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ACRONYMS

ADEQ - Arizona Department of Environmental Quality **CAP** - Central Arizona Project CAWCD - Central Arizona Water Conservatin District Cfs - Cubic feet per second COP - City of Phoenix DOC- dissolved organic carbon DBP - disinfection byproduct FPA -GAC - granulated activated carbon GC/MS - gas chromatography/mass spectroscopy HAA- haloacetic acids HPA -MCL - Maximum Contaminant Limit MWD - Metropolitan Water District of Southern California MIB - 2- methylisoborneol MPI - Malcolm Pirnie Inc. NAWQA - National Water Quality Assessment program (USGS) PAC- powdered activated carbon SPME - Solid Phase Micro-Extraction SRP - Salt River Project T&O - taste and odor T&OCS - Taste and Odor control Study THM - trihalomethane USEPA - U.S. Environmental Protection Agency USGS - United States Geological Survey UV - ultraviolet WTP - Water Treatment Plant

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EXECUTIVE SUMMARY

The goal of this project was to develop a comprehensive management strategy to reduce algaerelated water quality problems for drinking water supplies in arid environments. Algae can cause problems in water supply lakes, water distribution canals, and water treatment plants. The primary focus was the taste and dor problem. However, because algae also produce dissolved organic carbon (DOC), which reacts to form disinfection by-products (DBPs) and contribute other in-plant operational problems, these issues will also be addressed. This final report includes a summary of findings related to research and field-scale activities aimed at algae-related problems. Specific sections include:

- Summary of research report (Tasks 1 through 5)
- Implementation report and Overview of Guidance Manual (Tasks 6 through 8)
- Summary of Research Products
- Future Research Needs
- Recommendations for T&O Control and regional T&O management

RESEARCH REPORT (TASKS 1 THROUGH 5)

The research aspect of this project included five tasks. The major findings of each task will be summarized. The five tasks included:

- Task 1 Monitoring program
- Task 2 Field scale experiments to evaluate T&O control measures
- Task 3 Assessment of in-plant controls
- Task 4 Controlled laboratory experiments
- Task 5 Studies of DOC source, characterization, and treatability

Task 1 – Monitoring Program

The initially selected set of 20 baseline monitoring sites proved to be well-selected, with only a few additional sites added to the monthly monitoring program in order to obtain a comprehensive evaluation of the raw water system for the City of Phoenix. The hydraulic operation of this system is complex and dynamic. During the period of study, precipitation and watershed runoff was below average, and therefore represented a "drought" condition. Results differing from those encountered and reported here may occur during wetter years in the watershed. The work conducted during this task has lead to an improved understanding of the factors leading to T&O production in arid region surface water systems.

MIB and Geosmin concentrations exhibited seasonal patterns (highest in summer and fall) and

significant spatial variability. MIB data are shown in Figure E.1 as contour plots with respect to concentration (ng/L). MIB was the dominant T&O compound observed in the watershed and finished drinking water systems. Geosmin occurred at lower concentrations. MIB and Geosmin spatial and temporal trends followed predictable patterns with regards to water temperature and nutrient conditions. The highest MIB concentrations (>50 ng/L) were found in the reservoir epilimnion and downstream points of the canal systems. The algae species responsible for T&O compound production ("culprit" algae) represented only a very small percentage of the total algae numbers or biomass.

Intensive monitoring indicated "hot spots" for MIB production. For example, plankton in the open water of Saguaro Lake appeared to be the source of MIB, rather than pockets of benthic algae in shallower portions of the lake. In contrast, periphytic algae attached to the concrete-lined canal walls at two locations was a major source of caused MIB production in Arizona Canal.

Task 2 – Field Scale Experiments to Evaluate T&O Control Measures

Due to access limitations to reservoirs and non-site specific T&O spatial occurrence in the reservoirs, field-scale experiments were focused on MIB and Geosmin production in the canals. Experiments focused on (1) mechanical canal brushing of canal walls, (2) chemical liquid copper application to the canals, and (3) polymeric biocides fixed to canal walls. Mechanical brushing removed over 80% of the periphyton biomass from the canal walls and essentially lead to zero net MIB production along the length of the treated canal section. Copper addition lead to a gradual decrease in biomass, but a more rapid decrease of in-canal MIB production. In the weeks after both mechanical brushing and copper treatment biomass regrowth occurred, followed by MIB production. The treatments appear effective for two to three weeks. A combination of first mechanical brushing followed one week later by copper treatment would be a recommended course of action for MIB control in reaches of canals identified to produce T&O compounds.

Task 3 – Assessment of In-plant Controls

An assessment of each City of Phoenix WTP was conducted. No in-plant production of MIB or Geosmin was documented at any of the City of Phoenix WTPs which all practice periodic prechlorination, although reports of such production have been noted at City of Tempe and Chandler which do not prechlorinate. Conventional WTPs offer limited potential to control MIB and Geosmin present in the raw/influent water. The COP therefore has four options to minimize MIB and Geosmin in the finished water:

- 1. Minimize raw water T&O levels through upstream controls (e.g., canal treatments)
- 2. Optimize PAC brand selection, feed rates, and feed capability
- 3. Allow filters to operate in a biological mode
- 4. Upgrade treatment processes to include advanced oxidation processes or nanofiltration/reverse osmosis membranes.

Task 4 – Controlled Laboratory Experiments

Experiments were conducted in the laboratory to (1) screen parameters important for implementation at field- or full-scale and (2) gain insights into a biological process or mechanism. Powder activated carbon (PAC) tests demonstrated PACs ability to remove MIB and Geosmin from surface waters in Arizona. Performance of PAC brands varied and was lower in surface water than distilled water. Kinetics tests for MIB adsorption requires at least one hour of contact time. Ozone and advanced oxidation processes that produce hydroxyl radicals can oxidize MIB and Geosmin, and are more effective than chlorine dioxide; chlorine did not oxidize MIB or Geosmin. Two biocide coatings fo the canal walls were evaluated. Copper biocides can kill MIB-producing algae, but organically-complexed copper products should be avoided since they react with free chlorine to form organic chloramines. Inorganically complexed copper products are recommended. Coating concrete canal walls with biocides or photo-reactive paints offer potential to reduce periphytic biomass and reduce in-canal T&O production.

Environmental factors (temperature, light intensity, growth phase, and nutrient conditions) affected culprit algae growth and production and release of MIB and Geosmin into water. Ten (10) culprit algae (six taxa) were isolated from the water supply system which produced MIB or Geosmin, from over 1000 cultures. MIB and Geosmin biodegrade in reservoirs between the months of November and January at rates on the order of 0.5 to 5 ng/L/day. MIB and Geosmin degradation in the lower parts of the canal system have also been observed. Soils, especially irrigated and vegetated soils, can leach MIB and Geosmin during rainfall and runoff events. This may be a significant factor for "pulses" of T&O compounds that occurs shortly after precipitation.

Task 5 – Studies of DOC Source, Characterization, and Treatability

The DOC component of this study provided a linkage between regulatory issues (DBPs formed during disinfection) and aesthetic issues (T&O from algae). The study clearly shows an impact of algae on the production and structure of DOC in the reservoirs, and ultimately in raw and finished water at the WTPs. The following points summarize the DOC study:

- DOC concentrations and characteristics of the source water vary temporally and spatially. Mean DOC concentrations within each cluster were 2.85, 2.85, 2.35, and 1.93 mg/L in the CAP, Salt River, SRP canal, and Verde River clusters, respectively.
- DOC concentrations increase during runoff (upper reservoir systems). Although the study was conducted during three years of below average rainfall or watershed snowpack, historic data suggests that DOC concentrations increase during wetter than normal years.
- DOC from the CAP system (65/35) is less reactive to DBP formation than from the Salt (115/50) or Verde (85/40) Rivers. Values in parentheses indicate mean (µg/L) THM-SDS/HAA₉-SDS concentrations. Verde River system has the lowest DOC concentrations, but most reactive (to DBP formation) DOC compared to the lower Salt and CAP system.
- The effect of algal-derived DOC in the reservoir system may be small in comparison to

terrestrial DOC load during high runoff periods because algal-produced DOC degrades rapidly.

- However, algal-produced DOC can be significant during summer storage (low input from upstream runoff). Fulvic acids isolated from the Verde cluster were more closely related to algal-derived fulvic acids, especially during storage (no release from Horseshoe Reservoir) and low flow in the Verde River (~ 100 cfs upstream of Horseshoe Reservoir) during the summer (6/03/00 to 8/15/00).
- Mass balances on the reservoir systems show significant DOC production in upstream reservoirs (Horseshoe Lake).
- There is no significant temporal trend in the net rate of production or degradation; although Bartlett Lake exhibits net DOC production during late fall and winter and net degradation in the late summer-early fall.
- The results of the DON studies indicated that DON is present in raw and finished drinking water (0.1 to 0.3 mgN/L), and DOC removal across the COP WTPs could be used to roughly estimate DON removal.
- DOC removal ranged from 5% to 55%, but a median value of 15% was observed for all three WTPs.
- During certain periods of the year or reservoir operation algae in the reservoirs can contribute from 5% to 30% of the DBP precursors to downstream WTPs.

IMPLEMENTATION REPORT (TASKS 6 THROUGH 8)

The implementation aspect of this project included three tasks, and were intended to have a significant effect on drinking water quality for the public. Each task will be summarized for the major findings:

- Task 6 Midcourse Evaluation
- Task 7 Phased-in implementation controls
- Task 8 Guidance document

Task 6 – Midcourse Evaluation

Technical feasibility, economic factors, and political infrastructure of approximately 20 T&O control options were evaluated for potential use in the metropolitan Phoenix region. This evaluation served as the baseline for decisions on which activities to conduct in the field during Task 7 (Phased-in Implementation). A multiple-barrier approach for controlling T&O was developed, comprising (1) watershed controls, (2) source water controls, (3) canal distribution controls, and (4) in-plant controls. Achieving T&O control higher in the watershed would have the greatest benefit to the largest number of WTPs. Political obstacles associated with water rights and timing of water releases complicated implementation of regional controls, although the project has initiated efforts to evaluate such obstacles in the future. In-canal management

and in-plant controls were deemed highly effective and were therefore the focus of Task 7 activities.

Task 7 – Phased-In Implementation Controls

Six management practices were implemented at the operational scale: (1) modified operation of Lake Pleasant, (2) source water switching to avoid T&O episodes, (3) blending of SRP and CAP water at the head of the Arizona Canal, (4) copper treatment of the canals, (5) mechanical brushing treatment of the canals, and (6) PAC addition within the WTPs. The timing and location of these activities were highly dependent upon a seventh and critical implementation practice: process control monitoring; nearly weekly sampling and rapid communication/decision making allowed timely implementation of the management practices. This project demonstrated the effectiveness of these implementation controls.

The impact or benefit from the implementation activities were quantified by evaluating the number of drinking water consumer days below various MIB thresholds, and the cumulate effect of each "downstream" implementation activity. The implementation activities added between 100 million to 130 million consumer days below 20 ngMIB/L. This is 33% to 44% increase over prior years without such implementation activities. The implementation activities also increased the number of days that the drinking water public received water with MIB concentrations below 10 ng/L, a commonly reported threshold for sensitive populations. The implementation activities were therefore considered a success at improving the quality of water delivered to consumers.

Task 8 – Guidance Document

A Guidance Document was prepared as a separate report from this Final Report. The Guidance Document was written for application by WTP operations personnel, and provides the key decision making information required to establish a monitoring program, identify "hot spot" locations of MIB production, select T&O control measures, and implement the T&O control measures. An important portion of the monitoring program included a photo-documented guide for identification of T&O producing culprit algae.

OVERALL IMPACT OF THE T&O MANAGEMENT PROGRAM

The overall impact of the T&O management program for 2001 was computed two ways, first by subtracting "likely consumer days without management" from observed consumer days below the 10 and 20 ng/L thresholds, and second, by summing the impact of each T&O treatment measure. In theory, these two values should be the same, but because of slightly erroneous assumptions, they are somewhat different.

T&O management appears to have added between 102 million (by difference) to 132 million CDBT-20s (by summing terms) Phoenix's water supply. This is 33% to 44% more CDBT-20s than would have occurred in the absence of the T&O management program. T&O management added 85 million to 113 million CDBT-10s, a gain of 36% to 47% compared to the no-management option.

An approximate allocation of total system-wide consumer days is presented in Figure E.2. In the absence of a T&O control program, we estimate that about 64% of consumer days would

have been < 20 ng/L and 36% of the consumer days would have had MIB > 20 ng/L. The T&O management program dealt with about 3/4 of the problem. In 2001, MIB exceeded 20 ng/L for only 7% of consumer days. Source switching had the largest impact at reducing MIB in water delivered to consumers, reducing the number of consumer days above 20 ng/L by 20%. PAC treatment reduced MIB < 20 ng/L for 9% of total consumer days. Modified operation of Lake Pleasant contributed no CDBT-20s in 2001, but would have contributed to a decrease in CDBT-20s in 1999 and probably in many other years.

Without the T&O management program, only 48% of consumer days would have been below the 10 ng/L threshold. The T&O management program reduced the number of total consumer days with MIB < 10 by another 25%. About one fourth of total consumer days remained above 10 ng/L. Source switching and modified operation of Lake Pleasant provided the greatest increases in CDBT-10s. PAC treatment was not very effective at increasing CDBT-10s, mostly because COP's WTPs are not yet using PAC as effectively as they could. Infrastructure improvements in PAC delivery systems would greatly increase the CDBT-10s.

In summary, implementation of the T&O reduction program in 2001 significantly improved the quality of water delivered to consumers.

SUMMARY OF RESEARCH PRODUCTS

The following list includes journal articles, presentations, and graduate theses/dissertations that directly relate to the support from this project:

- 1. Baker, L., P. Westerhoff, et al. (1999). <u>Multi-barrier concept for taste and odor control</u>. North American Lake Management Society Conference, Reno, NV.
- 2. Baker, L., P. Westerhoff, et al. (2000). <u>Multiple barrier approach for controlling taste and</u> <u>odor in Phoenix's water supply system</u>. AWWA WQTC Conference, Salt Lake City, UT.
- 3. Brawley-Chesworth, A. and P. Westerhoff (2000). <u>Fate of MIB and Geosmin in surface</u> water treatment plants. AWPCA Annual conference, Mesa, AZ.
- Bruce, D., P. Westerhoff, et al. (in-press). "Removal of MIB and Geosmin in surface water treatment plants in Arizona." <u>Journal of water supply: Research and Technology</u> (AQUA).
- 5. Bruce, D., P. Westerhoff, et al. (2000). <u>Occurrence and potential causes of Geosmin and</u> <u>MIB in Arizona drinking waters</u>. AWPCA Annual Conference, Mesa, AZ.
- Dawson, S. (2002 (expected)). Use of fixed-biocide coatings for algae control in SRP canals. <u>Department of Civil and Environmental Engineering</u>. Tempe, AZ, Arizona State University.
- Dempster, T., D. Lowry, et al. (2001). "Identification and isolation of organisms causing taste and odor problems in surface water supplies of metropolitan Phoenix, AZ." <u>Journal</u> <u>of Arizona-Nevada Academy of Science</u> **36**: 15.
- 8. Dempster, T., M. Sommerfeld, et al. (2001). "An overview of microorganism-related taste and odor problems in surface water supplies of metropolitan Phoenix, AZ." <u>J. Arizona-</u>

Nevada Academy of Science 36(15-16).

- 9. Hu, Q., T. Dempster, et al. (2000). <u>Algal-related T&Os in Phoenix water supply:</u> preliminary report (POSTER). Phycological Society of America, San Diego, CA.
- 10. Hu, Q., T. Dempster, et al. (2000). "Algal-related tastes and odors in Phoenix water supply: preliminary report." J. Phycology **36**(3): 32.
- 11. Hu, Q., M. Sommerfeld, et al. (in preparation). "Effects of environmental factors on intracellular and extracellular Geosmin production." J. Environmental Microbiology.
- 12. Hu, Q., M. Sommerfeld, et al. (2001). <u>Production and release of Geosmin by the</u> <u>cyanobacterium Oscillatoria splendida isolated from Phoenix water sources</u>. Phycological Society of America, Estes Park, CO.
- Nguyen, M. (2002). Sources and characteristics of dissolved organic carbon in aridregion water supplies. <u>Department of Civil and Environmental Engineering</u>. Tempe, AZ, Arizona State University: 221.
- 14. Nguyen, M., L. Baker, et al. (2000). <u>Production of DOC/DBP Precursors from algal</u> growth in arid region surface water supply (POSTER). AWWA WQTC Conference, Salt Lake City, UT.
- 15. Nguyen, M., L. Baker, et al. (2000). <u>Sources and transport of DOC/DBP precursors in the CAP and SRP canals</u>. AWPCA Annual Conference, Mesa, AZ.
- 16. Nguyen, M., L. Baker, et al. (2002). "DOC and DBP precursors in western US watershed and reservoirs." Journal American Water Works Association **94**(5): 98-112.
- 17. Rodriquez, M. (2002 (expected)). Modeling MIB in reservoirs. <u>Department of Civil and</u> <u>Environmental Engineering</u>. Tempe, AZ, Arizona State University.
- 18. Westerhoff, P. (2001). <u>Sources and control of T&O causing algal metabolites</u>. AWPCA Luncheon, Tempe, AZ.
- 19. Westerhoff, P., D. Bruce, et al. (submitted). "Production and degradation of algal metabolites in three water supply reservoirs." <u>Environmental Science and Technology</u>.
- Westerhoff, P., D. Bruce, et al. (2001). <u>Removal of MIB and Geosmin in surface water</u> treatment plants in Arizona (Quentin Mees Research Award Paper). AWPCA Annual Conference, Mesa, AZ.
- Westerhoff, P., D. Bruce, et al. (2001). <u>Role of Verde River reservoirs on water quality:</u> <u>From arsenic to algae</u>. Verde Watershed Symposium - State of the Watershed, Camp Verde, AZ.
- 22. Westerhoff, P., D. Bruce, et al. (2001). <u>Spatial occurrence and degradation of MIB in</u> <u>local surface waters</u>. AWPCA Annual Conference, Mesa, AZ.
- 23. Westerhoff, P., D. Bruce, et al. (2001). <u>Production sources and degradation of algal</u> metabolites (MIB/Geosmin) in Arizona reservoirs, rivers, and canals. AWWA Annual

Conference, Washington, D.C.

24. Westerhoff, P., W. Chen, et al. (2000). <u>Fluorescence characterization of NOM</u> AWWA WQTC Conference, Salt Lake City, UT.

FUTURE RESEARCH NEEDS

Numerous research needs were identified during this project. Many of the identified research needs have been focused and serve as the basis of external funding. This research has also lead indirectly to supplemental funding from the following projects, and includes partnerships between ASU and metropolitan Phoenix regional cities:

- AWWARF Tailored Collaboration Project: Cities of Phoenix, Scottsdale, and Tempe plus Arizona State University. "Developing a Customer-Driven Response Strategy for Dealing with Public Perception (taste and odors at the tap) and Potential Health Concerns (algal biotoxins)" April 2002-2004 (PIs: R.Gottler, P. Westerhoff) (>\$150,000).
- AWWARF Solicited RFP#2775: PIs: P.Westerhoff, Z. Chowdhury, S. Summers. "Ozone-enhanced Biofiltration for MIB and Geosmin Removal" February 2002-2004 (\$350,000).
- AWWARF Unsolicited Proposal: PIs: P. Westerhoff, H. Mash, P. Fox, G. Amy, J. Croue. "Dissolved Organic Nitrogen (DON) in Drinking Water and Reclaimed Waste Water" Announced June 2002 (\$169,000)
- City of Tempe PIs: P. Westerhoff, M. Sommerfeld "PAC screening study for MIB" Spring 2002 (\$4,000)
- City of Tempe PIs: P. Westerhoff, M. Sommerfeld "MIB and Geosmin Process Control Monitoring" July – December 2002 (\$26,000)
- Salt River Project PIs: Q. Hu, M. Sommerfeld, P. Westerhoff "Development of Gene Probes for Monitoring the Occurrence and Distribution of MIB/Geosmin Producing Cyanobacteria in the SRP Water Distribution System" July 2002- June 2003 (\$35,000)

RECOMMENDATIONS FOR T&O CONTROL AND INTEGRATION OF REGIONAL T&O MANAGEMENT

The central theme of the proposed T&O management strategy is the concept of multiple barriers. The multiple barrier concept in water treatment is widely used for pathogen control. "Barriers" in pathogen control include watershed management (for example, eliminating animal and human waste inputs into streams), sedimentation and filtration within water treatment plants to remove pathogens, initial chlorination to kill pathogens, and maintenance of chlorine residual to kill any pathogens that might enter the distribution system (by regrowth, plumbing malfunctions, etc.).

