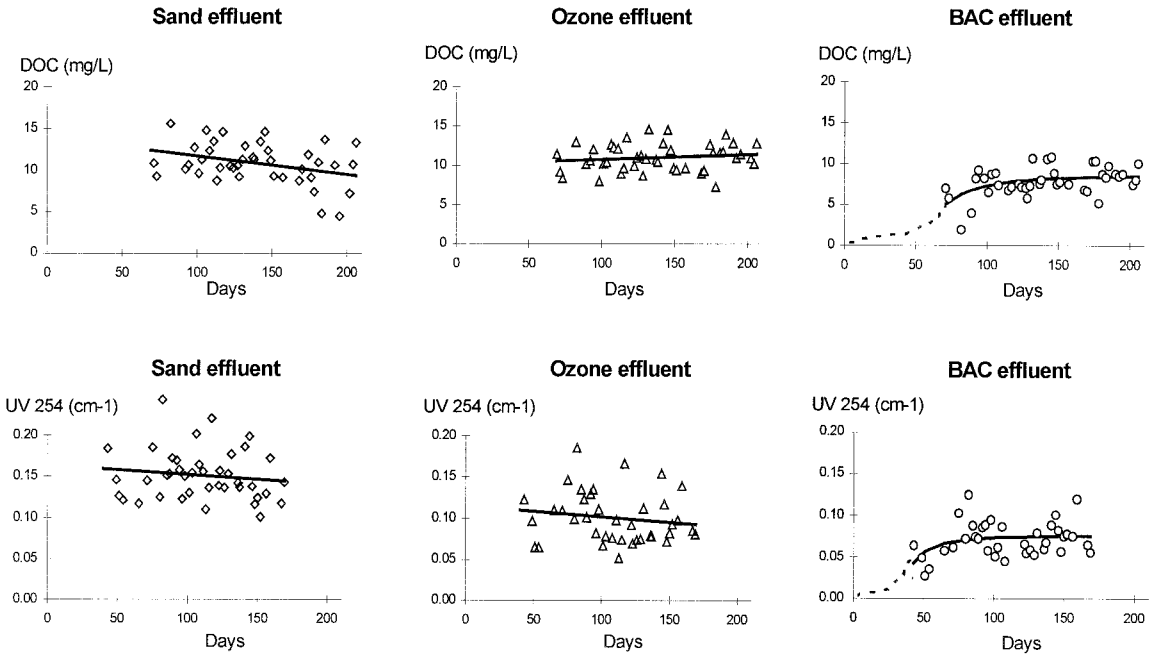

Figure 2—UV-254 nm and DOC analysis as a function of time for sand, ozone, and BAC effluent at the LAWRPP (dashed line illustrates possible BAC behavior before steady state).

through pattern is shown to take place simultaneously for many compounds.

To quantify this increase in concentration, each chromatogram was compared to its respective ozone effluent chromatogram for which a mass efficiency treatment calculation was performed for the five fractions. Table 2 presents the percent mass of trace organic compounds remaining after GAC treatment for each fraction as a function of time of BAC filter operation. An average of the percent mass remaining for the earlier and later eluting fractions (i.e., 300 to 1584 and 1585 to 2640) was performed that was then used to illustrate the treatment efficiency of the BAC filter as a function of time (Figure 7). At first, the lower molecular weight compounds are less efficiently removed than the later eluting compounds. Between 50 and 200 days after GAC treatment, both groups behave similarly, even though the early eluting compounds are more efficiently removed than the later eluting compounds. After 200 days, both base-neutral fractions seem to break through the filter. The higher scan index fraction or the higher molecular weight–lower volatility fraction indicates a greater breakthrough rate than the earlier eluting lower molecular weight–higher volatility compounds.