The concept is similar for T&O control. During the T&O study, more than 20 specific control measures were evaluated. Six control measures emerged as the key elements of an overall T&O management strategy:

- <u>Process Control Monitoring</u>. Frequent sampling, rapid analytical turnaround, and rapid data review are critical for implementing any control strategies. Experience indicated that MIB concentrations remained somewhat constant over 7 to 10 days, and that frequency of sampling is recommended. More fequent amling may be needed to monitor implementation of some control strategies, such as canal treatments. Timely and accurate data on the status of T&O levels in a water supply system was determined critical to maximize the economic benefits of implemented control strategies.
- <u>Reservoir management.</u> The main reservoir management practice found to be effective was blending of waters from the Colorado River and the two outlet structures (upper and lower) in Lake Pleasant. In a 1999 study, University of Arizona Researchers suggested modifying the depth of water released fro Lake Pleasant. Through blending waters from these three sources, CAWCD has been able to keep MIB and Geosmin in the CAP Canal below Lake Pleasant below 10 ng/L.
- <u>Canal treatments.</u> The goal of canal treatments was to remove T&O-producing algae growing on the sides of the Arizona Canal, thereby reducing the production of MIB. Because algae growing on the canal walls can be a major source of MIB, sometimes contributing > 50 ng/L MIB to water flowing through the canal, canal treatments to remove algae are a very important part of the overall T&O management program.
- <u>SRP-CAP Blending.</u> During the late summer and fall, CAP water generally has lower concentrations of MIB than SRP water. This provides an opportunity for blending the two source waters to reduce MIB concentrations in water delivered to the treatment plants. For most years, using more SRP water early in the season, and more CAP water later in the season, would improve the quality of water delivered to Phoenix's municipal customers. The opportunity for blending depends upon the hydrologic status of the system. Revisions in the legislation controlling the SRP-CAP Water Exchange Agreement in 2002 enhance the opportunity for blending as a T&O control measure, but still many institutional constrints exist.
- <u>Source switching.</u> Phoenix has several water treatment plants and will have a sixth within about five years. The idea behind source switching is that water with higher MIB/Geosmin can sometimes be avoided by switching production from a plant that is receiving high MIB/Geosmin water to one or more plants that are receiving water with lower MIB/Geosmin. For example, taking the Deer Valley WTP off line during 2001, shifting production to the Union Hills and Squaw Peak WTPs, avoided the problem of high MB in the lower end of the Arizona Canal and resulted in better quality of water delivered to consumers.
- <u>In-plant treatment.</u> PAC treatment in the WTPs has been an effective method of removing MIB from source waters. Although PAC treatment could theoretically keep MIB levels below 10 ng/L throughout the year with no upstream management, practical limitations constrain the effectiveness of PAC treatment. These limitations include limited storage capacity, problems with feed systems, and hydraulic short-circuiting. Furthermore, even if these limitations could be overcome, a multibarrier strategy would

be more cost-effective than reliance upon PAC treatment alone.

The surface water system that serves the City of Phoenix also serves every other municipality in the metropolitan Phoenix region. As can be seen in the above six effective control strategies, the first four would actually reduce T&O levels for all municipalities downstream of the implementation activity. A regional water sampling plan including locations, analytes, and sampling frequency has been developed in the Guidance Manual. Samples are collected by SRP, CAP, and a third party (e.g., ASU), analyzed at a central laboratory within 36 hours, and data reviewed within the following 48 hours. As this project ends, the Cities of Phoenix, Tempe, and Chandler are participating in an ongoing T&O monitoring project. Cooperation of multiple cities appears to be leading toward regional management of T&Os.



Figure E.1 Contour plot for MIB concentration as a function of sampling date and sampling site location



Figure E.2. Pie chart showing consumer days with MIB < 20 ng/L (A) and < 10 ng/L (B) for 2001 and allocation of causes.

SECTION 1: PROJECT OBJECTIVES

The overall goal of this project is to develop a multi-barrier management plan to control T&O problems, implement several algae control measures, and ideally also reduce other algaerelated problems. *Proactive controls* will be developed to minimize the growth of T&Oproducing algae. *Responsive controls* will be developed to treat T&O compounds if proactive measures are not effective. Implementation of control measures were phased in over the threeyear project period. The control measures implemented by Year 3 resulted in an actual reduction of T&O problem for areas served by the Arizona Canal. Changes in drinking water quality was documented by monitoring consumer complaints and actual concentrations of T&Ocausing compounds (MIB and Geosmin).

The results of this project is summarized in a guidance document that will allow water utilities to continue the implementation of a comprehensive T&O control program at the conclusion of the study. The role of algae in producing DOC in the water supply reservoirs, and the reactivity of this DOC in forming disinfection by-products (DBPs) upon chlorination was determined.

Specific goals were:

- 1. Develop a thorough understanding of conditions leading to T&O problems
- 2. Quantify the extent to which reservoir algae produce DOC and the reactivity of this DOC in forming DBPs.
- 3. Conduct a preliminary feasibility analysis for about 20 potential T&O control measures based on technical, economic, and political considerations.
- 4. Conduct controlled lab and field-scale experiments to evaluate specific T&O control practices.
- 5. Integrate results from the previous steps to begin implementation of a multiple-barrier approach for controlling the T&O problem.
- 6. Develop a long-term monitoring plan that will allow Phoenix and other municipalities to forecast the occurrence of T&O problems.
- 7. Develop a user-friendly taste and odor control manual that will help municipal water suppliers in arid environments develop effective T&O control programs.
- 8. Extrapolate applied research findings from Arizona to water treatment systems in other arid environments.

A comprehensive research program was undertaken that aims to understand the causes of Taste and Odor problems and to develop technically, economically, and politically feasible means of implementing measures to control its occurrence. The research and implementation plan is illustrated schematically in Figure 1.1. A schedule for project activities and milestones performed is presented in Figure 1.2. This is the final report and summarizes activities from August 1999 through June 2002.

SECTION 1 TABLES AND FIGURES

Figure 1.1. Schematic of Project Tasks



7						
	Jul/99 - Dec/99	Jan/00 - Jun/00	Jul/00 - Dec/00	Jan/01 - Jun/01	Jul/01 - Dec/01	Jan/02 - Jun/02
Task 1		-		-	-	1
Task 2			1	7		
Task 3						
		1				
Task 4			1	1		
Tubh T						
Task 5						
Task 6				-4		
Task 7						
Task 8						
Management						
Meetings	12-09-99	6-21-00	12-7-00	6-5-01	12-5-01	8-8-02
Riannual project	at	nual project	1-26-01	7_26_01	1-28-02	7-29-02
Diaminuar project	1-25-00	7-21-00	1-20-01	7-20-01	1-20-02	1-23-02
reports						
Quarterly status	10-27-99	4-25-00	10-25-00	4-27-01	10-29-01	4-29-02
reports						> •=

Figure 1.2. Schedule of project tasks.

SECTION 2: MONITORING PROGRAM (TASK 1)

The purpose of this task was to conduct baseline field monitoring in lakes, reservoirs, rivers, canals, and water treatment plants for selected water quality parameters, taste and odor compounds, and culprit algae species. The main text will include interpretation of trends in key parameters including MIB, Geosmin, algae species, nitrogen and phosphorus. Trends in DOC from baseline monitoring are presented in Section 6 along with other DOC related measurements. Appendix A contains raw data for all parameters collected during this study.

SITE DESCRIPTION

Reservoir Descriptions

The three reservoirs (Bartlett Lake, Saguaro Lake, Lake Pleasant) studied are major components of the water supply system for the >2 million inhabitants of the Phoenix, Arizona metropolitan area (Figure 2.1). They are all terminal reservoirs with some varying types of upstream impoundments. All three are located in the semi-arid Sonoran desert within 50 km of the Phoenix metropolitan area. The reservoirs are characterized as oligotrophic to mesotrophic with physical characteristics (Table 2.1) typical of reservoirs in the western United States, and semi-arid regions throughout the world. The reservoirs are operated very differently in ways that could affect both the production and degradation of MIB and Geosmin and the release of these compounds to downstream water treatment plants.

Bartlett Reservoir is an on-stream reservoir on the Verde River, located 2 miles downstream of Horseshoe Reservoir (maximum volume = $1.6 \times 10^8 \text{ m}^3$; maximum surface area = 11.4 km^2). Bartlett Reservoir has a single outlet near the bottom (hypolimnetic withdrawal). Most water enters the reservoir following snowmelt at higher elevations. Water is stored throughout the summer and released predominately after October 1, continuing through the winter. For the first half of this study Bartlett Reservoir was at approximately 50% of capacity, and then approached 75% capacity during the second half of the study (Table 2.1 and Figure 2.2).

Saguaro Lake is the lowest of five reservoirs on the Salt River. Three of the upstream Salt River reservoirs have hydropower generation facilities. Pump-back piping from Saguaro to upstream reservoirs is used during summer months to increase hydropower revenue. Water released from upstream reservoirs during peak demand periods (daytime) is pumped back to the upstream reservoirs upstream during off-peak periods (night-time). This operational mode is reflected in a very short hydraulic residence time (HRT = outflow/volume = ~0.25 years). Saguaro Lake typically remains at near capacity, with very little (2-4 m) variation in surface elevation throughout the year. Saguaro Lake also has one outlet near the bottom. Most releases occur in the summer (> 8.5 m³/s) and stop around early October, with minimal flow (~0.1 m³/s) between October through April. Water levels and storage volumes in Saguaro are maintained fairly constant for recreational, energy production, and maximal Salt River storage reasons (Figure 2.2).

Lake Pleasant is an off-stream water supply reservoir located near the Central Arizona Project (CAP) Canal. It is filled with water pumped from the Colorado River between October and April via a 200-km long open concrete canal. Water levels and storage volume vary significantly throughout each year (Figure 2.2). Water is released from Lake Pleasant between April and October through one of two outlets, near the bottom and surface, located ~30 m apart. Natural drainage from the Aqua Fria River supplies a small amount of additional inflow to Lake

Pleasant. This inflow was less than 5% of the total reservoir inflow during this study.

Hydraulic retention time (HRT) in the reservoirs emerged as one potential parameter that affects algae growth and metabolite production. Figure 2.3 illustrates that average HRT values (Table 2.1) only partially describes the operation of the reservoirs. Monthly HRT values computed for the study period vary from shorter than two months to longer than one year. In semi-arid regions water is captured when it is available, and released as reservoir storage approach full capacity. It is very important to state that during the period of this study rainfall / snowfall and associated watershed runoff was below normal. Wetter than average years may have dramatically different reservoir operation scenarios, affecting nutrient fluxes and algae growth dynamics.

Hydraulic Operation of SRP and CAP Systems

Central Arizona Water Conservation District (CAWCD), referred to herein as Central Arizona Project (CAP), and Salt River Project (SRP) operates canals, reservoirs, and pumps to deliver water to municipal, agricultural, and industrial users. CAP pumps water from the Colorado River to Lake Pleasant and into the CAP canal that serves the metro-Phoenix region before flowing southward towards Tucson, AZ. CAP can deliver water into the SRP canal system (Arizona or South canals) just below Granite Reef Dam (termed the "interconnect"). The City of Phoenix (C.O.P) has one water treatment plant (Union Hills WTP) located on the CAP canal, and is planning construction of another facility near Lake Pleasant.

SRP operates reservoirs on the Salt and Verde Rivers, with power generation capacity available only on the Salt River. SRP generally releases Salt River water from April through November, and Verde River water the remainder of the year. The confluence of the Salt and Verde Rivers is located approximately one mile upstream from a check-dam (Granite Reef Dam) that has control gates to release water to the South and Arizona Canals. A network of SRP canals (mostly concrete-lined open channel, gravity-flow) has wells located along the banks which can be used to pump groundwater into the canal. COP has two WTPs on the Arizona Canal (Squaw Peak and Deer Valley WTPs) and one on the South Canal (Val Vista WTP). Val Vista WTP is partially owned by the City of Mesa, and part of the treated water flow is delivered to the City of Mesa.

The SRP canals become hydraulically limited near Granite Reef Dam. To meet downstream water demands, groundwater wells are typically pumped into the lower part of the canal system. The decision for SRP to pump groundwater wells is based upon a minimum pumping requirement to maintain water rights, and increased pumping occurs during periods of high water demand or low storage in Salt and Verde River reservoirs. Figure 2.4 presents historic well pumping data for two wells located along the Arizona Canal between the COP Squaw Peak and Deer Valley WTPs. Beginning in 1999 pumpage of these two wells by SRP started due to decreasing storage in Salt and Verde River reservoirs; during prior years the reservoirs were nearer full capacity. Both wells contain nitrate (see figure caption), a limiting nutrient for algae production (see later sections). Groundwater pumping increases nitrate concentrations in this section of the canal by several theths of a mg/L, enough to encourage algae growth.

Sampling Locations

Field sampling sites included locations along the CAP and SRP canals and the Verde and Salt

Rivers including Bartlett Lake, Saguaro Lake and Lake Pleasant. Regular monthly baseline sampling sites are presented in Figure 2.1 and have a R# designation. Descriptions of the sites are listed in Table 2.2. Sampling sites were aggregated into four "clusters" that represent similar water quality:

- CAP cluster
- Salt River cluster
- Verde River cluster
- SRP Canal cluster

Locations along canals, rivers, and water treatment plants throughout the Valley region were selected as sample sites in order to assess taste and odor problems in the entire water collection system. A multi-barrier approach was taken to address taste and odor problems in drinking water supplies. Sample sites were selected to include locations along the entire water collection system in the Valley; from source water in rivers and lakes to finished water in water treatment plants. Water samples were collected monthly from August 1999 through June 2002 in the CAP, Verde River, Salt River, and SRP sample clusters.

Additional sample locations were monitored for selected parameters (namely MIB and Geosmin) as the study progressed. These include the following sites:

- R21 Arizona Canal at Central Avenue
- R22 Arizona Canal at 56th Street
- R25 Verde River at Beeline Highway
- R26 Cross-cut Canal at Washington Street

SAMPLING METHODS

Monthly samples of reservoir inflows and outflows and canals were collected as grab samples in a 1-liter stainless steel vessel attached to an extendable rod. Grab samples were collected from approximately 0.2 meter below the surface. Reservoir samples were collected using a Kemmerer sampler. Discrete samples were collected at roughly 5 m depth intervals. During stratification, discrete samples were composited (stainless steel container) into "epilimnetic" and "hypolimnetic" samples using thermal profiles as a guide. During non-stratified periods, discrete samples generally were composited from samples collected throughout the water column. On several occasions, discrete samples were collected at finer depth intervals to elucidate vertical profiles. Several parameters were measured in the field (Table 2.3). Secchi disc depth was only measured in the reservoirs.

Samples were collected and transferred to clean containers, stored in a cooler with "blue-ice," and transported to a central laboratory without preservation. At a central laboratory the samples were pretreated, preserved or split into separate samples. Analytical measurements were conducted within two weeks, with samples held at 4°C as appropriate.

Rigorous glass and plastic ware cleaning procedures were followed throughout the project. Labware was whshed with phosphate-free detergent (Citranox, Alconox Inc), rinsed with distilled water, soaked in dilute HCI, rinsed with distilled water, ashed (550°C for 4 hours for glassware only), and dried (100°C).

A periphyton sampler was developed to collect periphyton biomass (Figure 2.5). It is a rectangular chamber, measuring 25 cm long, 18 cm wide and 18 cm high. The upper part of the chamber was made of clear plexiglass plate whereas the bottom was a metal template with a 10 x 15 cm open area (0.015 m²). The side of the chamber facing the top of the canal has a small slot through which a wire pool brush inside the chamber is attached to a telescoping pole. The upstream side of the chamber has a large opening covered by a fine plastic screen that allows water to flow through the chamber. On the downstream side of the chamber is a large circular opening with a plankton-net (80 µm) attached. Two people are required to collect samples. The sampler is placed on the canal wall and held into position with the telescoping pole. A second individual brushes the wall a defined number of times. As periphyton mats are removed from the canal wall, they are carried by water flow into the plankton net. Because a vertical zonation of periphyton was evident on canal walls, sampling was done at three depths just below the surface and extending downward (ca. 40 cm apart). The three samples were composited and stored in a sterile Whirl-pak bag at 4 °C for analysis. To assess periphyton biomass, chlorophyll a was extracted and measured as described in the Analytical Methods below and expressed per m² of canal wall.

ANALYTICAL METHODS

Table 2.4 summarizes analytical methods used for laboratory analysis. It also includes glassware and sample pretreatment / preservation required prior to analysis. The remainder of this section includes more detailed methods on selected non-standard analyses.

MIB and Geosmin

MIB and Geosmin were measured using Solid-Phase Microextraction/Gas Chromatography Mass Spectroscopy (SPME-GC/MS) (Watson et al., 2000; Lloyd et al., 1998). Twenty-five ml of sample is added to a 40 ml septum capped vial that contains 8 gm desiccated sodium chloride and a magnetic stir bar. An internal standard (10 ng/L IPMP, Aldrich Chemical Co., Milwaukee, WI) is added through the septum and the vial is placed in a water bath on a magnetic stir plate heated to 50 \pm 1.5 °C. A SPME fiber (Supelco # 57348 U) is introduced into the head space gas through the septum and the sample is stirred for 30 minutes. The fiber is removed from the vial and inserted into the gas chromatograph injector at 250 °C for 5 minutes. The fiber was then retracted into the holder, removed from the GC inlet and reused for the next sample. Compounds are eluted from the column gas chromatograph to a mass spectrometer set for selective ion storage (selective m/z values: MIB = 95, Geosmin = 112 and IPMP = 124, 136). Calibration curves are generated using MIB and Geosmin standards (mixture standard: Supelco # 47525 U). Analysis of MIB and Geosmin was performed on a Varian Star 3400 CX gas chromatograph and mass spectrometer (GC/MS). Compounds from the fiber were desorbed in the gas chromatograph and eluted from a column (MDN-5 capillary column; Supelco, Pennsylvania) into the mass spectrometer for selective ion storage. QA/QC analysis of MIB measurements by the City of Phoenix and ASU labs has shown a nearly 1:1 correlation (actual slope was 0.95), and a statistical R^2 value of 0.72 for approximately 150 samples since inception of the project. These are acceptable statistical patterns for the project. The method detection limit (MDL) for MIB and Geosmin was 0.5 ng/L.

THM and HAA Tests

For Simulated Distribution System (SDS) THM and HAA tests filtered samples were buffered to pH 8.0 \pm 0.2 with phosphate buffer (at 0.02 M concentration). Chlorine dosage (NaOCI) was calculated from the different chlorine concentrations which would yield a residual Cl₂ of 1.0 \pm 0.2 mg/L following a 24 hour (25°C) chlorine demand test. The dosage and residual of chlorine (as Cl₂) were measured spectrophotometrically using the DPD Colorimetric Method (Method 4500-CI) using a HACH DR/2000 Spectrophotometer. Residual chlorine was quenched with sodium thiosulfate (Na₂S₂O₃) for THM analyses and with ammonium chloride (NH₄CI) for HAA analyses.

Algological Methods

Periphyton samples

Collection. Remove algae from predetermined surface area of canal wall using the periphyton sampling apparatus. Transfer algae with approximately 75 ml of canal water to an 8 or 12 ounce Whirl-Pak, seal it and store at 4° C until processing. In the laboratory, transfer the contents of the Whirl-Pak into a 125-mil glass jar with Teflon lined cap. Add Alga-Gro Freshwater medium to bring the final sample volume to 100 ml. Store samples at 4° C in the cold room until algal identifications and counts are completed.

Processing. Remove one ml aliquot from the 125 ml tall glass jar after vigorous shaking and transfer it into a 1 ml Sedgewick-Rafter counting cell (Wildlife Supply Co., Cat. No. 1801-A10). Place counting cell on inverted microscope and identify algae at 20 times magnification (20X). Observe and count the contents of at least two (2) 0.09 mm³ fields of the Sedgewick-Rafter counting cell. Repeat previous three steps twice for a total of three counting cells (or 3 ml of each sample) to increase observation of maximum species diversity.

Calculate the number of organisms per mm² of canal wall surface area using the raw data and the total volume observed on the inverted microscope as follows:

Total Sample Volume = 100,000 mm³ Total Canal Surface Area = 2,120 mm² Total Fields Observed = 15 (5 from each cell) Volume of each Field = 0.09 mm³ Total Volume Observed = 15 x 0.09 = 1.35 mm³ Fraction of Sample Observed = 100,000/1.35 = 74,074 Factor for Number of Organisms per mm² = 74,074/2,120 = 34.94 Total Number of Organisms per mm² = 507 x 34.94 = 17,717 Organisms/mm² **The total number of each alga multiplied by the factor above will give the total number of alga per mm² of canal wall surface.**

Phytoplankton samples

Collection. Collect one (1) liter of lake or canal water from each site and store on ice in the field followed by 4° C in the cold room until processing. Centrifuge 100 ml to a final volume of 10 ml by using two 50-ml plastic disposable centrifuge tubes and an International Portable Refrigerated Centrifuge (Model PR-2). Reduce volume of each 50-ml tube to 5 ml with an aspirator. Transfer the remaining contents of both 50-ml tubes to a 15-ml plastic disposable centrifuge tube and bring the final volume to 10 ml of concentrated sample. Store the 10-ml vials at 4° C until algal identifications and counts are completed.

Processing. Remove a 1 ml aliquot from the 10 ml plastic disposable centrifuge tube after

vigorous shaking and transfer it into a 1 ml Sedgewick-Rafter counting cell (Wildlife Supply Co., Cat. No. 1801-A10). Place counting cell on inverted microscope and identify algae at 20 times magnification (2X). Observe and count the contents of at least two 0.09 mm³ fields of the Sedgewick-Rafter counting cell. Repeat the three previous steps twice for a total of three counting cells (or 3 ml of each sample) to increase observation of maximum species diversity.

Calculate the number of organisms per ml of lake water using the raw data and the total volume observed on the inverted microscope as follows:

Total Concentrated Sample Volume = 10 ml Total Sample Represented = 200 ml Total Fields Observed = 15 (5 from each cell) Volume of each Field = 0.09 mm^3 Total Volume Observed = $15 \times 0.09 = 1.35 \text{ mm}^3$ Fraction of Sample Observed = 1,000/1.35 = 740.74Factor for Number of Organisms per ml = 740.74/200 = 3.7Total Number of Organisms per ml = $507 \times 3.7 = 1,878$ Organisms/ml **The total number of each alga multiplied by the factor above will give the total number of alga per mm³ of lake water.**

Algal identification and enumeration

Algae were initially identified using an Olympus compound microscope at 1000 magnification (1000X) with an oil immersion objective. Filamentous algae and diatoms were identified using wet mounts and burn mounts, respectively. Algae were identified at least to genera and to species whenever necessary using the following primary taxonomic sources:

Chlorophyll extraction and analysis

Collect one liter of lake water from each site and store on ice in the field with limited exposure to light followed by 4° C in the dark cold room until processing and analysis. Filter 200 ml of sample through 1.2 micrometer pore size Whatman GF/C glass microfibre filter. Place filter in a 15-ml centrifuge tube with 9 ml acetone and 1 ml magnesium carbonate solution (1 g finely powdered magnesium carbonate in 100 ml distilled water). Extract chlorophyll at 4° C in the dark coldroom for 48 hours. After 48 hours, centrifuge (500 rpm for 20 minutes) all of the tubes to concentrate filter and cellular debris at the bottom of the tube. Place a 3 ml aliquot from the 15-ml centrifuge tube into a quartz cuvette for spectrophotometric analysis. Record optical density measurements at 630,647 and 664 nm. Use the following equations to determine chlorophyll a, b and c concentrations in mg/l:

Chlorophyll a = 11.85(OD664) - 1.54(OD647) - 0.08(OD630)Chlorophyll b = 21.03(OD647) - 5.43(OD664) - 2.66(OD630)Chlorophyll c = 24.52(OD630) - 7.60(OD647) - 1.67(OD664)

Isolation of presumptive culprit organisms

Planktonic and periphytic algae collected from the field were transferred to several standard culture media including Alga-Gro freshwater medium, BG 11 medium and Bold's Basic medium enriched with soil-water medium (Carolina Biological Supply Company, 1978). These transfers were made on to both agar plates and into liquid medium. Growth temperature was 20-25 °C and light intensity was ca. 20-40 μ mol m⁻² s⁻¹.

To plate the algae on solid medium, 1% agar instead of 1.5% agar was used to obtain good growth. Cyanobacterial filaments rapidly migrate through 1% agar whereas motile bacteria do

not. The agar plates were incubated in unidirectional light. The filaments that are rapidly moving on front of the illuminated side of the plate are transferred to fresh agar plates or into liquid medium. In general, three to six passages through agar are sufficient for obtaining a unialgal isolate. For liquid medium culture, repeated liquid transfer of small amounts of material is necessary to obtain a unialgal culture.

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RESERVOIR LIMNOLOGY

All three reservoirs underwent seasonal stratification (April through September) and were destratified typically between November and April. Thermal stratification patterns for the reservoirs are presented in Figure 2.6. Maximum delta temperature (y-axis) represents the maximum difference in temperature between the warmest water (typically surface) and samples taken at 5-meter increments below the surface. The depth of SRP lakes does not influence maximum delta temperature. Saguaro Lake exhibits the weakest thermal stratification, probably due to pump-back operations from Saguaro that SRP employs to generate power during peak demand periods on upstream reservoirs. Representative vertical thermal and dissolved oxygen profiles from each lake are illustrated in Figure 2.7 for July 2000, and were typical of stratified periods. A sharper dissolved oxygen than thermal profile occurs between the epilimnion (upper

layer) and hypoliminion (lower layer). The epilimnion was generally considered to be 10 meters in depth.

Algae biomass and inorganic turbidity can result in varying degrees of reservoir water clarity. During this study, this was quantified using a Secchi disc measurement (Figure 2.8). Deeper Secchi disc measurements indicate water with higher clarity. The lowest Secchi disc depths typically occurred in late fall, approximately one to two months after thermal destratification.

NUTRIENTS (NITROGEN AND PHOSPHORUS)

Nutrient Concentrations and Trends

Nitrogen and phosphorus are key nutrients for algae production. A summary of total and dissolved nitrogen and phosphorus over the course of this study is presented in Table 2.5. The table includes data from all three reservoirs, include subsets of data only from the epilimnion during thermal destratification. Table 2.5 also includes statistics on one downstream site on the Arizona Canal (R14 – Deer Valley WTP raw water). Approximately 80% of the phosphorus and 90% of the nitrogen was present in the dissolved form. The particulate form includes algae cells and organic detritus. Nitrogen concentrations in the reservoirs generally ranged from 200 to 250 μ g/L and were higher than phosphorus concentrations (6 to 12 μ g/L). Downstream canal sites (e.g., R14) routinely had higher nitrogen (> 300 μ g/L) and phosphorus, especially particulate phosphorus, than the reservoirs.

The nitrogen to phosphorus ratio provides an indication for the limiting nutrients, and may affect algae specie distributions. N:P ratios in Bartlett ans Saguaro reservoirs sometimes decreased to approximately 10, indicative of nitrogen limitation. In contrast, Lake Pleasant nearly always had N:P rations of more than 20 and was nearly always P-limited. Since the SRP canals receive water from all three reservoirs, weekly or even daily differences in nitrogen or phosphorus concentrations will occur. Algae are capable of storing nutrients internally when available.

Nitrogen Speciation in Surface Water

Dissolved nitrogen distributions for surface water samples collected on March 2002 was conducted (Figure 2.9). The monitored drinking water supply systems showed significantly different nitrogen specie distribution. The CAP canal had the highest nitrate concentration (0.3 mg/l N-NO₃) (Figure 2.9a), whereas the Salt River and Verde River systems (Figure 2.9 b and c) had lower nitrate concentrations. DON remained fairly constant throughout the sampling clusters between 0.10 and 0.15 mg/l N, except for the Salt River System, which had the highest DON of 0.23 mg/l N (Figure 2.9c). A bloom of green unicell alga Platymonas that was observed throughout Saguaro Lake (Sites R8 and R9a) during the sampling trip may have caused this high DON. The algae bloom was not observed a month earlier and DON was only 0.09 mg/l N. DON is also the major form of nitrogen in Bartlett Lake.

Dissolved nitrogen distributions in the CAP system are constant throughout the length of the canal (Figure 2.9a). The distribution shifts when CAP water is mixed and stored in Lake Pleasant, where DON is dominant and NO_3 levels are reduced. This is most likely due to the influence of algae, that uptake nitrate and excrete nitrogen-enriched metabolites (e.g., algal DOC).

On the sampling day, the head of the Arizona canal water was comprised predominantly of Verde River water, and a small percentage of Salt River water. However, CAP water was also flowing into the Arizona Canal and was presumably a source of nitrate. Well pumpage or return flows into the Arizona Canal increased nitrate levels by the sampling point at Deer Valley WTP (R16) (Figure 2.9d).

Effect of Nitrate in the Canals

Elevated nitrogen levels in the canals are caused by well pumping. Total dissolved nitrogen (TDN) concentrations in surface waters are generally low. Average TDN concentrations at the upper end of the Arizona Canal were 0.32 mg/L at R11, 0.2 mg/L at R12, and 0.24 mg/L at R13 (Figure 2.10). By the time the AZ Canal reaches the Squaw Peak Treatment Plant, average TDN was 0.32 mg/L. A few miles further down, at the Deer Valley Treatment Plant, TDN reached 0.43 mg/L, nearly twice the average concentration observed at R13 (Figure 2.11a).

Average total dissolved phosphorus (TDP) does not exhibit a similar change. Average TDP was 20.1 ug/L at the head of the AZ Canal (R13), 23.3 ug/L at Squaw Peak (R14), and 19.2 ug/L at Deer Valley (R16). A reasonable conclusion from these observations is that the increase in TDN is caused by well pumping, which blends high-nitrate well water with low-nitrate surface water. Wells would normally have low TDP levels, so addition of well water to the canal would not increase TDP, and in fact may decrease TDP levels by dilution.

Elevated MIB levels are associated with increased TDN levels between Squaw Peak and Deer Valley (Figure 2.11b), suggesting that TDN may be causing elevated MIB levels. The basis of this hypothesis is:

- Nutrient ratios in the water in the AZ Canal indicate N-limitation, which means that addition of N would tend to increase algae abundance.
- MIB culprit organisms identified to date in this stretch of canal are not capable of N fixation, which means they require "fixed" N for growth.

The relationship is not a perfect correlation for several reasons. First, temperature plays a role. MIB levels increase in response to temperature, with concentrations > 20 ng/L generally occurring only when the temperature is > 20° C. However, the difference in temperature between Squaw Peak and Deer Valley is small, never more than a few degrees Centigrade (Figure 2.11c). Thus, temperature alone most likely does not account for the observed difference in MIB levels between the two treatment plant inlets but temperature certainly affects MIB throughout the year. Second, algae growth and MIB production may be out of phase. It is quite plausible that well pumping stimulates the growth of periphytic MIB culprits by supplying nitrate, but the actual MIB production peak occurs after well pumping ceases. For example, elevated TDN levels at Deer Valley during May-July of 2000 (average 0.6 mg/L) may have been responsible for elevated MIB levels in August and September, even though TDN levels had declined by half. Third, flow rates decrease in this section, which increase fluid retention times that allow increased MIB levels to accumulate following periphytic production.

There is an interrelationship among temperature, nitrogen, and MIB production in the Arizona Canal. At this time there is little doubt that well pumping increases TDN levels in the Arizona Canal between Squaw Peak and Deer Valley. This increase is very likely a stimulus to MB

production over this stretch of canal. It follows that reducing well pumping would likely decrease MIB production. One possible management solution would be to accomplish while still using well water would be to pump well water during cooler parts of the year, when low temperatures would keep MIB production low.

MIB & GEOSMIN SPATIAL AND TEMPORAL TRENDS

MIB and Geosmin concentrations exhibited seasonal patterns (highest in summer and fall) and significant spatial variability (Figures 2.12 and 2.13). MIB and Geosmin data are shown as contour plots with respect to concentration (ng/L). Elevated concentrations occur in the epilimnion of the reservoirs, especially Bartlett and Saguaro Lakes, and canal sites downstream of Squaw Peak WTP. Geosmin concentrations generally followed similar spatial and temporal patterns as MIB. MIB concentrations are generally greater than Geosmin concentrations (Figure 2.14), therefore, most of the discussion in this report focuses on MIB. Most exceptions when Geosmin > MIB occurred in nearly stagnant water (very low Salt or Verde River flows, Waddell Canal).

MIB in Reservoirs

MIB concentrations in the reservoirs followed predictable seasonal trends (Figures 2.15 and 2.16). The highest reservoir MIB concentrations occurred in the epilimnion. Vertical profiles at 5 meter increments had the highest MIB concentrations between the surface and 5 meters deep, with a vertical concentration profile similar to the thermal pattern down to the bottom of the reservoir. MIB was present in the reservoir inflow (R8 and R5) from upstream reservoirs, but was generally low – or represented an insignificant loading since the upstream flowrate was generally very low (e.g. R8 in March 2001 had high MIB but less than 3 cfs of flow).

Within the reservoir, MIB concentrations first exceed 10 ng/L in the epilimnion by May of each year. Since the reservoirs have hypolimnion release, with Bartlett and Saguaro release very close to the reservoir bottom, low MIB concentrations are observed in the downstream flow (R7 and R10). Throughout the summer MIB concentrations increase in both the epilimnion and hypolimnion. Epilimnion MIB is hypothesized to be produced from planktonic algae, rather than benthic periphyton production. Decaying cells settling into the hypolimnion may lyse and release MIB, or MIB may diffuse into the hypolimnion across the thermocliine from the epilimnion. Between September and November, when the reservoirs thermally destratify, MIB is mixed throughout the water column and increased downstream MIB concentrations occur. Starting immediately after destratification and proceeding for the next two to four months, MIB biodegrades and volatilizes from the reservoir such that by January of each year MIB concentrations throughout the water column are below detection limits. Hydraulic flushing was not adequate to account for the observed rates of MIB concentration decreases (see Task 4).

In year 2000, Bartlett Lake had higher MIB concentrations than Saguaro Lake, while the opposite occurred in the year 2001. Lake Pleasant always had the lowest MIB concentrations. We hypothesize that reservoir volumes (Figure1.2) impact epilimnion temperatures that are a major factor in controlling growth of cyanobacteria capable of MIB production. Nutrient levels were similar in both years, although in 2001 the DN/DP ratio (40) was higher than in 2000 (average DN/DP = 20) and may have affected the distribution of algae species. There were fewer blue-green algae and more diatoms in the epilimnion of Bartlett Lake in 2001 compared to 2000. In addition, the specific conductance (total dissolved solids) (see section below) were

elevated during the years of higher MIB concentrations.

MIB in Canals

Seasonal changes in canal operations affects MIB concentrations in the CAP and SRP canals. Elevated MIB concentrations occur seasonally in the CAP canal in late summer and fall of each year (Figure 2.17). There is no statistically significant increase in MIB between R4 (between Waddell Canal and Union Hills WTP) and R11 (near SRP cross-connect). MIB concentrations in the CAP Canal below Lake Pleasant (R4) vary depending on whether the waer is coming directly from the colorado river or from the Hypoliminion of Lake Pleasant. Site R1 is located upstream of the Waddell Canal and represents water pumped from the Colorado River. MIB levles at sites R4 and R11 were nearly always less than 10 ug/L

The influence of CAP water released into the SRP canals is illustrated in Figure 2.18. Site R12 represents water from Granite Reef Reservoir whereas R13 is downstream of the confluence with the CAP canal (R11). MIB concentrations at R13 were shown to be a conservative mixture of the two waters. To minimize MIB concentrations in the canals it would be advantageous to use primarily the water source with the lowest MIB concentrations – this was CAP water throughout this 3-year study.

In the SRP canals, MIB concentrations tended to increase with distance downstream of Granite Reef Dam (Figure 2.19). MIB concentrations gradually increase between R13 and R14 (Squaw Peak WTP). Significant MIB production was routinely observed between R14 and R16 (Deer Valley WTP), due to shallow water, low flows, and pumpage of wells that contained nitrate (Figures 2.4 and 2.11). During the summer of 2001 "hot spots" of MIB production between R13 and R14 were observed and implementation measures to control periphytic algae were rapidly deployed (see Task 7). During June and July of 2001 T&O control measures (see Task 7) were also conducted between R14 and R16, resulting in significant reductions in MIB production along this stretch (reference Figure 2.19). Without control measures along this section MIB concentrations and trends would have been similar to the summer of 2000 rather than the observed sharp decline present during June and July of 2001.

WATER TEMPERATURES

Water temperatures in SRP canal system ranged between 10°C and 30°C, with maximum water temperatures occurring in September or October (Figure 2.20). Water temperatures increased by less than 3°C over approximately 20 miles of canal length. Therefore the dominant factor affecting water temperature is upstream lake water temperature and thermal destratification of the reservoirs that results in increased downstream water temperatures (reference Figure 2.6).

Within the epilimnions of the reservoirs a general trend was observed between temperature and MIB concentrations (Figure 2.21). Above 20°C MIB production appeared to become significant. A weaker trend was observed between temperature and MIB concentration in the canal system (Figure 2.22). Therefore, other factors (i.e., nutrient inputs) appear to be more significant for MIB production within the canals.

SPECIFIC CONDUCTANCE

The Salt River has higher specific conductance than the CAP or Verde River systems, respectively (Figure 2.23). Specific conductance concentrations in the SRP canals varied seasonally, but generally reflected the higher releases of Salt River water (April through November) or Verde River water (November through April). CAP water was more commonly blended into the SRP system during the spring, summer, and fall seasons. No significant increase in conductance was observed between R14 and R16. Comparing 2000 against 2001 for the three reservoirs, the higher MIB concentrations in the reservoirs always occurred in the higher TDS year.

SPATIAL AND TEMPORAL TRENDS IN ALGAE OCCURRENCE

Algae collected from August 1999 through March 2002 at the 18 permanent sampling sites were routinely identified to genus. One hundred and seventy-three (173) different algae (including 116 diatoms, 30 chlorophytes, 17 cyanophytes, 2 dinoflagellates, 5 chrysophytes, 2 euglenophytes and 1 cryptomonad) have been identified from lake and canal plankton samples (Tables 2.6 and 2.7). Three blue-green algae genera identified during the project have previously been described as being associated with the production of 2-methylisoborneal (MIB) and/or geosmin (Table 2.8). Fifteen (15) additional taxa observed in the plankton samples have also been previously linked to tastes and odors other than earthy/musty odors (Table 2.8).

The total algal counts initially (August-October 1999) illustrated differences between the sample site clusters, but differences became less pronounced as the project progressed (Table A.26; CAP Cluster (Figure 2.24), Verde River Cluster (Figure 2.25), Salt River Cluster (Figure 2.26), and the SRP Cluster (Figure 2.27)). The highest organismal counts during the project were observed in October 2001 at the inlet of Saguaro Lake (R8) with 5919 organisms/ml, in July 2000 in the hypolimnion of Saguaro Lake (R9B), 5201 with organisms/ml and in December 2000 at the Deer Valley WTP Inlet (R16) with 2938 organisms/ml. With the exception of the inlet to Saguaro Lake (R8) in October 2001, diatoms were always the most abundant organisms throughout the system with counts generally between 100-1000 diatoms/ml (Table A.27). Diatom diversity varied greatly among sites. The SRP cluster sites generally had several taxa with similar abundances, whereas the other cluster sites were usually dominated by a single genus that occurred in high numbers. For example, the July 2000 Saguaro Lake hypolimnion had >1400 Achnanthes minutissima/ml, whereas sites from other clusters often had 812 different genera with abundances lower than 50 organisms/ml.

Although total plankton counts were relatively constant across the seasons, the major algae groups did exhibit seasonal patterns. Diatoms were typically most abundant during the cooler months (October-March), whereas cyanophytes were typically most abundant from mid-Summer through late Fall (July-November). Figures 2.28 through 2.31 illustrate these patterns for diatom abundance for each of the four sample site clusters: CAP Cluster (Figure 2.28), Verde River Cluster (Figure 2.29), Salt River Cluster (Figure 2.30), and SRP Cluster (Figure 2.31). Figures 2.32 through 2.35 illustrate these patterns for cyanophyte abundance for each of the four sample site clusters (Figure 2.33), Salt River Cluster (Figure 2.34), and the SRP Cluster (Figure 2.35).

Representatives of the Chlorophyta (Table A.28) and other algal divisions (no figure shown) occurred in low numbers (<100 organisms/ml) during the project with only two exceptions. In July 2000, counts of 122 chlorophytes/ml were observed in the epilimnion of Saguaro Lake and comprised exclusively of *Platymonas* sp. In October 2001, another bloom of *Platymonas* sp.

yielded cell counts of 5818 chlorophytes/ml at the inlet of Saguaro Lake (R8).

The number of cyanophytes or cyanobacteria throughout the system was generally <100 organisms/ml (Figure 2.32 to 2.35). The highest cyanophyte counts observed during the project were 439 cyanophytes/ml in June 2000 in the Verde River above Bartlett Lake (R5), 353 cyanophytes/ml in November 2000 in the Arizona Canal above the CAP Cross-Connect (R12), 252 cyanophytes/ml in July 2000 and 245 cyanophytes/ml in November 2000 in the epilimnion of Saguaro Lake (R9A), and 194 cyanophytes/ml in November 2000 at the inlet of Saguaro Lake (R8). Of the cyanophytes observed, the genera *Anabaena* sp., *Oscillatoria* sp., *Phormidium* sp. and *Pseudanabaena* sp. are known MIB-producers. *Anabaena* sp. and *Oscillatoria* sp. are also known geosmin-producers (Table 2.8).