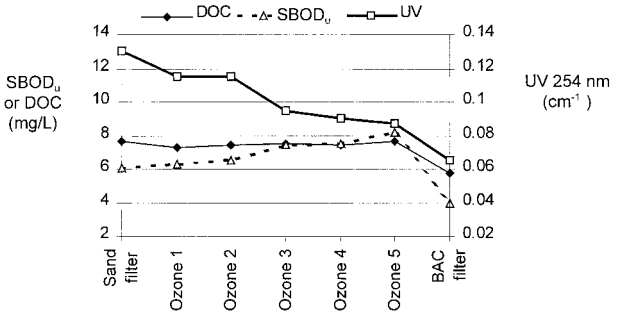

Figure 3—Sequential average $SBOD_U$, DOC, and UV-254 absorbance data at LAWRPP (adapted from Khan et al., 1996).

Table 3 lists the target and nontarget compounds that were tentatively identified by mass spectrometry in the DCM extracts before and after ozone and BAC treatment as a function of their scan index fractions and estimated concentrations. The primary groups identified were acids, ketones, trihalomethanes (THMs), aldehydes, alcohols, phenols, and polycyclic aromatic hydrocarbons (PAHs). This result indicates that (1) some of the larger alcohols and phenols identified in the sand extracts were not detected after ozonation, (2) most aldehydes present in the ozone effluent were not detected in the sand effluent and were readily removed by GAC treatment, (3) some compounds were found after each process (e.g., cholestanol and THM), and (4) the target compounds were less frequently detected after preozonation and GAC treatment.

Figure 8 shows that acetaldehyde, formaldehyde, glyoxal, and butanal were present after each process. The concentration of these four compounds increased after ozonation and decreased after BAC filtration. These data corroborate the trend highlighted by GC profile analysis. Formaldehyde and glyoxal were the compounds that had the greatest concentrations after ozonation, as great as 100 and 40 μg/L, respectively. Butanal was the aldehyde least affected by ozonation and was present at the lowest concentrations.

Discussion

Ozone Influence. Figure 3 corroborates the increase in concentration of biological organic matter after preozonation and the decrease in concentration of conjugated and aromatic compounds described by Chrostowski et al. (1982). In addition, DOC remains approximately constant across the ozone columns, indicating that DOC is transformed from unsaturated and aromatic organic com-