From August 1999 – March 2002, there were no obvious relationships observed between algae abundance and diversity, and MIB/geosmin production. These observations continue to illustrate the difficulty associated with identifying the source of taste and odor in large systems. MIB and geosmin production was very localized in areas of the canals or lakes. These "hotspots" were difficult to detect during routine baseline-monitoring. Thus, a positive correlation between algae abundance and diversity, and MIB/geosmin production was not observed during the project.

Although no obvious relationships were observed between algae abundance and diversity, and MIB/geosmin, some annual trends were observed in Saguaro Lake. Increases in cyanophyte counts appeared to precede increases in MIB concentrations by one to two months (Figure 2.36). More specifically, these trends were also observed when numbers of the cyanophyte known to produce MIB and geosmin (members of the cyanophyte Family Oscillatoriaceae) are compared to MIB concentrations (Figure 2.37). Similar trends were also observed when specific conductance in the water was related to MIB concentrations (Figure 2.38). An increase in specific conductance appeared to precede increases in MIB concentrations by one to two months. However, these observations continue to illustrate the difficulty associated with identifying contributing factors and the source of taste and odor in large systems.

In addition to actual counts of planktonic algae, chlorophyll a analyses were performed on each sample as an indicator or estimate of biomass accumulation. Plankton biomass (chlorophyll a concentration) remained relatively low throughout the system throughout the project (Table A.9). During the project, chlorophyll a concentrations only exceeded 10 μ g/L on 15 occasions. The three highest chlorophyll a concentrations were 66.9 μ g/L in October 2001 at the inlet of Saguaro Lake (R8), 21.0 μ g/L in September 2000 at the Verde River site above Bartlett Lake (R5), 15.6 μ g/L in July 2000 in the hypolimnion of Saguaro Lake (R9B) and 14.5 μ g/L in August 2000 in the epilimnion of Saguaro Lake (R9A). Chlorophyll a analysis appeared to be an overall reliable indicator of plankton biomass. For example, the highest chlorophyll a concentration (66.9 μ g/L in October 2001 at the inlet of Saguaro Lake) corresponded with the highest cell count (5919 organisms/ml).

The use of algae counts and algal biomass were not reliable methods for predicting MIB and geosmin episodes in the Metropolitan Phoenix area water supply system. Although some weak relationships were observed between algae abundance and diversity, and MIB/geosmin production, these associations do not provide sufficient benefit to justify the continuation of the time intensive process of identifying and counting algae throughout the system. Throughout the project, MIB and geosmin production has shown to be isolated in relatively small sections of the system, referred to as "hotspots". Location of these "hotspots" was not ascertained during

routine algae counts from monthly baseline-monitoring, rather "hotspot" locations were only identified as a result of intensive water sampling coupled with MIB/geosmin analyses using GC/MS. Thus, identification and treatment of "hotspots" by identifying and counting algae is not a reasonable expectation/outcome of a routine monitoring program. However, water treatment plant personnel may benefit from the ability to identify confirmed MIB and geosmin producers (as illustrated in the interactive taxonomic guide). The presence of confirmed producers in the supply water system at least suggests that a taste and odor episode is possible in the future if optimum environmental and chemical parameters for MIB and geosmin producers persist in the water storage and distribution system.

INTENSIVE MONITORING FOR MIB AND GEOSMIN

Saguaro Lake

MIB and Geosmin production were monitored at two baseline sites on Saguaro Lake, R-8 and R-9A/B, throughout the project period. Site R9-A was representative of the epilimnion (5 m-depth), and site R-9B was representative of the hypolimnion (20 m-depth). An additional of 11 special sampling sites were sampled on a semi-weekly basis during the 2001 peak MIB production period (Figure 2.39).

MIB was the predominant taste and odor compound produced in Saguaro Lake. MIB production was highest during late summer and early fall each year. The highest concentration observed was 114 ppt on September 13, 2001 at site SS-10 (Figure 2.40). Production of such high levels of MIB was episodic in nature. Concentrations of MIB doubled and returned to previous levels in only a four-week period (Figure 2.41). However, MIB concentrations of higher than 10 ppt were sustained for six to seven months each year.

Horizontal monitoring showed that the highest MIB production occurred in the open areas of the reservoir, such as at sites R9 and SS-10, rather than in coves or narrow canyon areas, as was originally expected (Figure 2.42). Vertical monitoring showed that during the late summer and early fall when MIB concentrations are highest, Saguaro Lake is stratified. Highest concentrations of MIB, as well as highest numbers of algae, usually occurred in the epilimnion, suggesting that most of the MIB is produced by phytoplankton in the upper 10 m of water (Figure 2.43). When MIB concentrations spike in the epilimnion, the downstream water supply system is not strongly affected, since the water released from Saguaro Lake comes from the hypolimnion. However, MIB production also occurs in the Salt River below Saguaro Lake. In March 2001, when R-9A MIB concentration was only about 4 ppt, R-10 in the Salt River at Blue Ridge had an MIB concentration over 51 ppt (Figure 2.44).

In late fall, when air temperatures cool and solar radiation is reduced, the lake "turns over" and becomes mixed. If MIB concentrations are still high in the epilimnion, following turn over, MIB is mixed throughout the water column and can be released into the downstream water system.

A total of 280 algae have been isolated from Saguaro Lake, with 27 isolates from R-8, 59 from R-9 and the remaining from the special sampling sites. Only one isolate (313), a *Pseudanabaena sp.*, was confirmed by GC/MS to produce MIB. Isolate 313 was collected in a periphyton sample on May 15, 2001 (Figure 2.45).

During the fall of 2001 and again in the spring of 2002, a flagellate green alga, Platymonas,

bloomed intensely throughout the reservoir making the water appear a bright green color. There was an extraordinarily high unit count of 6,750 cells/L at site SS-7 during the fall bloom. *Platymonas*, however does not appear to produce any taste and odor compounds.

Arizona Canal

After the MIB episodes were determined to occur seasonally within the Arizona Canal, it was necessary to localize the sections of the canal where MIB increased rapidly. Originally, samples were sparsely collected every 5 to 10 miles, which was not effective to locate the problematic canal sections. Samples were collected every 1 to 5 miles to better determine the location of "hot spots" before recommending in-canal treatments. Figure 2.46 shows the increase of MIB concentration at two identified "hot spots". The first "hot spot" between 24th Street and 29th Avenue was identified in 2000, whereas the hot spot between Beeline Highway and Mesa Drive was identified in 2001. Additional details on hotspots in the canals is presented in Section 3 along with copper treatment and mechanical brushing for algae removal.

SUMMARY

The initially selected set of baseline monitoring sites proved to be well selected, with only a few additional sites added to the monthly monitoring program in order to obtain a comprehensive evaluation of the raw water system for the City of Phoenix. The hydraulic operation of this system is complex and dynamic. During the period of study precipitation and watershed runoff was below average, and therefore represents a "drought" condition. Results differing from those encountered may occur during wetter years in the watershed.

MIB was the dominant T&O compound observed in the watershed and finished drinking water systems; Geosmin occurred at lower concentrations. MIB and Geosmin spatial and temporal trends followed predictable patterns with regards to water temperature and nutrient conditions. The highest T&O levels were found in the reservoir epilimnion and downstream points of the canal systems. The algae species responsible for T&O compound production (culprit algae) represented a very small percentage of the total algae counts or biomass.

Intensive monitoring indicated "hot spots" for MIB production. For example, plankton in the center of Saguaro Lake appeared to be the source of MIB, rather than benthic algae in shallower portions of the lake. In contrast, periphytic algae attached to the concrete-lined canal walls caused MIB production in the canals.

SECTION 2 TABLES AND FIGURES

Table 2.1 Physical characteristics of three reservoirs at maximum pool elevations and hydrologic data during study period.

	Bartlett Lake	Saguaro Lake	Lake Pleasant
Surface area (km ²)	11.2	5.1	40.3
Volume (m ³)	2.2x10 ⁸	0.85x10 ⁸	10.5x10 ⁸
Depth (m)	38	33	43
Surface Elevation (m)	532	466	519
Hydrology during study			
Average Annual Inflow (m ³)	2.8x10 ⁸	3.7x10 ⁸	7.2x10 ⁸
Average Annual Outflow (m ³)	2.6x10 ⁸	3.6x10 ⁸	7.0x10 ⁸
Average HRT (days)	139	80	438

Table 2.2. Baseline monitoring site description.

site #	Site description
	CAP Canal Cluster
R1	CAP canal above Waddell Canal
R2A	Lake Pleasant integrated sample
R2B	Lake Pleasant integrated sample
R3	Waddell Canal
R4	Cap Canal at 7th St.
R11	CAP Canal at Cross-connect
	Verde River Cluster
R5	Verde River btwn Horseshoe and Bartlett
R6A	Bartlett Lake near outlet
R6B	Bartlett Lake near outlet
R7	Verde River below Bartlett Lake
R20	Verde River at Tangle (USGS)
R25	Verde River at Beeline Highway
	Salt River Cluster
R8	Salt River inlet to Saguaro Lake
R9A	Saguaro Lake near inlet
R9B	Saguaro Lake near inlet
R10	Salt River below Saguaro (Blue Point Bridge)
	SRP Canal Cluster
R12	AZ Canal above CAP Cross-connect
R13	AZ Canal below CAP Cross-connect
R14	AZ Canal - Inlet to Squaw Peak WTP
R15	Squaw Peak WTP treated water
R16	AZ Canal - Inlet to Deer Valley WTP
R17	Deer Valley WTP treated water
R18	South Canal at Val Vista WTP
R19	Val Vista WTP treated water
R21	AZ Canal - Central Av.
R22	AZ Canal - 56th St.
R26	Cross-cut Canal - Washington St.
Table 2.3. Field measurement methods and equipment

Parameter	Method	Equipment
pH (pH unit)	Probe (SM 4500-H ⁺)	YSI Model 60 pH meter
Temperature (°C)	Probe (SM 2550 Temperature)	
Dissolved Oxygen (mg/L)	Membrane probe (SM 4500-O G)	YSI Model 50B DO meter
Secchi Disc Depth (m)	N/A	Ben Meadows Inc.

Table 2.4. Sample volumes, pretreatment/preservation and analytical methods (AG = amber glass bottle; NG = Nalgene plastic bottle; GF/F = filtration with ashed Whatman GF/F)

Parameter	Volume Collected	Pretreatment/ Prosorvation	Method	Equipment
MIB & Geosmin (ng/L)	40 to 250 ml	NONE	GC/MS	Varian Star
	in AG		00/100	3400CX
Total Organic Carbon (mg/L)	250 mL in AG	HCI A sidificanting	Medium-	Shimadzu
Disachuad argania aarban (mg/l.)			temperature	100 5050
Dissolved organic carbon (mg/L)		GF/F, NCI	ovidation	
		acidification	(SM 5310 B)	
UV Absorbance (m ⁻¹)			Ultraviolet	Shimadzu
			absorption at	UV160A
			254 nm	
			(SM 5910)	
Trihalomethane (μg/L)	500 mL in AG	GF/C; SDS chlorination	USEPA 551.2	HP5890 Series II GC
Haloacetic acid (µg/L)			USEPA 502.2	
Total Phosphorus (μg/L)	1L in NG	GF/C; HCI	Modified SM	TrAAcS 800
Dissolved Phosphorus (µg/L)			4500-P	Autoanalyzer,
Total Nitrogen (µg/L)		GF/C; HCI	SM 4500-N C	Bran-Luebbe
Dissolved Nitrogen (µg/L)				
Nitrate (μg/L)			SM 4500-NO3 ⁻ F	
Ammonium (µg/L)			SM 4500-NH ₃ G	
Specific conductance (uS/cm)	1 L in NG		SM 2510	
Chlorophyll-a (µg/L)		GF/C	SM 10200 H	Beckman
				Instruments
				Model DU-64
Planktonic algae taxa		<mark>???</mark>		

Location	Parameter	ТР	DP	TN	DN	TN/TP	DN/DP
		(ng/L)	(ng/L)	(ng/L)	(ng /L)		
Saguaro	Minimum	5.0	3.8	241	183	13	14
Lake	Average	17	11	335	267	26	31
Epilimnion	Maximum	73	26	715	426	54	59
(all Data)	Count	30	25	29	29	30	24
Saguaro	Minimum	5.6	5.4	257	183	14	14
Lake	Average	14	11	343	250	29	28
Epilimnion	Maximum	22	19	715	349	52	46
(stratified	Count	15	10	15	15	15	10
only)							
Bartlett Lake	Minimum	4.4	1.9	148	132	7.0	12
Epilimnion	Average	16	9.4	258	215	20	33
(all Data)	Maximum	35	21	378	350	43	110
	Count	30	28	30	30	30	28
Bartlett Lake	Minimum	4.4	1.9	148	138	12	12
Epilimnion	Average	12	8.5	256	218	24	41
(stratified	Maximum	28	18	355	347	43	110
only)	Count	15	13	15	15	15	13
Lake	Minimum	0.8	1.8	198	179	12	14
Pleasant	Average	8.0	6.3	298	264	64	57
Epilimnion	Maximum	24	15	376	404	335	153
(all Data)	Count	29	23	30	30	29	23
Lake	Minimum	0.8	1.8	198	190	17	20
Pleasant	Average	7.4	6.9	289	254	71	50
Epilimnion	Maximum	15	13	350	404	335	135
(stratified	Count	15	11	15	15	15	11
only)							
Deer Valley	Minimum	1.8	1.0	117	180	7.6	11
WTP	Average	23	11	351	311	24	51
Influent	Maximum	49	24	619	539	159	275
(R14)	Count	27	26	28	28	27	26

Table 2.5. Summary of nutrient levels in three reservoirs and downstream canal site

Achnanthes coffieformis	Denticula sp.	Hantzschia amphioxys	Nitzschia filiformis
Achnanthes linearis	Diatoma anceps	Mastogloia elliptica	Nitzschia fonticola
Achnanthes microcephala	Diatoma hiemale	Mastogloia smithii	Nitzschia frustulum
Achnanthes minutissima	Diatoma tenue	Melosira granulata	Nitzschia palea
Amphora ovalis	Diatoma vulgare	Melosira sp.	Nitzschia paradoxa
Amphora venata	Diploneis smithii	Melosira varians	Nitzschia parvula
Asterionella formosa	Entomoneis alata	Navicula accomoda	Nitzschia sigma
Bacillaria paradoxa	Entomoneis paludosa	Navicula cari	Nitzschia sigmoidea
Biddulphia laevis	Epithemia argus	Navicula cocconeiformis	Nitzschia sinuata
Cocconeis diminuta	Epithemia intermedia	Navicula cryptocephala	Nitzschia sp.
Cocconeis pediculus	Epithemia sorex	Navicula cuspidata	Nitzschia tryblionella
Coscinodiscus denarius	Epithemia turgida	Navicula decussis	Nitzschia vermicularis
Cyclotella bodanica	Eunotia sp.	Navicula exigua	Pinnularia brebissonii
Cyclotella meneghiniana	Fragilaria arcus	Navicula mutica	Pleurosigma delicatum
Cymatopleura solea	Fragilaria brevistriata	Navicula pupula	Rhizosolenia sp.
Cymatopleura sp.	Fragilaria chains	Navicula radiosa	Rhoicosphenia curvata
Cymbella affinis	Fragilaria construens	Navicula secreta	Rhopalodia gibba
Cymbella mexicana	Fragilaria crotenensis	Navicula sp	Rhopalodia gibberula
Cymbella minuta	Fragilaria leptostauron	Navicula tripunctata	Stephanodiscus sp.
Cymbella muelleri	Fragilaria sp	Nitzschia accendans	Surirella brightwellii
Cymbella norvegica	Gomphonema acuminatum	Nitzschia acicularis	Surirella ovalis
Cymbella prostrata	Gomphonema intricatum	Nitzschia acuta	Surirella pseudovalis
Cymbella pusilla	Gomphonema olivaceum	Nitzschia apiculata	Surirella striatula
Cymbella sp.	Gomphonema parvulum	Nitzschia bicrena	Synedra actinostroides
Cymbella tumida	Gomphonema sp.	Nitzschia bita	Synedra affinis
Cymbella turgida	Gomphonema subclavatum	Nitzschia capitellata	Synedra goulardii
Cymbella ventricosa	Gomphonema truncatum	Nitzschia communis	Synedra rumpens
Denticula elegans	Gyrosigma sp.	Nitzschia denticula	Synedra sp.
Denticula rainierensis	Gyrosigma spencerii	Nitzschia dissapata	Synedra ulna

Table 2.6. Comprehensive list of diatom taxa observed in phytoplankton.

Chlorophyta (30)	Chlorophyta (cont.)	Cyanophyta (17)	Other (10)
Ankistrodesmus sp.	Pandorina sp.	Anabaena sp.	Ceratium sp.
Chlamydomonas sp.	Pediastrum sp.	Aphanothece sp.	Cryptomonas sp.
Chlorella sp.	Platymonas sp.	Chroothece sp.	Dinobryon sp.
Chlorococcum sp	Pyramimonas sp.	Cylindrospermum sp.	Euglena sp.
Cladophora sp.	Rhizoclonium sp.	Gloeocapsa sp.	Mallomonas sp.
Closterium sp.	Scenedesmus sp.	Gomphosphaeria sp.	Ophiocytium sp.
Coleochaete sp.	Selenastrum sp.	Merismopedia sp.	Peridinium sp.
Cosmarium sp.	Spirogyra sp.	Microcystis sp.	Phacus sp.
Eudorina sp.	Staurastrum sp.	Oscillatoria agardhii	Synura sp.
Franceia sp.	Tetracystis sp.	Oscillatoria sp.	Vaucheria sp.
Golenkinia minutissima	Tetrahedron sp.	Oscillatoria splendida	
Golenkinia sp.	Ulothrix sp.	Oscillatoria tenuis	
Gonium sp.	Zygnema sp.	Phormidium sp.	
Microspora sp.		Pseudanabaena sp. #1	
Mougeoutia sp.		Pseudanabaena sp. #2	
Oedogonium sp.		Pseudanabaena sp. #3	
Oocystis sp.		Spirulina sp.	

Table 2.7. Comprehensive list of taxa (excluding diatoms) observed in phytoplankton.

Table 2.8. Known taste and odor causing organisms observed in phytoplankton.

MIB Producers	Associated with Other Tastes & Odors		
Anabaena	Anabaena	Mallomonas	
Oscillatoria	Asterionella	Pandorina	
Phormidium	Ceratium	Peridinium	
Pseudanabaena	Chara	Staurastrum	
	Chlamydomonas	Synedra	
Geosmin Producers	Diatoma	Synura	
Anabaena	Dinobryon	Tabellaria	
Oscillatoria	Gomphosphaeria		

Figure 2.1. Overview of watershed and locations of baseline monitoring sites ($\triangle R$ #) and location of COP water treatment plants (\bullet)



Figure 2.2. Cumulative volume of water input, release and in storage for the three reservoirs: Lake Pleasant (A), Bartlett Reservoir (B), and Saguaro Lake (C) from August 1999 to July 2001.



Figure 2.3. Frequency distribution of monthly hydraulic residence time for the three reservoirs during the 1999-2001 study.



Figure 2.4. Groundwater pumping into Arizona Canal by two SRP wells between Squaw Peak and Deer Valley (Well#12.5E13.1N has 12.6 mgNO3-N/L; Well#12E13.3N has 7.0 mgNO3-N/L)



Figure 2.5. Diagram of the periphyton sampler. Sampler consists of A, a rectangular chamber with an open window (10 x 15 cm) on the bottom plate; B, a plankton net; C, a plastic screen with metal frame (D); E, two telescoping poles; and F, a wire pool brush.









Figure 2.7. Verticle profiles in three reservoirs for temperature (upper) and dissolved oxygen (lower).



Figure 2.8. Secchi disc depth in three reservoirs.

Figure 2.9. Dissolved nitrogen speciation (Dissolved organic nitrogen DON, nitrate NO_3 , ammonia NH_4) for surface water and drinking water samples during the month of March 2002. Error bars represent one standard deviation (n = 3). TDN = DON + NO_3 + NH_4 .



Figure 2.9 (continued) Dissolved nitrogen speciation (Dissolved organic nitrogen DON, nitrate NO_3 , ammonia NH_4) for surface water and drinking water samples during the month of March 2002. Error bars represent one standard deviation (n = 3). TDN = DON + NO_3 + NH_4 .