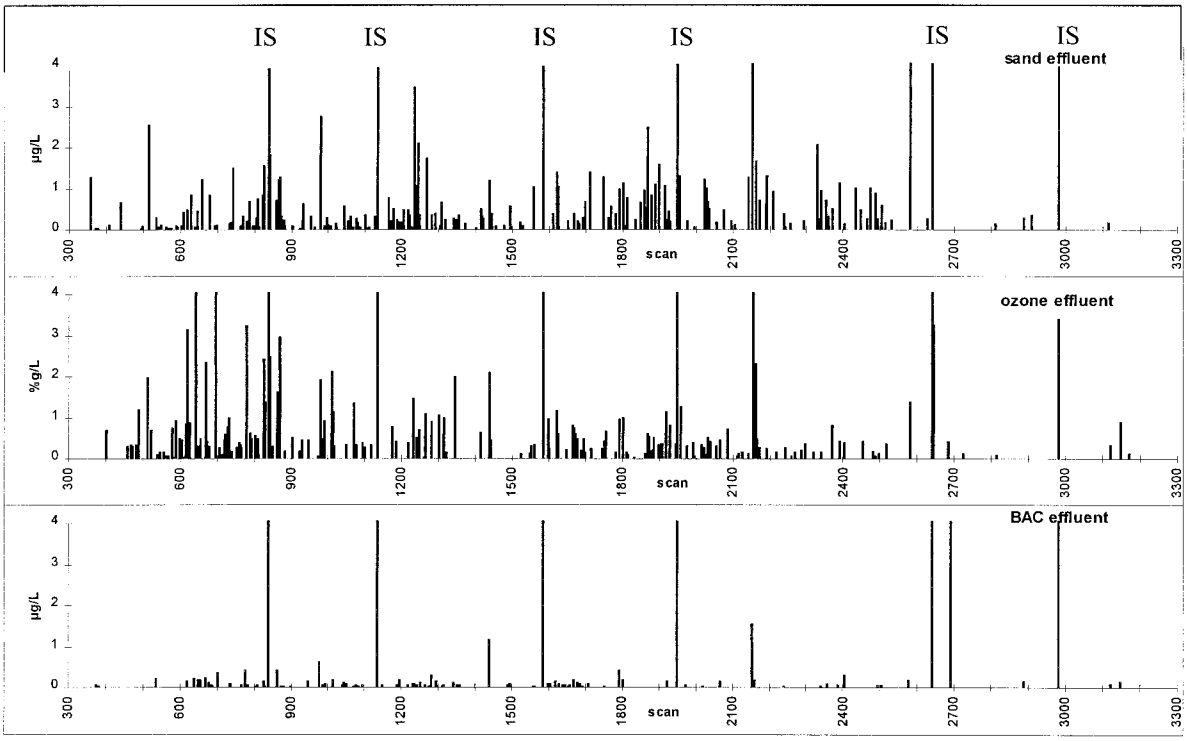

Figure 4—Computer reconstructed GC–MS profiles of the Lake Arrowhead Wastewater Treatment Project sampled 125 days after BAC startup.

pounds to more biodegradable organic compounds and is not degraded to carbon dioxide.

The most typically identified ozonolysis products were aldehydes, ketones, acids, and alcohols. According to Rice (1989), these compounds are typically smaller, more polar and more biodegradable than their parent compounds. The increase in concentration varied as a function of the compound's physicochemical properties and the sampling period. In addition to ozonolysis, specific compounds such as cholestanol were affected by ozonation and underwent a decrease in concentration.

Gas chromatography profile analysis was used to study ozone influent and effluent as a fractionation technique comparable to gel permeation chromatography or UF separation. However, the key difference with the more typical techniques is the apparent molecular weight (AMW) range. Traditional AMW characterization protocols range from 500 daltons (Da) to 50 000 Da (Amy et al., 1987). Gas chromatography profile analysis groups compounds that are extractable by DCM and for which the AMW spectrum ranges from 50 to less than 1000 Da.

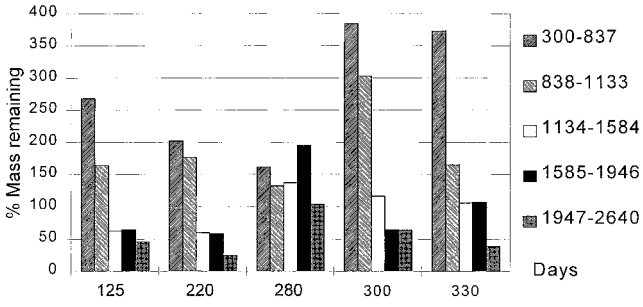

Figure 5—Percent mass remaining after ozonation as a function of the elution group after fractionation of the different chromatograms.

Figure 5 illustrates the shift in mass from the higher molecular weight fraction of the BNAs to the lower molecular weight fraction. This is the first time such a relationship is shown for low-molecular-weight compounds. Yet Sierka et al. (1989) and Grady et al. (1984) have already reported this phenomenon for higher molecular weight organic material using gel chromatography or UF separation. These authors have also shown the existence of a positive relationship between the ozone dose and the magnitude of the shift. This positive relationship could be an explanation for the lack of shift on day 280.

Biological Activated Carbon Influence. Figure 3 shows that all three general organic parameters are affected by BAC treatment. According to van Leeuwen (1986), the startup of a BAC filter takes place in two phases. In the early stage of operation, physical adsorption is the only mechanism involved in the removal of trace organic compounds. During this first stage, GAC adsorption efficiency varies with the chemical composition of the water, type of GAC, and its history.

Biological activated carbon efficiently removed both organic and trace organic compounds from the effluent. Steady state for DOC and UV-254 was reached between day 50 and 100. Dissolved organic carbon and UV-254 breakthrough took place before that time, whereas the BNA breakthrough point was estimated to be 200 days after BAC startup. The time difference between general organic parameters and trace organics is associated with the nature of the compounds.

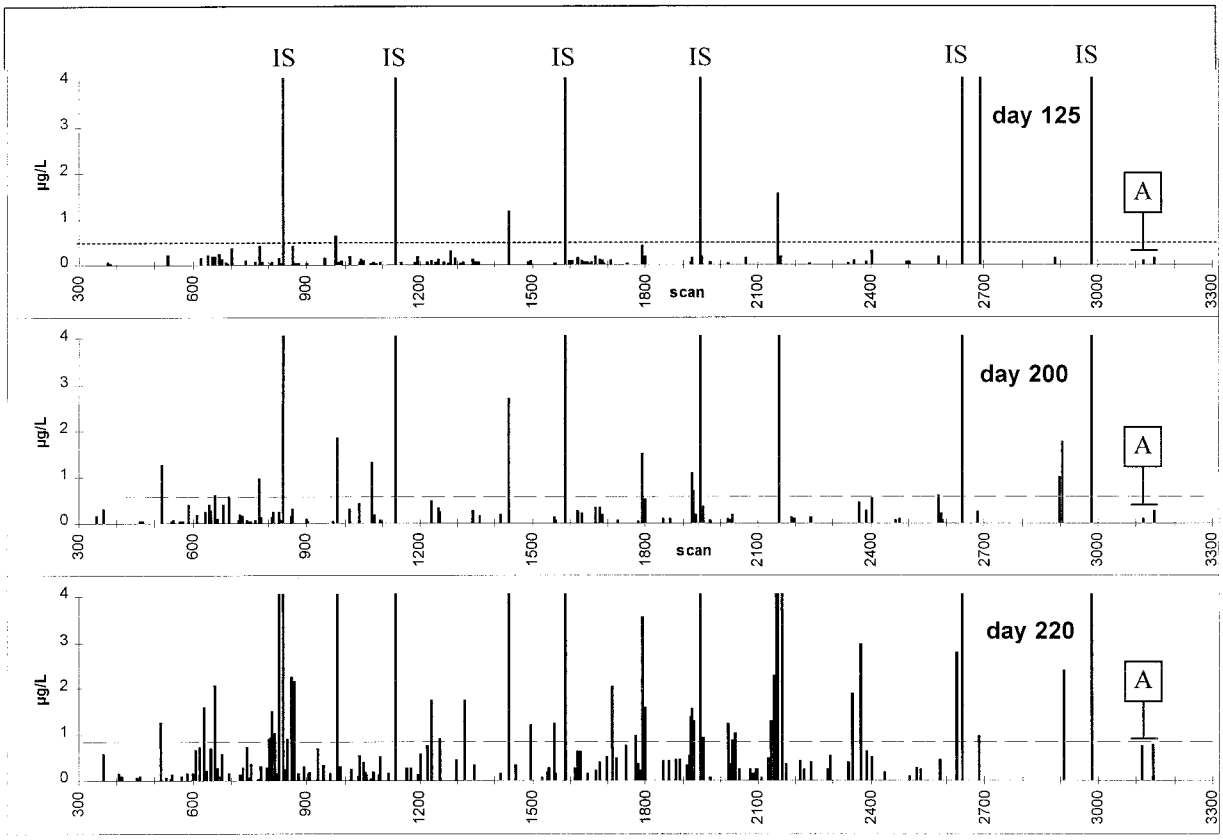

Figure 6—Computer reconstructed GC–MS profiles of four BAC effluent samples from the Lake Arrowhead Wastewater Treatment Project sampled 125, 200, and 220 days following the startup of the GAC filter.

In wastewater treatment applications, the complexity and variability of influent quality make it difficult to develop models to predict breakthrough of individual solutes. However, the fate of these compounds is a function of the influent organic mixture, its reactivity, its affinity to adsorb to GAC, and its adsorption equilibrium status at a given time. Therefore, on the carbon surface, less strongly adsorbed species are displaced by those that present a greater affinity to GAC (Baker and Suffet, 1989). As long as the adsorption equilibrium is favorable to the more strongly adsorbed compounds, this remains true. If the concentration of the more strongly adsorbed compound were to drop below adsorption equilibrium, reequilibration would occur through the release of that specific compound. Depending on the relative extent of these organic displacements, this situation can lead to temporarily greater concentrations in the GAC effluent than in the influent for any given species. This phenomenon has been identified as the chromatography effect by Suffet (1980).