Figure 2.10. Total Dissolved Nitrogen (TDN) at the upper end of the AZ Canal. TDN at R11 (CAP Canal at the Cross-Connect), R12 (Arizona Canal above the CAP inlet), and R13 (Arizona Canal below the Cross-Connect, reflection the blend of CAP and SRP waters).



->-R11 - CAP at X-Connect --R12 - AZ Canal above X-Connect --R13 - AZ Canal below X-Connect

Figure 2.11. Changes between Squaw Peak and Deer Valley: (A) Total Dissolved Nitrogen (TDN), (B) MIB, and (C) temperature.



Figure 2.12. Contour plot for MIB concentration as a function of sampling date and sampling site location.



Figure 2.13. Contour plot for MIB concentration as a function of sampling date and sampling site location.



Figure 2.14. Comparison of MIB and Geosmin concentrations throughout baseline monitoring program.







A-99 N-99 F-00 M-00 A-00 N-00 F-01 M-01 A-01 N-01 J-02 M-02





Figure 2.17. MIB in CAP canal.













Figure 2.20. Temperature trend in the Arizona canal (SRP system).

Figure 2.21. Relationship between water temperature (5-m below surface) and MIB concentration in the epilimnion of three reservoirs.



♦ R14 🗆 R16 Canal Water MIB (ng/L) • ф Canal Water Temperature (°C)

Figure 2.22. Relationship between water temperature and MIB concentration in the Arizona canal (SRP system).



Figure 2.23. Specific conductance (uS/cm) in three watersheds and two WTPs located along the Arizona canal. Todal dissolved solids (mg/l) = $0.64 \times \text{Specific conductance (uS/cm)}$.



Figure 2.24. Total plankton counts for the CAP Cluster.

Figure 2.25. Total plankton counts for the Verde River Cluster.





Figure 2.26. Total plankton counts for the Salt River Cluster.

Figure 2.27. Total plankton counts for the SRP Cluster.





Figure 2.28. Total diatom counts for the CAP Cluster.

Figure 2.29. Total diatom counts for the Verde River Cluster.





Figure 2.30. Total diatom counts for the Salt River Cluster.

Figure 2.31. Total diatom counts for the SRP Cluster.





Figure 2.32. Total cyanophyte counts for the CAP Cluster.

Figure 2.33. Total cyanophyte counts for the Verde River Cluster.





Figure 2.34. Total cyanophyte counts for the Salt River Cluster.

Figure 2.35. Total cyanophyte counts for the SRP Cluster.





Figure 2.36. Saguaro Lake MIB concentrations and cyanophyte counts.

Figure 2.37. Saguaro Lake MIB concentrations and Oscillatoriaceae counts.





Figure 2.38. Relationship between MIB and specific conductance (R14 - Squaw Peak WTP intake).

Figure 2.39. Saguaro Lake, location of sampling sites. Sites R-9A/B and R-8 are baseline sites. Sites SS-1 through SS-11 are intensive sampling sites monitored from May to November, 2001.



Figure 2.40. MIB production in Saguaro Lake during project period, August 1999 to May 2002. Peak MIB production occurred during late summer and early fall in the epilimnion, R-9A. The highest concentration of MIB was measured on September 13, 2001.


Figure 2.41. MIB concentration at sites R-9A and SS-10 from June 18 to November 15, 2001. MIB production was episodic. In only two weeks (August 30 to September 13), MIB concentrations doubled, then within the next two weeks, returned to previous concentrations.



Figure 2.42. Horizontal monitoring across Saguaro Lake showed that the highest concentrations of MIB occurred in the open areas of the reservoir. MIB concentrations were lowest at the top of the reservoir and in narrow canyon areas.



Figure 2.43. Vertical monitoring at site R9. Higher concentrations of MIB, as well as highest numbers of algae, usually occurred in R-9A, the epilimnion. This suggests that most of the MIB is produced by phytoplankton in the upper level of water, and then diffuses down into the lower depths of water.



Figure 2.44. MIB concentrations near Stewart Mtn Dam in the epilimnion of Saguaro Lake (R-9A) and downstream in the Salt River at Blue Point Bridge (R-10). MIB concentration spikes in R-9A do not impact MIB concentrations in the downstream water supply, since the water released from Saguaro Lake comes from the hypolimnion. However, MIB production occurs in the Salt River below Saguaro Lake.



Figure 2.45. Micrograph of young filaments of isolate 313, collected from Saguaro Lake site SS-4. A *Psuedanabaena sp.*, 313 was confirmed to produce MIB. B. Mature filaments. (Both images at 100x.).





Figure 2.46. Location of two "hot spots" at two different sections of the Arizona Canal.

SECTION 3: FIELD SCALE EXPERIMENTS TO EVALUATE T&O CONTROL MEASURES (TASK 2)

These tasks involved collaborative research to assess the effectiveness of T&O Control measures at the field scale level. Data from full-scale implementation (Task 7) is shown here to present a comprehensive evaluation of the two major efforts. The major activities included:

- Canal brushing in the Arizona Canal
- Copper treatment in the Arizona Canal

MECHANICAL CANAL BRUSHING

The objective of canal brushing is to prevent or reduce culprit organisms from proliferating on canal walls and thus reduce MIB and Geosmin production in the canal system.

Background

The Arizona Canal from the CAP cross-connect to 76th Avenue spans a distance of ca. 38 miles. There are four water treatment plants (WTPs) along the canal that provide drinking water for over one million people. During our baseline and intensive monitoring, we have observed that the Arizona Canal experienced major episodes of MIB and Geosmin production especially in the late summer-early fall (July through November). The gradients of MIB and Geosmin concentration along the canal suggest net production of these odorous compounds in the Canal system rather than being carried over from the source water. The production of these odorous compounds was attributed to vigorous growth of periphyton along the submerged canal walls. Indeed, several MIB and Geosmin producers were isolated from the Arizona Canal and all were identified as periphytic filamentous cyanobacteria primarily attached to the canal walls.

Removing canal wall-associated periphyton physically using a mechanical approach, such as brushing was first quantitatively assessed in the summer of 1999. The preliminary results were very encouraging. Over 80% of periphyton was removed by brushing. The first large-scale implementation of canal brushing was conducted in the summer of 2000. In the summer of 2001, brushing has been implemented in conjunction with copper treatment in the Arizona Canal to enhance the effectiveness of canal treatment. Detailed information presented here about the canal implementation was obtained in the summer and fall of 2000 and 2001.

Methodology

A section spanning ca. 3 km between Central Avenue and 19th Avenue of the Arizona Canal were subjected to brushing treatment. A tractor mounted custom-designed metal brush from the Salt River Project (SRP) was employed. The brush measured 150 cm long and 80 cm in diameter. The rotation of the brush was about 60 rpm and speed of brushing operation was about 1-2 miles/day. Figure 3.1A shows a SRP designed tractor-mounted brushing system and a close-up photograph of the metal brush in operation (Figure 3.1B). Both sides of the canal walls were brushed during the implementation.

Within the 3-km canal stretch, six sampling sites were established for monitoring changes in periphyton biomass and MIB and Geosmin concentrations before and after brushing. For

comparison, four sampling sites along a 4km section downstream just below the brushed section were also monitored for the same parameters. Brushing was conducted once every two weeks from September 21 through November 20, 2000 (Figure 3.2). Algal and water samples were taken at each of the sites one, four, seven and fourteen days following brushing. In order to assess the periphyton biomass, the periphyton sampler previously described (Figure 2.5). was used.

Results

Removal of periphyton from the submerged canal walls by brushing

Planktonic microalgal biomass in the Arizona Canal was typically below 100 ug chlorophyll *a* m⁻² during the summer months. In contrast, over 2,000 ug chlorophyll *a* m⁻² was associated with the periphytic algal community. Periphyton were distributed all over the submerged canal walls from top to the bottom of the canal with the highest density appearing between 5 to 30 cm below the water level. It was also observed that more periphyton appeared in the downstream- than upstream regions of the canal. Figure 3.3A and B are photographs of the canal wall taken before and after brushing, illustrating that the majority of periphytic cyanobacteria and microalgal biomass were removed from the canal wall by brushing. The brushing removed over 80% of periphyton from the submerged walls, based on chlorophyll *a* analysis (Figure 3.3).

Reducing production of MIB and Geosmin by brushing

Figure 3.4 shows the concentration of MIB and Geosmin, respectively, along the 3-km stretch shortly before the brushing treatment. Before brushing, an increase of over 140% in Geosmin was detected between sites 2 and 7. After brushing the doubling of the MIB concentration between sites 2 and 7 was no longer observed (Figure 3.4.A). The net increase in Geosmin concentration downstream was eliminated after brushing (Figure 3.4B). Three additional consecutive brushing treatments carried out in early-October through mid-November gave results consistent with these illustrated in Figure 3.4B. Brushing was effective in removing algal biomass and reducing the production of MIB and Geosmin in the treated section of the Arizona Canal.

Effectiveness of canal wall-brushing over time

How long does the effect of canal brushing persist? To answer this question, both periphyton biomass and concentrations of MIB and Geosmin were monitored over time following brushing. Figure 3.5 shows the changes in periphyton biomass as chlorophyll *a* concentration along the brushed section as a function of time. Periphyton biomass in the brushed section increased gradually over time and reached the level of the unbrushed section within two weeks. Along with the increase in periphyton biomass, periphyton composition underwent a noticeable change. Pigment analysis indicated an increase in chlorophyll *c* concentration and chlorophyll *c* to *a* ratio following brushing. Light microscopic observation also revealed that periphytic diatom populations increased after brushing. Conversely, a decrease in the amount of MIB- and Geosmin-producing cyanobacteria was evident. MIB and Geosmin concentrations remained low and constant in the brushed section over the two weeks (data are not shown). During the two months of brushing, the production of MIB and Geosmin remained low in the brushed section.

Brushing of the short canal stretch reduced MIB and Geosmin concentrations in the lower reach of the Arizona Canal

In order to evaluate the impact of upstream brushing on downstream concentrations of MIB and Geosmin and to demonstrate that the upstream site was a point source of production, a 4-km unbrushed canal section just below the brushed section was monitored for the changes in MIB

and Geosmin concentrations. As shown in Figure 3.7, upstream brushing reduced the overall concentration of MIB at the downstream sites. A similar trend was also observed for Geosmin production (data are not shown). During the brushing period from mid-August through November 2000, MIB and Geosmin concentrations at the Deer Valley WTP site were significantly lower than that prior to the brushing in early August (Figure 3.6).

Discussion

Various conventional and innovative control measures have been evaluated and adopted by water utilities to reduce the off-flavors. However, in-plant techniques and technologies are generally applied on either a small scale or are very expensive. Control of surface source waters has generally been considered to be a long-term management strategy. Where practical, source control might be a more efficient and cost-effective means of reducing taste and odor problems.

We demonstrated that canal wall brushing can be an effective source control measure for taste and odor-producing cyanobacteria. With brushing, over 80% of the periphyton biomass was removed from the submerged canal walls of the Arizona Canal, with a concomitant reduction in MIB and Geosmin production.

Brushing not only effectively removed nuisance periphyton from the canal walls, but also appeared to selectively reduce the rate of colonization of MIB- and Geosmin-producers of this habitat. Although the periphyton biomass recovered after two weeks following brushing, MIB and Geosmin concentrations remained low. Brushing appears to have changed species composition of the community. In the Arizona Canal, MIB- or Geosmin-producing periphytic cyanobacteria were not the dominant species, but rather appeared as discontinuous patches along the canal walls intermixed with other taxa. Such a phenomenon was also observed in other water bodies with taste and odor incidents. Our laboratory studies have revealed that several MIB- and Geosmin-producing cyanobacteria isolated from the Arizona Canal showed specific growth rates significantly lower than other non-odor producing strains from the same habitats. This might be a reason for the difficulty encountered in isolating MIB- and/or Geosmin-producing cyanobacterium from field samples.

While net production of MIB and Geosmin was eliminated in the canal sections brushed, there was some concern that brushing might exert a negative impact in the lower reach of the canal. MIB- and Geosmin producers detached from the canal walls by brushing could be carried downstream and eventually end up in water treatment plants. Or, it might be possible for detached periphyton mats to sink to the bottoms of the canal, releasing MIB and/or Geosmin by cell lysis and decomposition. These scenarios did not occur. Neither the algal biomass in the water nor the concentrations of MIB and Geosmin notably increased at the downstream Deer Valley water treatment plant, some 4 km downstream of the brushed section. Instead, both MIB and Geosmin concentrations declined significantly at the water treatment plant during the threemonth brushing implementation from mid-August through mid-November 2000 compared to prior to brushing. The biomass removed from the canal walls by brushing was perhaps too diluted in the flowing water to cause a measurable contribution to the overall concentrations of MIB and Geosmin in the downstream section. It should be noted that our baseline monitoring data collected in 1998 and 1999 indicated that peak production of MIB and Geosmin in the Arizona Canal occurred in September and October. Clearly, the significant decline in MIB and Geosmin concentration during the late summer and fall months in year 2000 may be attributed to the brushing treatment.

Cost for brushing operation was estimated, under our treatment conditions, to be ca. \$1,000 per mile of canal section. This cost may be substantially reduced if brushing could be applied on a regular basis in the canal network serving metropolitan Phoenix. Therefore, brushing appears not only to be an efficient, but also a cost-effective technique for source water taste and odor control. It can be particularly applicable to the southwest region of the United States, such as California, Nevada, Utah, New Mexico and Arizona, where surface water supplies are stored in lakes and reservoirs and transported in open but lined canal/aqueducts.

COPPER TREATMENT

Background

Copper-based algicides are the most popular chemical approach to control the growth of algae in aquatic environments. The mechanism of toxicity of copper on algae is that copper ions, particularly in a form of Cu²⁺, may inhibit or disrupt photosynthetic and respiratory reactions, resulting in death of cyanobacteria and microalgae. Effectiveness of copper on algae depends largely on water chemistry (pH, hardness, conductivity, etc), temperature and light intensity, as well as algal composition. Little information was available about effectiveness of copper on algae in the Phoenix canal system in which pH and hardness of the water are usually high.

Methodology

Cutrine-Plus copper solution was injected into the canal at a radial gate to ensure sufficient mixing of copper with water. The maximum copper concentration was controlled to provide a concentration of 0.5 mg Cu L⁻¹.

Water and periphyton samples were taken at various sites before and following copper or brushing treatment. MIB, Geosmin and chlorophyll concentrations were also measured, and algal counts and species classification were also conducted.

Results

Copper concentration in the water system following copper addition

The first copper application was conducted at 7th Street on 9 July, 2001. Cutrine-Plus solution was continuously injected for six hours into the canal near the radical gate. Copper concentration in the water downstream was monitored during copper injection. Four sampling sites each 0.6-mile apart were selected and water samples were taken every 10 to 30 min. Results show that copper was being carried over a 2.4-mile distance without significant loss in total copper. In addition, a copper concentration of ca. 0.3 mg Cu/L was detected some 5 miles downstream at 29th Avenue (Figure 3.7). A concentration of 0.3 mg Cu/L was also detected some 10.5 miles downstream at 51st Avenue during and shortly after copper addition at 7th Street.

Reduction of periphyton biomass and MIB production by copper treatment

Reduction of MIB concentration was detected within first 24 hours following copper application, indicating inhibition of the MIB-producing organisms by a copper concentration of 0.3-0.5 mg

Cu/L (Figure 3.8). On 10 July, 2001, copper was added at the same site for 8 hours. Over a one-month period following the copper addition, MIB concentration decreased gradually at each sampling site. Since a decrease in MIB concentration was also observed between 29th- and 67th Avenues following the copper addition, Glendale and Peoria WTPs located further downstream of the Arizona Canal also benefited from reduced MIB concentrations from the copper application.

Reduction of MIB concentration by copper application resulted from its effect on the periphyton community in the canal. Periphyton grow vigorously at submerged canal walls in early summer, forming thick algal mats (Figure 3.9A). These algal mats periodically detach from the canal walls and are carried downstream (Figure 3.9B) to accumulate at radial gates (Figure 3.9C). While there are a number of factors, such as flow rate, structure and composition of soil and the microbial community, temperature and light conditions, that influence this phenomenon, oxygen bubbles generated by periphyton photosynthesis may be a major factor in the detachment of the algal mats from the canal walls. The detached floating algal mats continue producing taste and odor compounds, representing a secondary source of water problems. Algal mats, however, can be reduced or eliminated by copper treatment. The periphyton algal mats essentially disappeared from the canal walls two to three days after copper application. No major spikes in MIB/Geosmin concentrations were detected during and after copper treatment, suggesting that the MIB/Geosmin producers were likely present in relatively small populations or in limited biomass, but vigorously produced and released odorous compounds. The contributions of MIB/Geosmin to the canal water from lysis of MIB/Geosmin-producing organisms appear to be relatively minor, and a short-term phenomenon in the canal water system.

As expected, algal numbers were affected by copper treatment. Figure 3.10 shows that the number of cyanobacteria, green algae and diatoms were gradually reduced following copper application. Green algae were found to be most sensitive to copper with limited recovery of the biomass for up to one month after copper application. Cyanobacteria and diatoms were initially inhibited but began recovering about three weeks after copper application.

In concert with reduced periphyton mats and algal numbers, gradual decreases in chlorophyll concentration (or periphyton biomass) were also observed following the copper treatment (Figure 3.11). Since MIB concentration remained low even after one month following copper treatment (Figure 3.12), the MIB-producing species appeared to have a slower process of recovery from copper application than other non-MIB-producing species.

COMBINATION OF COPPER AND BRUSHING

Background

In 2001, over 50 ng MIB/L was first detected downstream at 29th Avenue in mid-June. A comparable level of MIB did not occur until mid August in 2000 (3.13). The earlier occurrence of high MIB concentrations downstream might relate to the changes in hydraulics and periphyton algal communities in the canal during 2001 compared to the past two years. Since June 2001, the Deer Valley WTP downstream of the Arizona Canal was out of operation. Accordingly, the amount of water delivered from the Granite-Reef Dam and also from the CAP canal into the Arizona Canal was reduced. As a result, the water depth and flow rate, especially at the downstream sites was also reduced (Figure 3.14). Such changes in the hydraulic character of the Arizona Canal resulted in the formation of dense periphyton mats along the submerged canal walls and on the bottom of the canal.

Furthermore, a new "hot spot" was identified in 2001. It was located between Highway 87 and Mesa Drive, a 3.5-mile canal stretch. Over 30 ng L⁻¹ increase in MIB concentration was observed over this stretch in September (Figure 3.15). This was unexpected since the flow rate was relatively high and there was little silt on the canal walls in this region. The algal composition, however, was different in this region from that observed at the downstream sites of the canal. In fact, a filamentous green alga, *Cladophora* sp. was the dominant periphyton at the upstream location. Canal brushing had little effect on removal of the algal biomass. These larger filamentous algae harbored microscopic MIB/Geosmin producers.

A combination of copper application and canal brushing was used between August and mid-November 2001 to determine whether the two techniques were more effective when used in concert.

Methodology

In addition to Cutrine-Plus, another manufactured copper product, Earthtec, was applied in the summer of 2001. The latter was applied due to increased consumption of chlorine by the former product in WTPs during and shortly after copper addition. The maximum copper concentration for Earthtec application was subsequently reduced to 0.3 mg Cu L⁻¹.

Results

Copper addition and canal brushing were implemented periodically in August through November 2001 to reduce periphyton algal growth and MIB concentrations in the Arizona Canal. Six copper applications and five canal brushing events have been applied to the Canal at various locations over this period. Although it was difficult to quantitatively assess, separately, the role of each method in reducing MIB production, it appeared that the two methods worked well in concert to reduce increases in MIB production in this upstream section (Figure 3.16). Likewise, by combining copper addition with canal brushing, net production of MIB was largely reduced and even eliminated in the lower Arizona Canal prior to the October shutdown of Deer Valley WTP and cessation of canal treatments (Figure 3.17).

Unlike canal brushing, which mainly affects the canal stretch brushed, copper addition may affect algal growth and MIB production in a canal stretch of up to 10 miles. Therefore, copper application may serve as a "systemic" implementation measure, whereas canal brushing as a "localized" control method.

SUMMARY

Due to access limitations to reservoirs and non-site specific T&O spatial occurrence in the reservoirs, field-scale experiments were focused on MIB and Geosmin production in the canals. Experiments focused on (1) mechanical canal brushing of canal walls, and (2) chemical liquid copper application to the canals. Mechanical brushing removed over 80% of the periphyton biomass from the canal walls and essentially led to zero net MIB production along the length of the treated canal section. Copper addition lead to a gradual decrease in biomass, but a more rapid decrease of in-canal MIB production. In the weeks after both mechanical brushing and copper treatment biomass regrowth occurred, followed by MIB production. The treatments

appear effective for two to three weeks. A combination of first mechanical brushing followed one week later by copper treatment would be a recommended course of action for MIB control in reaches of canals identified to produce T&O compounds.