The second stage of operations for BAC takes place once the GAC has been colonized by bacteria. In this case, the removal of synthetic organic substances is performed by both biodegradation and sorption. Biodegradation enhances the efficiency of GAC sorption (Somiya et al., 1986); therefore, when compounds undergo desorption and resorption in the GAC column, biodegradation of organic compounds takes place across the column. The

Table 2—Percent mass remaining of the trace organic after BAC treatment at the LAWRPP as a function of time and of the eluting fraction.

	Time, d					
Fraction	**3**	**60**	**125**	**200**	**280**	**300**
300–837	23.9	5.3	4.5	14.9	31.9	43.5
838–1133	13.8	7.5	6	29.7	21	13.9
1134–1584	8.7	14.3	11.5	13	22.1	18.3
1585–1946	6.5	10.9	10.5	28.3	49.1	45.9
1947–2640	3.7	16.2	16.9	10.7	73.5	66.8

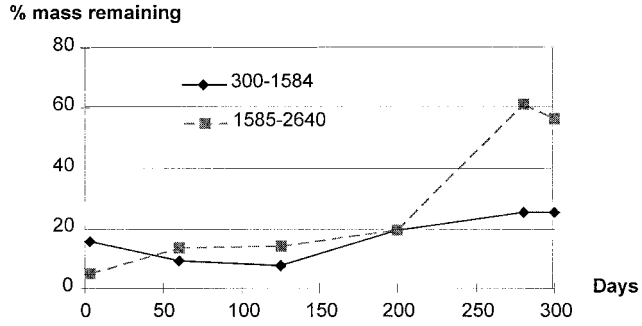

Figure 7—Trace organic percent mass remaining after BAC treatment as a function of the eluting fraction and days of operation after BAC startup.

Table 3—Average estimated concentration of target and nontarget compounds at the LAWRPP before and after preozonation and BAC filtration (Group: represents the retention time group of the compound, the first group being the first eluting fraction).

Compound type	Group	Sand, μg/L	Ozone, μg/L	Carbon, μg/L
THM				
Bromodichloromethane	1	1.2		0.4
Tribromomethane	1	1	0.7	0.5
Trichloromethane	1	0.7	0.4	0.5
Dibromochloromethane	1	2.7	2	1.3
Alcohols and phenols				
2-Methoxy-1-propanol,	1	0.4		
3 Hexanol	1	2.8		2.4
3-Chloro-2-butanol	1			0.2
2,5-dimethyl 2-hexanol	1	1.2		
Diacetate, 1,2 ethanediol	1		9.1	0.6
2,2 Dimethyl 3-pentanol,	1			0.6
Cyclopentanol 1,2-dimethyl-3-(methylethenyl)	2	0.5		
1-Propanol, 2-(2hydroxypropoxy)	3	2.8		
Phenol,2,4 (bis(1,1 dimethylethyl)	3	1		0.6
Phenol4,4(1,2-diethyl-1,2-ethanediyl)bisphenol nonyl (grouped)	4	1		
	4	1.7		
Ethanol, 2-butoxy-phosphate (3:1)	5		5.9	0.6
Cholestanol	>5	—	0.7	0.4
Hydrocarbons				
1,3,5-Cycloheptatriene	1			0.1
Decahydro naphthalene	2	0.6		
3-Methoxy-3methyl-hexane	2			1.1
Benzene, 1-methyl-4-2(methyl propyl)	3	1		
Octadiene,4,5 dimethyl-3,6 dimethyl	3	1.4		
Acids				
Propanoic acid 2 methyl-,2,2-dimethyl-1-(2-hr...)	3	1.2		
Octandecanoic acid	5	9.4		
vTetradecanoic acid	5		4.5	1.3
Hexadecanoic acid	5		9.4	3.4
Butyl 2-methylpropyl ester 1,2-benzene dicarboxylic acid	5		5.7	
Ketones				
Cyclohexanone[a]	1		0.6	0.1
2-Propanone, 1-(1-cyclohexen-1-yl)	2	0.5		
Cyclohexanone,4-(1,1-dimethyethyl)	2	0.9		
1-Phenyl ethanone	2		0.6	0.4
2-Heptanone,3 hydroxy-3 methyl	3	0.9		
2-cyclohexen-1-one[a]	3	1.9		
Benzophenone	4		0.3	0.1
Ethanone 1-(2-naphthalenyl)	4	0.5		
Aldehydes				
Benzaldehyde (ACD) (DOT)	1	0.2	2.4	0.2
Hexanal	1		8.4	
Heptanal	1		13.8	1.1
Octanal	1		4	0.2
Nonanal	2		11.9	2.2
Decanal	2		1.7	
Tetradecanal	4		1.2	
Miscellaneous				
Benzothiazole,2-2(methylthio)	4	2.5		
Ethyl citrate	4	1	1.8	1
N,N-Diethyl-3-methyl benzamide	4		0.9	0.8
Target				
2-Methylnaphthalene (day 1)[b]	3	<0.1	<0.1	<0.1
Benzoic acid (day 20)[b]	2	0.2	0.1	<0.1
Fluoranthene	5	<0.1	<0.1	<0.1
Fluorene	4	<0.1	<0.1	<0.1
Naphthalene (day 1)[b]	3	<0.1	<0.1	<0.1
Nitrobenzene (day 125)[b]	2	<0.1	<0.1	<0.1
Phenol (day 200)[b]	1	<0.1	<0.1	<0.1
Pyrene	5	<0.1	<0.1	<0.1