SECTION 3 TABLES AND FIGURES

Figure 3.1. SRP designed tractor-mounted brushing system (A) and a close-up photograph of the metal brush in operation (B).



Figure 3.2. Schematic of the Arizona Canal illustrating location of water treatment plants (WTP), the canal stretches brushed and unbrushed, and sampling sites along the canal. Black circles: water treatment plants; Hatched bar: brushed section (ca. 3 km, between central Avenue and 19th Avenue); Open bars: unbrushed sections; Open arrows: sampling sites (S1 to S10 on the Arizona Canal).



Figure 3.3. Photographs of the canal wall taken before (A) and after brushing (B), illustrating that the majority of periphytic cyanobacteria and microalgal biomass were removed from the canal wall by brushing (C).







Figure 3.5. Increase in periphyton biomass, as indicated by chlorophyll *a* concentration, on the canal walls over time following brushing treatment (in August 2000).



Figure 3.6 Effect of upstream brushing treatment on downstream MIB concentration in the Arizona Canal in August 2000. Solid bar, MIB concentration before brushing treatment; Open bar, MIB concentration after brushing treatment. S8, sampling site at 19th Avenue (end of the brushing treatment section); S9, sampling site at 25th Avenue, 2 km downstream from 19th Avenue; S10, sampling site near the Deer Valley WTP, 4 km downstream from 19th Avenue.



Figure 3.7. Copper concentration as a function of distance and time following copper dosing in the Arizona Canal. Arrows indicate the time when the copper plume reached each sampling point.





Figure 3.8. Effect of copper on MIB production in the lower Arizona Canal. Copper was applied at 7th street continuously for 6 hours.

Distance (miles)

Figure 3.9. Periphyton mats grown along the submerged Arizona canal walls (A); detached floating algal mats (B); and accumulation of algal mats at a radial gate (C).





Figure 3.10. Changes in population density of three major algal groups (cyanobacteria, diatom and green algae) before and after copper treatment. Algal samples were collected at 19th Avenue, Central Avenue and 29th Avenue.

Figure 3.11. Changes in chlorophyll *a* concentration at various sampling sites along the lower Arizona Canal before and after copper treatment.





Figure 3.12. Decrease in MIB concentration over one month in a canal section following copper application.

Distance (miles)



Figure 3.13. Early occurrence of elevated MIB in the Arizona Canal (D.V. WTP), 2000 vs 2001.

Figure 3.14. Flow rate in the Arizona Canal was 17 % less this summer than last summer. A) Flowrate measured near the head of the Arizona Canal, B) Flow rates measured right below the Arizona Falls.



Months of the year

Figure 3.15. A new "hotspot" of MIB production was identified upstream between Highway 87 and Mesa Drive, a 3.5-mile canal stretch in the Arizona Canal.



Figure 3.16. Net production of MIB in the Arizona Canal at the upstream "hot spot" between Beeline Highway and Mesa Drive.



Months of the year

Figure 3.17. Net production of MIB in downstream Arizona Canal between Squaw Peak and Deer Valley WTPs throughout the season.



SECTION 4: ASSESSMENT OF IN-PLANT CONTROLS (TASK 3)

The purpose of this task was to (1) summarize current T&O control activities at each COP WTP, (2) quantify T&O removal at several WTPs, (3) evaluate alternative T&O control measures, and (4) provide recommendations for continued T&O control in the future.

T&O CONTROL STRATEGIES PRIOR TO PROJECT INITIATION

A series of plant tours and interviews of lead operators was conducted during October 1999 by Paul Westerhoff and Darlene Bruce from ASU. The purposes of the interviews were as follows:

- Identify current algae conditions in plant and discuss problems associated with alga growth.
- Summarize current practices and potential in-plant strategies for controlling alga and taste and odors
- Discuss the potential for conducting full-scale experiments targeted at in-plant alga control and/or removal of MIB/Geosmin

The interviews included twenty-three specific questions. During the interviews/tours at Deer Valley and Squaw Peak samples were collected and later analyzed for comparison against alga growing in the canals and reservoirs. Table 4.1 provides a summary for the odors and characterization of collected alga from the two plants. Data on alga in the canal and reservoirs were presented in earlier sections. In some cases higher diatom levels and different alga, some of which are suspected MIB/Geosmin producers, were found within the plants. Responses to the interviews / plant tours are summarized in Tables 4.2 through 4.6. The lead operators were very candid during the tours that facilitated useful insight, and potential strategies to address inplant alga control. Statements by the operators were not checked for their approval, and ASU takes responsibility for any comments that may have been misinterpreted. The general impression was that this project would improve taste and odor and alga related operational issues, since previous COP studies had not been conducted on these issues.

Each plant visited had varying degrees of alga growth in the plant. Each facility had a unique approach for controlling in-plant alga growth. The consequences of alga growth was also variable at each plant, with some noticing significantly shorter filter run times that were attributable to alga growth. Below is a general description of the alga in each plant, relative to alga growth in the other COP plants:

- Union Hills had the lowest level of visible alga growth, although it was noted that the water in the plant was "beginning" to turn a greenish color. The most significant location of alga growth was the 140-MG on-site impoundment. Accumulation of nutrient-rich sediments and poor circulation may in the long term increase algae growth.
- Val Vista was feeding PAC and copper during the visit and had limited alga growth. In addition to the algaecide action of the copper, PAC may have been providing "shading" that prevented light penetration needed for alga growth in the basins.
- Squaw Peak had considerable visible alga growth in the presedimentation and

sedimentation basins, especially on the weirs. Submerged mats were also visible in the sedimentation basins. The large presedimentation basin was considered a "nursery" for alga. The plant practices prechlorination on weekends as its main approach for alga control.

• Deer Valley had the most severe visible alga growth problem, with large floating and submerged mats of alga present in the presedimentation and sedimentation basins. With low level continuous chlorine addition and shock prechlorination on weekends, inplant alga were still noted as a cause for reduced filter run times.

T&O PRODUCTION WITHIN THE TREATMENT PLANTS

There was no evidence of T&O production within the WTPs. T&O concentrations were lower in WTP effluents compared to influent concentrations (Figures 4.1 through 4.3). Intensive sampling conducted at multiple locations in parallel treatment trains and across all processes also confirmed no net production of MIB or Geosmin within the COP WTPs. Likewise return flows to the head of the WTP did not contain MIB or Geosmin above influent levels.

Periodic prechlorination in presedimentation basins (approximately one time per week when water temperatures exceed 22°C) aids in controlling in-plant algae growth. Algae growth within the plant could allow T&O-producing algae to colonize. For example, the City of Tempe does not prechlorinate and has experienced in-plant T&O production. Prechlorination can produce DBPs. A study of DBP formation just prior to and during prechlorination period at Deer Valley was conducted (Figure 4.4). Prechlorination (4 to 5 ppm chlorine added to presedimentation basins) was being conducted approximately every other weekend. The chlorine residual in the filter influent and effluent was < 1 ppm; finished water had a chlorine residual of 1.04±0.09 ppm. Raw water TTHM concentration was $< 5 \mu g/L$. Chlorine was applied just prior to filtration throughout the study. Prior to prechlorination (Period#1: 6/19-6/23) approximately 25-30 µg/L was present in the filter effluent and into the reservoir inlet; between 55 and 60 µg/L of TTHM formed after retention in the reservoir (pump bay). During prechlorination (Period#2: 6/24-6/25) TTHM concentrations were roughly equivalent at all three sample locations and averaged 80 µg/L. TTHMs were formed prior the presedimentation, flocculation, and sedimentation basins in the presence of elevated chlorine residuals. After prechlorination (Period#3: 6/26-6/28) TTHM concentrations returned to levels similar to Period#1 prior to prechlorination. The conclusion of this study is that prechlorination increased TTHM formation leaving the plant to levels above the Stage I MCL of 80 mg/L for TTHMs.

Alternative methods for in-plant algae growth could be (1) copper addition or (2) application of biocide coatings to concrete and metal surfaces. Based upon experience at Val Vista and with canal treatments, copper sulfate products (e.g., Earthtec) addition at the head of WTPs should be able to control periphytic algae growth. Continuous copper addition is not recommended, rather pulse addition on a weekly basis (similar to prechlorination) would be effective. A copper dose of 0.5 mg/L is below USEPA regulatory levels and sufficient to kill most algae. One copper product manufacturer (Earthtec) suggested that the product also removed MIB and Geosmin. In laboratory tests in distilled and natural waters this was not observed. In the field, this could be an indirect observation if prior to copper addition algae were present that produced MIB; adding copper would kill those organisms, thereby preventing release of T&O compounds into the water.

Coating concrete and steel surfaces in WTPs with a biocide could significantly limit periphytic algae growth. Preliminary experiments conducted with polymeric coatings and titanium oxide paint coatings both showed some effectiveness at reducing periphytic algae biomass on clay tile surfaces (see Task 4). Neither type of coatings currently have NSF approval, and therefore could not be tested in WTPs. Callow and Fletcher (1994) reviewed how polymers reduced bioadhesion through reductions in surface tensions and coatings, including silicone elastomers and fluoropolymers. Surface tensions between 20 and 30 dynes/cm minimized long-term adhesion, although immersion in natural waters resulted in the formation of "conditioning films" which lead to algae or bacteria attachment after prolonged exposure. Destais et al. (2000) and Sauvet et al. (2000) indicated that guaternary ammonium salts that were covalently-bound to epoxy resins showed good bactericidal activity against *E. coli* even after 6 months of immersion in water. Scott et al. (1996) used SEM and cytochemical staining techniques to investigate the progression of algae colonization on surfaces, and found that blue-green algae were rapid colonizers of both toxic and non-toxic surfaces and that colonization was first characterized by the production of extracellular polysaccharides (EPS). Layers of EPS and inactivated algae covered the surface until other organisms could colonize on top of these layers and away from the toxic coatings. The City should continue investigation of biocide coatings, which should gain NSF approval in the near future.

A combination of practices (chlorine, copper, biocide coatings) that control algae growth in WTPs would have multiple benefits. First, reduced algae cell counts would lengthen filter run times. Second, reduced algae biomass would decrease the likelihood that algal MIB/Geosmin producers colonize the WTP.

MIB AND GEOSMIN REMOVAL AT WTPS

Conventional treatment (flocculation, sedimentation, filtration, chlorination) with alum and polymer coagulants does not remove MIB or Geosmin. Plots of MIB and Geosmin removal at three WTPs over the course of the study are presented in Figure 4.1 through Figure 4.3. In general MB or Geosmin were only removed during periods of PAC application. WTP plant shut-downs for canal maintenance occurred roughly from November through February of each year; Deer Valley WTP was shut-down late summer-fall 2001 for construction. During WTP shut-down only influent samples were available. In 1999 and 2000, Val Vista WTP was just about the only COP WTP adding PAC (summer-fall season). In 2001 (summer-fall), all three WTPs added PAC. For the most part, after late summer 2001 the PAC brand was switched from Norit HDB to Norit 20B. With longer HRT in the presedimentation basins and good PAC addition, MIB concentrations in effluent water could be lowered to 10 to 15 ng/L.

PAC experiments were conducted in the presence and absence of alum coagulant. At high alum doses, MIB and Geosmin removal efficiency decreases as PAC becomes enmeshed with alum floc. At the relatively low alum doses used by the COP WTPs, no difference was observed in MIB or Geosmin removal in the presence of alum (5 ppm).

Simultaneous prechlorination and PAC addition is not advised. PAC will rapidly react with chlorine, resulting in oxidized surface functional groups on the PAC. This will lead to elevated chlorine demand. Furthermore, oxidized PAC is significantly less effective than virgin PAC in adsorption of MIB and Geosmin.

GAC FILTER CAPS FOR MIB AND GEOSMIN REMOVAL

GAC filter caps for MIB control may be an additional implementation option for the City of Phoenix's WTPs. Granular activated carbon (GAC) replaces anthracite coal as the upper layer in dual media filters; the bottom sand layer is unchanged. The GAC layer provides removal of dissolved organic material (e.g., MIB) and serves to remove particulate material (e.g., turbidity). Changing to GAC capped filters, rather than anthracite filters, may result in increased headloss and shorter filter runs due to the roughness of the media in comparison to anthracite. A GAC depth of 24" to 50" is common.

GAC filter caps provide short-term absorption for DOC (DBP precursors) and MIB/Geosmin, and sustainable MIB removal via biodegradation if chlorination is performed after filtration. Chlorination reduces the biological activity in GAC capped filters. Malcolm Pirnie Inc (MPI) performed a Taste and Odor Control Study (T&OCS) (September 1995) for the City of Chandler to investigate GAC caps at that conventional WTP facility. The report was analyzed to determine if the conclusions could benefit the City of Phoenix, and what additional work may be required.

ASU concluded, after analyzing the T&OCS, that the methodology used and results obtained by MPI were appropriate for comparison to the City of Phoenix WTP operation. The plant was considered a conventional WTP (coagulation, flocculation, sedimentation, filtration, chlorine disinfection), and applied PAC prior to coagulation for T&O control. The MPI study was planned to evaluate the effect of a higher filtration rate on the removal of T&O compounds. MPI performed several rapid-small-scale-column-tests (RSSCTs) under a wide range of hydraulic and operational (GAC origin) conditions. Figures 4.5 and 4.6 show that GAC removed 100 percent of MIB and Geosmin for < 10,000 bed volumes (BVs). A sharp breakthrough of MIB and Geosmin occurred. GAC preloaded with DOC from natural water had an earlier breakthrough, due to sorption competition between DOC and T&O compounds. The RSSCT column effluent concentration of MIB and Geosmin remained at a steady removal of 40% (C/C₀~0.6) and 80% (C/C₀~0.2), respectively, between 50,000 and 400,000 BVs. It was speculated that the steady removal was a result of biological activity on the GAC filter media because of the use of non-chlorinated feed water. Absorption was only the dominant MIB and Geosmin removal mechanism during the first few thousand BVs, after which biodegradation was the dominant mechanism. GAC caps would be better than anthracite caps since biological growth and biosorption are enhanced on GAC.

Intensive sampling at a full-scale WTP (Chandler WTP) was also performed to verify the results of the MPI study. MIB removals of 30-40 % were measured at Chandler WTP, which corroborated the RSST results. ASU and MPI teamed up in 2001 to write a AWWARF project on biofiltration for MIB and Geosmin control, which was recently awarded and the project will start in 2002. This project will, in part, compare GAC versus anthracite as biofilter material. Starting in 2002, the City of Tempe will also be conducting pilot studies on biofiltration for MIB and Geosmin control.

MPI also determined that the life expectancy of the filter caps were highly dependent on the filter depth, filtration rate and targeted removal. Figure 4.7 shows that the GAC filter caps will last proportionately longer at lower filtration rates, percent removal and deeper filter media.

It was concluded that GAC filter caps are a feasible alternative for in-plant control of MIB and Geosmin and DBP precursors; data for DBP precursors was included in MPI report. The MPI

report supported the recommendation for implementing GAC caps at the City WTPs, without further need for bench-scale testing. PAC addition prior to GAC-capped filters would still be desirable, and together the two integrated systems would provide excellent T&O control. It is specifically recommended that the City implement GAC filter caps at the WTPs with the shorter PAC contact times and highest influent MIB or Geosmin levels. Accordingly, this leads to the recommendation that the City should evaluate GAC filter caps at Deer Valley WTP first and then Squaw Peak WTP. Union Hills WTP could benefit from a GAC cap upgrade since it has minimal contact times for PAC addition, although T&O levels in the raw water for this facility have historically been low. Replacement timing of GAC filter caps could be optimized such that PAC addition requirements are minimized. The City would need to hire a professional consulting firm to design and install the GAC filter caps, as it would likely affect disinfection strategies since the point of chlorination would have to be moved to after filtration, and GAC filter caps would likely reduce filter run times.

RECOMMENDATIONS

Conventional WTPs offer limited potential to control MIB and Geosmin present in the raw/influent water. The COP therefore has four options to minimize MIB and Geosmin in the finished water:

- 1. Minimize raw water T&O levels through upstream controls (e.g., canal treatments)
- 2. Optimize PAC brand selection and feed capability
- 3. Allow filters to operate in a biological mode
- 4. Upgrade treatment processes to include advanced oxidation processes or nanofiltration/reverse osmosis membranes.

As part of a multiple barrier T&O control strategy, reducing MIB and Geosmin in the raw water is critical. Approaches for upstream T&O controls in canals and reservoirs are described under Task 7 and 8.

Selection of the PAC brand should be based upon two parameters. First, different PAC brands (manufacturer and products) adsorb significantly different amounts of MIB or Geosmin in local Arizona waters, compared against distilled water tests or natural waters from elsewhere. For Arizona waters, PAC brands with smaller internal pores and pH zero points of charge near the natural water pH appear to the best at removing MIB and Geosmin while minimizing competition for adsorption sites from DOC. Second, the unit cost of the PAC affects the economics of T&O control. Often, the most effective PAC brand at removing MIB and Geosmin is not the least expensive. ASU recommends an Index Value approach, where the Index Value is computed as follows:

Index Value = [% MIB Remaining]x[Price per pound]

The PAC brand with the <u>lowest</u> Index Value represents the most cost effective supplier of PAC. A performance-based specification should be used for the selection of a PAC supplier.

PAC feed capabilities at most COP WTPs should be improved. This includes onsite storage, day storage, feed pumps, and mixing systems. ASU recommends that COP have a 7 to 10 day

onsite storage capability to feed 40 mg/L at the maximum design flowrate. Onsite storage can be dry or slurry form. Batch adsorption experiments found no reduced performance of PAC slurry stored for six months compared against a freshly prepared PAC slurry. The 7 to 10 day supply is based upon logistics of process control monitoring for MIB and Geosmin levels in raw water, and the ability to schedule PAC deliveries. Currently, the COP WTPs have maximum feed rates of 15 to 20 mg/L, which is inadequate to achieve high MIB removal efficiencies. In order to achieve 90% removal efficiencies, a minimum PAC feed rate capability of approximately 40 mg/L is necessary.

GAC capped filters operated in an adsorption or biologically active mode will remove MIB and Geosmin. Existing anthracite filter caps would be replaced by GAC caps. The point of chlorination would have to be changed to after filtration, which would affect CT disinfection credits. Depending upon operating conditions 20% to > 90% MIB and Geosmin removal can be achieved. PAC addition may not be required when operating in adsorption modes only, while it would be required under biologically operated (exhausted adsorption capacity). GAC caps operated under adsorption mode, and to a lesser extent under biological mode, would provide TOC removal and removal of synthetic compounds (e.g., estrogenic compounds and pharmaceuticals). COP may want to consider conducting an evaluation of upgrading existing anthracite filters to GAC-capped filters. This is especially true for WTPs with short presedimentation contact times for PAC and/or high influent T&O concentration (e.g., Deer Valley WTP).

Free chlorine does not oxidize MIB or Geosmin under WTP conditions. Prechlorination was found not to affect MIB or Geosmin concentrations, but increased TTHM levels leaving a WTP during one study from approximately 60 to 80 μ g/L (the Stage I MCL). Alternative strategies for in-plant algae control (chlorine dioxide, chloramines, copper, biocide surface coatings) are needed.

Advanced treatment processes are capable of MIB and Geosmin removal. Ozone can provide in excess of 95% oxidation of MIB and Geosmin, provide CT inactivation credits, but forms bromate. Chlorine dioxide slowly oxidizes 10% to 30% of the MIB and Geosmin, and may be a pre-disinfectant. UV-photolysis can oxidize MIB and Geosmin, but requires dosages approximately 100 times greater than doses required for microbial inactivation. Deep-bed GAC adsorption efficiently removes MIB, Geosmin, and other trace micropollutants. Nanofiltration and reverse osmosis require extensive pretreatment, but can remove MIB and Geosmin along with pathogens and some salts.