[a] The compound may be a solvent impurity.
[b] The compound was regularly found in the BAC effluent after the given number of days once the BAC column was on-line.

organics that are most likely to be biodegraded are the compounds that have the least affinity for GAC and therefore are the most likely to be found in the aqueous phase. Shi et al. (1995) attribute these compounds with high adsorption–desorption characteristics because they tend to desorb rapidly once adsorbed to the GAC. Therefore, compounds that have a greater affinity for activated carbon are less likely to be biodegraded and have a low adsorption–desorption rate because the compounds are less likely to be released in the aqueous phase.

The probable explanation is that microorganisms preferentially metabolize molecules that are free flowing in the aqueous phase rather than metabolizing molecules that are already sorbed to the GAC. This choice can be motivated by the fact that molecules sorbed to the GAC offer greater resistance to biosorption than nonsorbed compounds because of the bonds existing between the molecule and GAC. In conclusion, biodegradation and sorption are complementary mechanisms that extend the life of the GAC and delay organic breakthrough (Speitel and DiGiano, 1987).

The difference in treatment efficiency between the lower and higher scan index fractions shown in Figure 7 after breakthrough of the BNA trace organic compounds shown in Figure 7 can be the result of biological activity that preferentially removed the lower

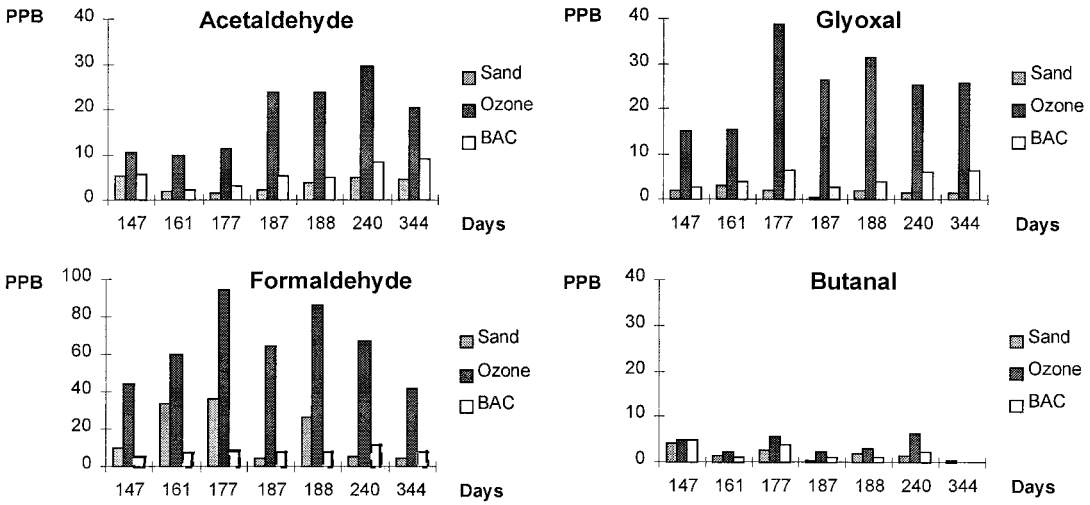

Figure 8—For sequential concentration data at LAWRPP as a function of days after BAC startup for four aldehydes (formaldehyde, acetaldehyde, glyoxal, and butanal) and after sand filtration, ozone pretreatment, and BAC filtration.

molecular weight compounds from the effluent while the higher molecular weight compounds were no longer sorbed by the GAC. This observation is corroborated by Figures 8 and 6. Low-molecular-weight compounds such as those analyzed in Figure 8 are readily removed by the BAC filter, and their concentrations remain fairly constant. On the other hand, the concentration of compound A in Figure 6, which can be considered as a high-molecular-weight compound, is constantly increasing after the 25th day.

Trace Organic Analysis. This work could be the basis for the development of a new water quality parameter for wastewater reuse regulations. Currently, trace organic compounds are regulated through specific lists of compounds that are typically derived from existing drinking water or groundwater standards (Levine et al., 1996). The drawback associated with this approach is the development of long lists of compounds for which positive identification must be performed to guarantee public safety.

Gas chromatography coupled with a flame ionization detector is particularly well suited for measuring the lower molecular weight organic compounds of the DOC spectrum (between 50 and 700 Da), ensuring broad spectrum organic analysis of potentially hazardous compounds. This approach can be considered as a complimentary analysis to more general analytical tools such as DOC or UV-254.