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SECTION 4 TABLES AND FIGURES

Table 4.1.	Summary	of alga	samples	from	Deer	Valley	and	Squaw	Peak

Plant Name	Odor description	Alga ID and relative abundance
Deer Valley (10/11/99)	Intake: dried seaweed odor	Intake: Cladophora covered with Cocconeis; filamentous mat Sed Basins: Some Diatoms
	Sed Basins: No odor	Navicula, Amphora Weirs: Blue green mats had
	Weirs: No odor	MANY Nostoc (thick without heterocysts); much dead Oscillatoria – Achnanthes minutissima; some Rivularia – Navicula; some Gloeocapsa - Synedra
Squaw Peak (10/11/99)	Head of Sed Basins: No odor; much sediment and debris; many trapped particles	Head of Sed Basins: Many Oscillatoria and filamentous diatoms; some Cocconeis, Amphora, Lg. Synedra, Navicula; a little Anabaena and Scenedesimus
	End of Sed Basins: No odor	End of Sed Basins : Oscillatoria and Oedogonium in thick rigid brown mass; Oedogonium in light green filaments
	Sed Basin Floating Patties: No odor; trapped particles	Sed Basin Floating Patties: Much Spirulina; Oscillatoria, dead Cladophora, Spirogyra, Biddulphia diatom, Synedra Navicula, Gomphonema Amphora, Cocconeis, Nitzschia

Table 4.2. WTP Plant Surveys

WTP	When does T&O	Where in plant is T&O most	What have you done to control / treat T&O?
Interviewed	problem occur?	noticeable?	
Deer Valley (10/11/99)	May Sept/Oct Based upon nose and customer complaints	Most noticeable at weirs	Shock Cl2 (4-5 ppm) for 48 hr every weekend to control in-plant alga (May-Nov); large Cl2 demand noticed during the day; Cl2 added prior to filters (~1ppm) PAC added in the past, but not in last 2 years
Squaw Peak (10/11/99)	Usually in the fall	Haven't noticed them in the plant – may be a distribution issue (Dick Mussel cultured some actinomycetes a few years ago) Clearwell is gravity feed and limits plant to ~ 100MGD and water can return to clearwell and may affect T&O During interview – headworks and weirs had most noticeable odor	 Shock Cl2 prior to flocculation for 48 hours on weekends – does not appear to make T&O problem worse (target is finished water residual) – a 5ppm residual after presedimentation would control alga, but forms too many DBPs now. PAC added in past, but in last 2 years
Val Vista (10/14/99)	Aug - Oct	Some fishy odors in presed basins Solids (shells/ sand) from grit pumps have musty / moldy odor TON conducted 6 times daily (see daily datasheets)	Prechlorination (1ppm residual after filters for 24 hours) improves filter operation with less alga in presed, floc, and sed basins; not required this year with constant Copper feed Since May 1999 constant copper application (0.25 ppm) at head of plant – visibly equally effective as pre-Cl2 PAC added as needed from customer complains – adding from Aug-Oct in 1999; also added in 1998 Co-owned with Mesa (Allen Martindale) and often drives customer complaints
Union Hills (10/27/99)	Sept/Oct is typically worst month when Lk Pleasant turns over or they start changing over to CRW (canal holds a lot of stagnant water	Noticeable at aeration basin; no odor during interview - just a chlorine odor	Added 225 white Amor to impoundment Pre-Cl2 with 0.5 ppm to impound Add 0.25 ppm of copper pentahydrate (60 ug/L as Cu) to impound Had ClO2 feed at one time, but due to high demand ClO ₂ ⁻ was > 1 mg/L (equipment removed); had KMnO4 feed but no longer applied Aeration removes some T&O

Table 4.3. WTP Plant Surveys (pretreatment)

Water Treatment	What chemical	Is there any presed	What is your experience with PAC
Plant Interviewed	pretreatment options exist?	basins?	addition?
Deer Valley	Alum (22ppm) + Catfloc currently feed. Acid feed capabilities	Yes – 3.5 MG total; typical plant flow 100 to 130 MGD (Max day = 130 MGD)	PAC selected based upon low bid. Norit Hydrodarco B. Stored onsite until needed. No PAC feed in last 2 years
	Copper feed (~0.2 ppm) has been	Approximately 3 hr residence time from head through filters.	PAC added prior to presed for contact time, but alum added simultaneously
	impact lead and copper rule	Presed is considered a "nursery" for alga	Historically used in May & Fall based upon customer complaints for 2 weeks to 90 days
	Stated KMnO4 may be a viable preoxidant for T&O		Historical records available & may be able to cross reference with lab
Squaw Peak	Pretreatment in presed is limited to PAC	Yes – unsure of exact size but may be ~ 5MG	PAC addition (~ 1 month) is controlled by customer complaints
		Presed water is "green" and may be a "nursery" for alga	Plant observed benefits from PAC in the form of reduced customer complaints
			PAC selected based upon low bid
Val Vista	220 MGD plant. Copper, chlorine, PAC, alum, polymer feeds exist	4 MG for each train; with 140 MGD on East side – 48 min retention; West side with 80 MGD	PAC selected based upon low bid. Norit hydrodarco B
		 – 2 hr retention time 	PAC added to presed up to 20 ppm; no change in turbidity loading onto filters
Union Hills	Ferric chloride (2-4 ppm) at a target pH of 7.6 to 8.1 for lead an copper rule in the future	65 MG in impoundment is typical, although its capacity of 140 MG is only used 0 to 4 times per year. Impoundment has not sludge	Direct filtration plant has limited contact time. Some in aeration system. Could possibly add PAC to impoundment.
	Cationic polymer (S308P)	removal (possible nutrient sink)	Have added PAC at 2-5ppm almost every year during Sept/Oct
	requirements, except at lower pH levels		PAC should be used immediately and not stored for long periods dry or as a slurry
Water Treatment	What is your	What is your filtration	What is done with sludge and
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Plant Interviewed	coagulation process?	process?	backwash water?
Deer Valley	Alum + Catfloc added prior to presed and then added again at flash mixers Jar tests are run daily to minimize chemical usage Some floating alga / alum mats in sed basins Weirs covered with alga	Dual media – anthracite over sand Nonionic polymer added continuously as a filter aid	 Pumped daily for 2 hours per basin and clarifier to canal (nearly constant discharge) 3-6 MGD of water including filter backwash returned to canal; Backwash at 20,000 gpm for 20 min A composite sampler exists at channel prior to canal Sludge handling (centrifuge) will be online in Jan 2002 and return 2.5 to 5.5 MGD back to head of plant (may carry over MIB/Geosmin)
			Some chemical treatment of future return flow may be helpful
Squaw Peak	pH depression (~ 7.2) + alum 15-18 ppm) + cationic polymer Recently the plant started operating at low pH and limited chlorine addition to reduce DBP formation – termed enhanced coag by Mr Martin	Nonionic filter aid used. Dual media anthracite over sand Run times fairly constant throughout year (~75 hr @ 60MGD and 40 hr @ 100 MGD) Cl2 added to sed collection flume to target 1ppm residual after filters	Returned to canal. Centrifuges going on line Fall 2001 with supernatant returned to head of plant or sewer (not to canal) Total retention time through plant is 3 hr at 100 MGD, and up to 6 hr otherwise
Val Vista	Alum(18-20 ppm) + acid + cationic polymer	Cl2 residual of 0.1 to 0.5 ppm leaving filters Approximately 3 hr retention time through plant	Onsite treatment with supernatant and some settled-only material returning to presed basins
Union Hills	Ferric chloride (2-4 ppm) at a target pH of 7.6 to 8.1 for lead an copper rule in the future Cationic polymer (S308P)	30 hr runs on MOD1 – monomedia 18 hr runs on MOD2 – dual media Diatoms in CAP seem to have an effect on filter run time	Series sludge settling – supernatant returns to impoundment and sludge is disposed onsite on mesquite trees

Table 4.4. WTP Plant Surveys (Coagulation and Filtration)

Table 4.5. V	WTP Plant Surveys	(Algae issues)
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Water Treatment	Where does alga grow	What are the associated	What do you do to control in-plant alga?
Plant Interviewed	in your plant?	problems?	
Deer Valley	Visible growth of patties in presed and sed basins – rise from bottom during the day due to photosynthesis Green filamentous alga growth on walls of presed and sed basins	Clogging of weirs Significantly reduced filter runs times due to in-plant alga(May- Sept); increased turbidity during this time Prechlorination doubles filter runs and decreases effluent turbidity	Manual removal 3-4 times per week – worst in sed basins and inlet weirs Pressurized washing of alga Weekend shock chlorination
Squaw Peak	Prior to "enhanced coag", chlorine addition prevented alga growth in plant. Presed is about the same, but sed basins are much worse now. Problem is not as severe as Deer Valley	Alga and fungi are fairly uniform on sed basin walls and weirs	Limited effort available for manpower in removing alga During shutdown, used to powerwash walls with CuSO4, but not recently due to reduced manpower – now just hose down
Val Vista	Normally along walls – no floating matts typically Pre-Cl2 results in sloughing	Reduced filter run times. With pre-Cl2 filter run times increased and turbidities decreased; no complaints this year with copper replacement of pre-Cl2 18-36 hr filter run times Customer complaints from Mesa	Historically – preCl2, but this year mainly copper addition PreCl2 would cause sloughing that required weir cleaning; otherwise maintain weirs 2x / week ASU – PAC addition my block out light for alga
Union Hills	Plant is starting to get green now (Oct). Seems to be Phosphorus related	Diatoms from canal are difficult to treat / charge neutralize Nitrification occurs in sed basins with low DO at bottom of basins	Some copper addition and pre-Cl2; most of Cl2 demand goes to forming DBPs was stated Alga identification / counting is used as a process control parameter

Water Treatment Plant Interviewed	What do you recommend for controlling T&O?	Could full-scale experiments be conducted at this facility?
Deer Valley	Suggested something post filtration (GAC/membrane) rather than chemical addition Addition of PAC after low lift pumps (80,000 lb of onsite storage)	Could run east-side presed separate from west-side All floc basins are connected and common downstream of presed basins
		Very reluctant NOT to add alum prior to presed for PAC study (alum + PAC added together reduces sorption)
Squaw Peak	Increased manpower to take a train out of service and thoroughly clean it	Pilot plant was removed for Val Vista – check with COP equipment group; should have one for Lake Pleasant testing during Spring 2000
	Most of the problem is in distribution system where changing water sources (GW/SW) may make problem more noticeable	The plant has many common flumes so partial treatment of plant would be difficult
	~1" of sludge in clearwell may have some fungi growth	Could add pretreatment of presed basins
Val Vista	Wanted to know how effective copper is along with PAC addition; plans to add copper next year	Copper could be added to either the East and/or West plants
	Copper prevents alga growth, while pre-Cl2 only slowed it down	PAC could be added to either the East and/or West plants
	PAC addition helps, based upon feedback from Mesa labs (Matt Rexing) and Mesa customer complaints	
Union Hills	Addition of sed basins would allow contact time and solids removal for PAC addition	Quantify role of aeration of MIB/Geosmin
	T&O problem must be quantified with GCMS and FPA	
	Storage of PAC slurry is problematic	
	Role of distribution system should be quantified	

Table 4.6. WTP Plant Surveys (T&O controls)





Val Vista WTP









Deer Valley WTP





Figure 4.4. THM concentrations before and during prechlorination at Deer Valley WTP.

Figure 4.5. Breakthrough curves from RSSCTs for MIB.



Figure 4.6. Breakthrough curves from RSSCTs for Geosmin.





Figure 4.7. Life expectancy of GAC filter caps.

SECTION 5: CONTROLLED LABORATORY EXPERIMENTS (TASK 4)

Experiments were conducted in the laboratory to (1) screen parameters important for implementation at field- or full-scale and (2) gain insights into a biological process or mechanism. This section is organized into two subsections, plus a recommendation subsection, to address the above objectives. Background, methods, and results for experiments are presented.

PARAMETER SCREENING

Powder Activated Carbon (PAC)

MIB and Geosmin can be removed from drinking water through adsorption to PAC. The rate and extent of adsorption can vary dependent upon water chemistry.

Methods. Activated carbon adsorption studies with MIB and Geosmin were conducted in the laboratory with ten commercially available brands of PAC (Table 5.1). PAC samples were obtained from PAC manufacturers in amounts sufficient to run all experiments. Arizona Canal, Salt River and CAP water (250 or 50 ml) was spiked with MIB and Geosmin. MIB and Geosmin concentrations ranged from 25 to 150 ng/L, while PAC concentrations ranged from 1 to 50 mg/L (slurry at 2500 mg PAC/L ultra-pure water mixed for 24 hours). Either centrifuge vials (50ml) or jars (250 ml) were used for treatments and were shaken on a wrist shaker (Multi-wrist® shaker, Lab-Line, Melrose Park, IL) using a separate container for each replicate. Controls contained MIB and Geosmin, but no PAC. Two controls were used including one taken at time zero and the other placed on the mechanical shaker and taken after 240 minutes. Contact times for the adsorption experiments were 5, 10, 20, 60 and 240 minutes. Activated carbon was removed from the samples by centrifuging for 10 minutes (3500 rpm; Marathon 10K centrifuge, Fisher Scientific, Pittsburgh, PA) and then filtering by syringe with a 0.2 um nylon filter (Acrodisc® 32 Supor® 0.2 um syringe filters, Pall Corporation, Ann Arbor, MI).

Results. The removal of MIB and Geosmin was evaluated in ultrapure water and SRP/CAP waters using several PAC brands. The samples were spiked to have initial MIB or Geosmin concentrations of 30 ng/L. The results are summarized in Table 5.2. After a contact time of three hours, MIB was removed nearly completely from nanopure water (pH = 7 with 10 mg/L sodium bicarbonate) upon addition of 15 mg/L of most PAC brands. However, a large range of MIB removal performance was observed in the natural water. The presence of DOC in the water competed against MIB and Geosmin for PAC adsorption sites. Geosmin removal by PAC followed similar trends as that for MIB (results not shown). Geosmin removal was always higher than MIB removal. Geosmin has a higher K_{SW} value (3.7) than MIB (3.1) and the increased hydrophobicity of Geosmin caused improved removal by PAC (Pirbazari et al., 1992). Similar patterns of PAC performance were observed in SRP and CAP waters.

In general the bituminous coal based PAC performed better than lignite- or wood-based PAC. Pore size distribution is a critical factor for MIB or Geosmin removal in natural waters (Pendleton et al., 1997; Manes, 1998), and manufacturers commonly provide surrogate measurements (e.g., molasses, tannin or iodine numbers (Table 5.1)) for pore size distributions. Other research conducted in distilled water matrices concluded that lower oxygen content of PAC, along with a higher iodine number, also leads to improved MIB and Geosmin removal since a low oxygen content increases the hydrophobicity of the PAC surface (Pendleton et al., 1997;

Considine et al., 2001). Oxygen content and hydrophobicity are influenced by the composition of the PAC, and jointly influence the point of zero charge (pH_{ZPC}) of PAC. PAC can exhibit a wide range of pH_{ZPC} values. For example, Norit HDB has a pH_{ZPC} of ~ 3.5 while many other PACs have pH_{ZPC} values between 6 and 8 (Siddiqui et al., 1996). PACs with a pH_{ZPC} near the natural water pH will have less ionization potential and have a greater affinity for hydrophobic compounds (e.g., MIB or Geosmin) (Newcombe, 1999). Furthermore, microporous PAC is less likely to allow DOC molecules to sorb into the pores while smaller molecular weight compounds (e.g., MIB and some DOC) can access the internal surface sorption sites and therefore minimize the competitive sorption effects between DOC and MIB (Kilduff et al., 1996). However, large molecular weight DOC can block small pores. Overall microporous, hydrophobic PACs with pH_{ZPC} values near the pH of the water should perform best for MIB or Geosmin removal, and the net effects of the presence of DOC on PAC sorption sites can be significant (e.g., Table 5.2).

The PAC brand historically used by the City of Phoenix WTPs for removal of taste and odor compounds (MIB and Geosmin) is HDB. Similar adsorption kinetics were observed for Norit HDB and 20B (Figure 5.1). Adsorption kinetics do not vary significantly as a function of PAC dose. After 4 hours at a HDB dose of 10 mg/L, about 42 percent of the MIB was removed as compared to 82 percent of the Geosmin. In addition, the majority of MIB and Geosmin were removed within the first hour. MIB and Geosmin removal also increased with higher PAC doses, since more adsorption sites were available. MIB is removed less effectively than Geosmin. Most of the field monitoring (Task 1) indicated higher MIB than Geosmin concentrations. Therefore, the higher raw water concentrations, slower adsorption rate, and lower extent of removal for MIB compared against Geosmin would indicate that MIB removal controls selection of PAC dose. If MIB is removed to less than 10 ng/L, so would Geosmin be removed to even lower concentrations.

Two of the best performing PAC types from the evaluation presented in Table 5.2 (WPM and 20B) along with HDB were used to generate adsorption curves in SRP water (Figure 5.2). MIB and Geosmin concentrations ranged from 25 to 150 ng/L. MIB and Geosmin percent removals were not a function of the MIB or Geosmin concentrations in the raw water influent, which agrees with previous research (Knappe et al., 1998). Geosmin percent removals were significantly higher than MIB percent removals for all three PAC types. MIB percent removals were highest for 20B as compared to HDB and WPM. At a dose of 15 mg/L PAC and contact time of 4 hours, the percent removal for 20B was about 86 percent as compared to 72 and 55 percent for HDB or WPM, respectively. For Geosmin, 20B had a slightly higher removal rate at 93 percent as compared to 87 and 90 percent removals for HDB and WPM, respectively. Doseresponse curves can be used to optimize the PAC dose to achieve a desired percent removal. Since MIB and Geosmin are micropollutants, occurring at nanogram per liter levels compared to DOC at milligram per liter levels, the percentage of MIB or Geosmin removed is independent of their initial concentrations (Knappe et al., 1998).

A field implementation study was conducted at Val Vista water treatment to determine if switching to a better performing PAC type could enhance MIB removal rates, and to verify that bench-scale results could be used to predict full-scale performance. The study was conducted for seven days from October 3 - 10, 2000 and HDB was fed to the west treatment train while 20B was fed to the east treatment train. During the testing period the HRT of the presedimentation, flocculation, and sedimentation basins were approximately 2 hour, 30 minutes, and < 2 hour, respectively. Laboratory batch tests were conducted with water from the field and PAC with a contact time of 4 hours. Kinetic differences between full-scale evaluation and batch tests were probably negligible given that pseudo-equilibrium between MIB and PAC

was achieved within 1 hour (i.e., Figure 5.1). Raw water influent MIB concentrations to both treatment trains were the same and decreased from 46 ng/L to 22 ng/L during this period (Figure 5.3). Average PAC feed rates to the treatment trains were similar for both 20B and HDB and ranged from 4-17 mg/L throughout the implementation. Removal rates for MIB ranged from 18 to 53 percent for the West train with HDB and from 35 to 77 percent for the East train with 20B (Figure 5.4). MIB removals for 20B were from 9 to 34 percent higher than removals for HDB. Geosmin concentrations ranged from less than 2 to 8 ng/L throughout the study and removal rates were slightly better with 20B as compared to HDB. The majority of the MIB removal occurred in the pre-sedimentation basins and removals were about 10 percent lower in the field as compared to laboratory and were likely due to incomplete mixing or sedimentation in the presedimentation basins.

To implement using 20B at Val Vista WTP, theoretical curves of final MIB concentration (ng/L) versus 20B PAC dose (mg/L) for varying influent MIB concentration (ng/L) were generated using field data (Figure 5.5). For a given influent MIB concentration, determined from water sampling, a PAC dose can be selected based on a desired final effluent MIB concentration. Based upon a PAC slurry of Norit 20B from the field the following regression was obtained to generate Figure 5.5:

$$PACDose(mg/L) = \frac{-\ln\left[0.95 * \left(\frac{MIB_{finished}}{MIB_{raw}}\right)\right]}{0.079}$$
 Equation 5.1

or to achieve 10 ng/L MIB in finished water:

PAC Dose
$$(mg/L) = 12.7xln(MIB_{raw}) - 28.5$$
 Equation 5.2

Where the raw (MIB_{raw}) and finished (MIB_{finished}) water MIB concentrations are in ng/L. For example, if the influent MIB concentration is 40 ng/L and the desired effluent MIB concentration is 10 ng/L, a 20B PAC dose of about 27 mg/L would be required. Theoretical PAC curves can be generated from either laboratory dose response curves or field removal rates. In this research, the laboratory rates were about 10 percent higher and therefore the curves were generated using field data since it was available. Furthermore, higher PAC doses during prechlorination may be required to maintain high MIB or Geosmin removals since chlorine oxidizes PAC sorption sites (Gillogly et al., 1998a).