In addition, this approach favors a visual and semiquantitative representation of the trace organic contaminants present in the water. Therefore, once the GC analysis has been performed, comparison between chromatograms can be used to assess the treatment efficiency of a process and evaluate the changes in concentration of trace organics over time (Gibs, 1983; Stevens et al., 1981; and Suffet et al., 1978).

Conclusions

The purpose of this paper was to analyze the effect of ozone–BAC processes on high-molecular-weight organics and trace organic compounds (BNAs $<$1000 Da) as part of the treatment chain developed at the Lake Arrowhead potable water reuse project. To achieve this goal and satisfy quality assurance requirements, the CLLE extraction protocol was adapted from potable and environmental applications and applied for the first time to wastewater as a broad spectrum analysis of base-neutral compounds with molecular weight varying from 50 to 700 Da.

The ozone–BAC process behaved as has been previously published in the literature. Ozone treatment favored the production of $SBOD_U$ and lowering of the UV-254 absorbance and did not affect the DOC concentrations. A change in composition of the water matrix was indicated by a shift in mass of low-molecular-weight base-neutral compounds from the higher to the lower scan index fraction. This is the first time that this phenomenon was observed at the low molecular weight level. Aldehydes underwent a significant increase in concentration, whereas other compounds such as the larger alcohol compounds were oxidized.

Biological activated carbon treatment efficiently removed both high-molecular-weight and trace organic compounds from the effluent. The data showed that trace organic compounds eluted from the carbon filter after 200 days, which was reflected in DOC or UV-254 parameters after approximately 50 days. This time difference was associated with (a) the nature of the compound because large AMW compounds (50 000 Da) are not readily sorbed by GAC but directly affect DOC data, (b) the fact that GAC is continuously reequilibrating itself with the water phase, requiring more time for lower molecular weight compounds to break through, and (c) the fact that extremely low-molecular-weight compounds are preferentially biodegraded, therefore requiring even more time for them to break through.

In this project, GC profile analysis was used as a monitoring tool for research purposes. However, this approach can also be used as a process-monitoring tool or, in wastewater reuse regulations, as a means for controlling trace organic compounds. In either case, broad spectrum analysis should be used as a screening tool in addition to more traditional parameters such as $SBOD_U$ and UV-254. Additional work is needed to standardize and officially validate this approach as a standard protocol in the wastewater reuse field.

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