MIB and Geosmin behave as micropollutants in natural waters that contain mg/L levels of DOC, and as such their percentage removal is nearly independent of initial concentrations (Knappe et al., 1998). PAC addition preferentially removed Geosmin over MIB, and was attributed to the higher K_{ow} value of Geosmin and a hydrophobic removal mechanism by the PAC. Screening tests for the performance of different PAC brands for MIB and Geosmin removal at a specific WTP should be done in the natural water at the facility that contains ambient levels of DOC (Cook et al., 2001; Gillogly et al., 1998b, 1999b; Graham et al., 2000; Newcombe et al., 1997a,b). The best performing PAC brand in ultrapure water (no DOC) was not necessarily the best PAC in the natural water, due to competition between DOC and MIB or Geosmin for PAC sorption sites. Bituminous coal performed better than other coal or wood based products investigated. MIB and Geosmin have molecular size of approximately 6 Å and should be adsorbed in the micropores of activated carbon (< 20 Å). In ultrapure water relatively higher

oxygen content of the PAC, and associated higher hydrophilicity, as potentially indicated by lower pH_{ZPC} of the PAC, could lead to lower MIB uptake. Selection of a microporous PAC with a pH_{ZPC} close to the raw water pH may be the best selection criteria in the absence of PAC performance testing for MIB or Geosmin removal in site-specific raw waters. However it remains unclear how DOC interactions with PAC surfaces impact the ability to a priori predict PAC performance for MIB removal in natural waters that contains DOC. Therefore WTPs should develop PAC dosing requirements to achieve certain taste and odor threshold goals. Based upon the work herein those goals should be selected for MIB, since it always occurred at higher concentrations than Geosmin and was more difficult to remove by PAC. During this study PAC doses far above levels needed to reach a threshold that would not be noticeable by most consumers (e.g., 8 ng/L) were applied. Many times the MIB concentrations in the effluent of the WTPs were less than 2 ng/L. Overdosing of PAC results in excessive sludge production, shorter filter runs, and larger operating costs. Over expenditure of PAC related operating costs may range from \$10,000 to \$200,000 annually. Therefore we recommend frequent (e.g., weekly) monitoring of influent MIB levels to select appropriate PAC doses, using a guide similar to Figure 5.5, to optimize PAC feed rates and reduce operating costs.

As part of implementation tasks for T&O control an approach to selecting PAC suppliers was developed for COP bid process. PAC brands from suppliers covers a range of costs (\$/pound), and preliminary cost estimates (not formal bids) were obtained from the suppliers for the PAC used in the above testing (Figure 5.6). There is not always a direct correlation between more expensive PAC (higher \$/lb) and higher performing (% T&O removal) PAC brands. The PAC with the lowest performance (Norit HDB) was the least expensive. We recommend the use of an Index Value to rank PAC brands, based upon the following equation:

Index Value = [% MIB Remaining]x[Price per pound]

Equation 5.3

The PAC brand with the lowest Index Value represents the most cost effective supplier of PAC.

Ozone

Batch ozonation experiments were conducted to evaluate a benefit of adding ozone to a conventional WTP for taste and odor control.

Methods. Ozonation experiments were conducted in batch reactors where a liquid ozone stock solution was added to a 500 mL mixed reactor containing the water sample with MIB or Geosmin (Westerhoff et al., 1999). Ozone decay and loss of MIB and Geosmin were monitored over time. Tertiary butanol (t-but) was added during select experiments to scavenge hydroxyl (HO) radicals, and thus only allow molecular ozone to oxidize the taste and odor compounds.

Results. Application of ozone to MIB and Geosmin spiked into CAP water rapidly oxidized both MIB and Geosmin within the first 3-5 minutes of reaction (Figure 5.7). Geosmin was removed slightly better than MIB. In order to identify the mechanism for oxidation, t-butanol was added during a parallel experiment to scavenge hydroxyl (HO) radicals. During ozonation molecular ozone decays and forms HO radicals, which are powerful oxidants (Hoigne, 1997). Molecular ozone serves as a disinfectant, while HO radicals do not. In the presence of t-butanol the HO radical concentrations are much lower than in its absence. Addition of t-butanol, and subsequent quenching of HO radicals, resulted in less MIB or Geosmin oxidation. The results imply that HO radicals participate in a major mechanism for oxidation of MIB and Geosmin during ozonation. Higher pH, lower alkalinity, and higher hydrogen peroxide levels increase HO

radical concentrations, and would lead to improved taste and odor treatment.

Both molecular ozone (O₃) and hydroxyl radicals (HO) play important roles in oxidation of taste and odor compounds (T&O), yet reaction rate constants (k_{O3} , k_{HO}) between these oxidants and organic compounds are not well documented:

O_3 + T&O \rightarrow by-products	d[T&O]/dt = - k _{O3} [T&O][O ₃]	Equation 5.4
HO + T&O \rightarrow by-products	d[T&O]/dt = - <i>k_{HO}</i> [T&O][HO]	Equation 5.5

 K_{HO} for reactions with MIB and Geosmin were estimated from ozonation experiments in the presence of hydrogen peroxide as 8.2×10^9 and 14×10^9 M¹s⁻¹, respectively (Glaze et al., 1990). Values for k_{O3} are lacking from the literature, but values on the order of 5 to 100 M¹s⁻¹ seem appropriate for MIB and Geosmin based upon unpublished data by the investigators and others (von Gunten, personal communication). Both values are consistent with laboratory and field observations supporting the fact that Geosmin oxidation is more extensive than MIB oxidation (Lundgren et al., 1988).

The relative importance of the molecular ozone and HO radical oxidation pathways are presented for a model simulation in Figure 5.8. The predictions were developed using a simple process model accounting only for ozone decomposition at an observed rate of 0.1 min⁻¹ (halflife of 7 minutes) that is representative for natural water, and a R_{ct} ratio of 10⁸ ($R_{ct} = [HO]/[O_3]$) which is appropriate for most full-scale ozonation systems. Elovitz and von Gunten (1999) developed an approach that demonstrated the ratio of HO radicals to O₃ was relatively constant during ozone decomposition. Values for this ratio are $10^7 < R_{ct} < 10^9$. The model is currently set up in ACUCHEM that solves sets of differential equations via the Jacobean algorithm. Figure 5.8 shows ozone decay and MIB oxidation (solid lines). Dashed lines indicate the models ability to track HO radical and O₃ MIB oxidation byproducts, indicating whether HO or O₃ was responsible for MIB oxidation. MIB oxidation by-products are probably polar and no reported odors are associated with them. Based upon the rate constants used in this simulation (k_{03} = 15 M¹s⁻¹; $k_{HO} = 8.2E9$ M¹s⁻¹) approximately 83% of the MIB was oxidized via HO radical pathways, and the remaining 17% by molecular ozone (Westerhoff et al., 1999). These simulated results are close to observed experimental data that indicated 90% MIB removal 20 minutes after ozone addition, compared against only 37% in the presence of excess t-butanol (HO radical scavenger). More accurate rate constants and slight model adjustment would provide a very useful mechanistic optimization tool.

Ozone addition effectively and rapidly oxidized MIB and Geosmin. The primary oxidation mechanism was identified to involve HO radicals. However, better rate constants are needed for molecular ozone oxidation of MIB and Geosmin. Higher HO radical concentrations could be achieved through the addition of hydrogen peroxide (H_2O_2) during ozonation. The downside of H_2O_2 addition during ozonation is that lower dissolved ozone concentrations would occur, and hence less disinfection credit would be available. Significant capital and operating costs are associated with ozone addition and multiple benefits (oxidation of Fe/Mn, disinfection) and tradeoffs (bromate formatin; MCL = 10 µg/L) of ozone addition to a WTP would have to be considered, as opposed to use of ozone solely for taste and odor control.

Chlorine Dioxide

Chlorine dioxide can be an effective disinfectant, but is a weak oxidant for T&O compounds.

Methods. A stock solution of ClO_2 (~3000 mg/L) was prepared as instructed by representatives from Vulcan Technical Technologies (Vulcan) from material called "V-Charge". V-Charge contains two packets, that when mixed together with 1 liter of Nanopure water produces ClO_2 . The two packets were dissolved in 1 liter of water, and slowly agitated for 20 minutes. The stock solution was stored at 4°C. The concentration of the stock solution was measured prior to use by UV absorbance at 360nm and by a Hach colorimetric method. The initial stock solution concentration was verified with titration by Vulcan personnel and agreed with the other two methods. Different doses of ClO_2 were added to a 1-L cylinder reactor with 500 mL of source waters and then cover the top of water surface with Teflon mesh. Water samples were collected at 0, 5, 10, 20, 30, 45, and 60 minutes and ClO_2 residual was measured using a HachTM colorimetric method or UV absorbance at 360nm. Residual ClO_2 was quenched with sodium thiosulfate, and MIB and Geosmin analyzed on samples.

Results. Arizona Canal water was spiked with MIB (80 ng/L) and Geosmin (426 ng/L) prior to CIO_2 addition. A CIO_2 dose of 2.45 mg/L was selected based upon previous work to achieve 1-log cryptosporidium inactivation; previous work associated with the COP Lake Pleasant WTP bench-scale testing program. Over the course of 60 minutes only 10% to 20% of the MIB or Geosmin was oxidized. CIO_2 is not recommended for T&O oxidation in Arizona waters.

Copper Biocides

T&O Oxidation by Copper Products. At the December 2001 periodic presentation, Reb Ferrell (Representative from Earthtec), suggested that Earthtec copper may react with MIB over time in water treatment plants. The proposed reaction would degrade / remove MIB. A simple set of experiments to test this hypothesis for possible use of Earthtec in water treatment plants was developed. Approximately 50 ngMIB/L solutions were prepared in Distilled Water (DI) and in Central Arizona Project water (CAP). Initial MIB concentrations were measured in triplicate. Approximately 1 mg/L as copper of Earthtec was added and copper concentration was measured by colorimetric analysis. This copper concentration was recommended by Mr. Ferrell. MIB was measured immediately after 3.1, 3.8, and 6.1 hours. These contact times were selected to represent maximum contact times within City of Phoenix water treatment plants. The triplicate initial MIB concentrations (no copper) were used to develop error bars (Figure 5.12). Over time there was no statistical change in MIB concentration in the presence of the Earthtec product. The conclusion of the study was that Earthtec application under typical drinking water treatment plant practices would <u>not</u> remove MIB.

Chlorine Consumption by Copper Products. Cutrine-Plus and Earthtec are two different types of copper-based algicide. The former is a chelated elemental copper with triethanolamine, whereas the latter is a copper sulfate-based acidic solution (pH 0.5).

Both copper products reduced the production of MIB and Geosmin in the Arizona Canal. However, application of Cutrine-Plus in the canal resulted in a significant increase in chlorine demand in the WTPs downstream shortly after copper application. In contrast, little chlorine demand was observed when Earthtec was introduced. This phenomenon was confirmed by laboratory experiments in which chlorine demand was tested in pure water and water from the Arizona Canal spiked with either Cutrine-Plus, Earthtec or copper sulfate. A large increase in chlorine demand was detected in water containing the Cutrine-Plus solution (Figure 5.10). Cutrine-Plus contains organic triens (organic nitrogen) that complexes copper ions, allowing copper to remain dissolved rather than precipitate. Reactions between organic triens and chlorine form organic chloramines. Inorganic and organic chloramines were detected by the total-chlorine DPD test, whereas free-chlorine can be quantified separately. Earthtec or copper sulfate solutions did not consume chlorine or form organic chloramines (Figure 5.11).

Fixed-surface Biocides

Background. Gu et al. (1998) investigated degradation of materials to be used on the International Space Station and found that the biocide diiodomethyl-p-tolylsulfone impregnated into a polyurethane coating was ineffective against microbial colonization and growth, and that a biofilm containing *Pseudomonas*, *Ochrocatrum*, *Alcaligenes*, *Xanthomonas*, and *Vibrio* formed. Electrochemical impedance spectroscopy indicated that degradation of the coating occurred in several stages. The initial decrease in impedance was due to the transport of water and solutes into the polymeric matrices, and further decreases were a result of polymer degradation by the microorganisms themselves. This work clearly demonstrates two important issues related to presumed biocide-enhanced surface coatings: (1) not all presumed formulations will endure continued use, and (2) a standardized protocol for evaluating surface colonization was useful in testing the effectiveness of the surface coating.

Clarkson and Evans (1995a, b) tested a silicone elastomer polymer (3-trimethoxysilyl propyloctadecyldimethyl ammonium chloride (DC5700 enhanced silicone polymer) for resistance to algae growth. Short-term experiments demonstrated that a metal-coated surface was toxic to a test alga (*Amphora coffeaeformis*). Continual leaching tests and subsequent soxhlet extraction indicated that uncrosslinked polymers were leachable, that they were predominantly responsible for the toxicity, and that once these polymers were completely leached into solution the surface was no longer toxic to the test alga.

Cheung and Beech (1996) observed that planktonic algae were less resistant to three different biocides, compared against sulphate-reducing bacteria. Clarkson and Evans (1995) observed gradual foiling on surfaces coated with a polymeric biocide over a 13-week test period. Therefore it is possible that extracellular polysacchoorides (EPS) production by less resistant bacteria could provide a layer for algae colonization, since the algae would not have to contact the biocide surface directly.

Estarlich et al. (2000) documented increases in hydrophilicity with some biocide-enhanced silicone elastomers (General Electric RTV11, RT160, RTV655) and fluorosilicones (-(Si(CH3))((CH2)3-O(CH2)(CF2)(x)CF3)-O)(n)-, x=5,7,9). The biocide-enhanced polymers showed very little, and patchy attachment of bacteria and algae after 16 weeks in flowing seawater, compared against mature biofilms which were formed on the polymer without the biocide-enhanced functional groups.

Wynne et al. (2000) reported reduced adhesion of barnacles, and easier removal, upon coating of surfaces with a non-biocidal silicone (polydimethylsiloxan) polymer. Wood et al. (2000) observed similar data for silicone polymers and commented that surface coverage was important for good performance. Furthermore, they commented that fouling organisms were easily removed from treated surfaces by water pressure. This work demonstrates that polymeric surface coatings alone, without the biocide-enhancement, may be quite effective at reducing organism accumulation due to enhancement of the bulk modulus and other mechanical properties.

Testing of three silicone foul-release coatings (allow fouling, but are easily cleaned) at the US Navy's Office of Naval Research Biofouling program found significant differences in

performance between the polymers (Holm, 2000). This suggests the need for a standard protocol to screen the effectiveness of future biocide-enhanced polymeric coatings.

Callow and Fletcher (1994) reviewed how polymers reduced bioadhesion through reductions in surface tensions and coatings, including silicone elastomers and fluoropolymers. Surface tensions between 20 and 30 dynes/cm minimized long-term adhesion, although immersion in natural waters resulted in the formation of "conditioning films" which lead to algae or bacteria attachment after prolonged exposure. Destais et al. (2000) and Sauvet et al. (2000) indicated that quaternary ammonium salts that were covalently-bound to epoxy resins showed good bactericidal activity against *E. coli* even after 6 months of immersion in water.

Rittschof (2000) reviewed the use of natural product biofoulants, and projected that in the near future the necessity to replace toxic-metal based antifoulants with natural polymeric organic biocides will lead to innovations in anti-fouling coatings. Brady (2000) reviewed the replacement of non-toxic antifoulants with polymers that reduce foulant adhesion, and are self-cleaning on ships due to fluid shear.

Scott et al. (1996) used SEM and cytochemical staining techniques to investigate the progression of algae colonization on surfaces, and found that blue-green algae were rapid colonizers of both toxic and non-toxic surfaces and that colonization was first characterized by the production of extracellular polysaccharides (EPS). Layers of EPS and inactivated algae covered the surface until other organisms could colonize on top of these layers and away from the toxic coatings.

Methods. Laboratory experiments were conducted to determine the effectiveness of biocidal surface coatings for controlling growth of periphytic algae in concrete lined canals, concrete water treatment plant tanks, and possibly steel structures (e.g., weirs) in water treatment plants. An organic silicone elastomer polymeric coating (3-trimethoxysilyl pro-pyloctadecyldimethyl ammonium chloride - DC5700 enhanced silicone polymer) and an antifouling TiO2 pant (EP2000) were applied to test tiles and evaluated over a period of time in a recirculating reactor containing algae. A background review on organic biocide coating is provided as a basis for conducting and evaluating the laboratory results.

The active ingredients in Alphacoat 454 (Alphacoat), manufactured by Coating Systems Inc., are quaternary ammonium compounds containing a trihydroxy silicone moiety. This ingredient is water-soluble and exists as a hydrated species. Thus the biocide is both water-soluble and becomes an insoluble polymer when bonded to a surface, by the process of evaporation of the water molecule. If there are hydroxy groups present in the substrate there will be better bonding as in the case of concrete and masonry. The insoluble long chain polymer (- $C_{18}H_{37}(CH_3)_2N^+CH_2CH_2Ci(OH)_3CI$ -) imparts water repellency and he ammonium chloride gives the biocidal effectiveness.

EP2000 is a marine antifouling paint used on the hulls of boats to prevent algae and other marine microorganisms from attaching onto the surface of the boats thus reducing the efficiency of the marine vehicles. It was determined that EP2000 produces hydrogen peroxide on the surface, a mild disinfectant. Excess hydrogen peroxide can lead to chlorine consumption in water treatment applications, but was not considered significant at the low levels that may be produced in full-scale applications.

The biocides (Alphacoat and EP2000) were applied to clay tiles, from a home supply store, cut

into 6cmx6cm squares. The tiles were placed into a continuous flow reactor with a hydraulic retention time of 3.5 hrs. The recycle reactor comprised a rectangular tank made out of polypropylene having dimensions of 56 cm X 8.5cm X 39 cm. Weirs were attached on both ends of the reactor with holes drilled into them for the smooth and even flow of the liquid medium into the core of the reactor. The sample tile substrates were kept in the middle of the reactor. The reactor was seeded with a mixed algae culture taken from the Arizona Canal with tiles being used as the simulated growth substrate. The liquid algae-growth medium (BG-11) was used since it would promote rapid growth of the algae (no limiting nutrient concerns). The algal biomass densities were measured by scraping algae off each test tile after a two-week incubation period in the reactor. Chlorophyll *a* was then measured on the scraping, and assumed to represent the live algae biomass concentration on the surface of the tile.

Results. Periphytic biomass was estimated by the chlorophyll-a concentration of biomass removed from the surface of the tiles. Figure 5.9 presents chlorophyll-a concentrations of a control (no biocide coating), Alphacoat coated-tiles, and EP2000 coated-tiles after 3 and 4 weeks within the recycle reactor. Chlorophyll-a concentrations of the control tiles increased from 60 to 120 mg/m² between the 3rd and 4th weeks. Alphacoat treated-tiles had statistically lower biomass densities after 4 weeks than the control tiles. The EP2000 treated-tiles had less than 15% of the biomass on the control tiles. Therefore, the EP2000 antifouling paint appears to be a viable surface biocide. Field experiments are underway, but results will be available until Fall 2002 in the form of a Masters Thesis, which will be provided to the City of Phoenix.

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BIOLOGICAL PROCESSES

MIB and Geosmin Biodegradation

Background. MIB and Geosmin are produced by some phytoplanktic and periphytic cyanophytes or some actinomycetes, and can be produced in storage reservoirs, rivers, canals, and within treatment plants (Gerber and LeChevalier, 1965; Izaguirre and Taylor, 1995; Suffet et al., 1995). Treatment plants generally accomplish T&O removal by carbon adsorption or ozonation, adding considerably to the cost of water treatment (Mouchet and Bonnelye, 1998; Lawton et al., 1998). This has led to efforts to control the production of MIB and Geosmin at their sources (Izaguirre and Taylor, 1995; Means and McGuire, 1986). MIB and Geosmin often accumulate in surface water reservoirs. Knowledge regarding production and degradation of these compounds would be valuable in developing management strategies to reduce their concentrations in upstream reservoirs before water is delivered to water treatment plants.

Soil and aquatic bacteria are capable of biodegrading MIB and Geosmin, with the cam-operon serving as the primary gene responsible for biodegradation of these alicyclic alcohols and ketones (Hoehn, 1965; Izaguirre etal., 1998; Oikawa et al., 1995; Trudgill, 1990). Although kinetics of biodegradation of algal metabolites in biological treatment systems have been evaluated and modeled (Rittmann et al., 1995; Nerenberg et al., 2000), there are limited published studies of MIB or Geosmin degradation in natural systems.

This section provides field and laboratory estimates for the rates of MIB and Geosmin biodegradation in reservoirs. Our in situ modeling analysis is based on physical and chemical data collected over a three-year period for three water supply reservoirs near Phoenix, Arizona, augmented by detailed hydrologic data. Mass balance analysis on MIB and Geosmin in the reservoirs indicated a gradual production that could not be attributed to any specific cyanophyte blooms, followed by rapid biodegradation following reservoir destratification. Degradation rates of MIB and Geosmin in laboratory tests were similar to those calculated from reservoir mass balances. Taken together, field and laboratory data suggest that bacterial degradation of these metabolites is enhanced by enhanced nutrient supply during and after thermal destratification.

Mass Balance and Reaction Rate Analysis for Field Data. Mass balances on MIB were developed for each of the three reservoirs to estimate net MIB production or loss rates. The mass of MIB stored in the epilimnion and hypolimnion was computed for each month as the

product of MIB concentration and volume of the layer. Based upon measured parameters, the field reaction rate for MIB (R_F) was calculated using the following equation:

$$\frac{dM}{dt} = Q_{in}C_{in} - Q_{out}C_{out} + \forall R_F$$
 Equation 5.6

Where M is the mass of MIB (ng) in the reservoir, C_{in} and C_{out} are the MIB concentrations (ng/L) of water entering and leaving the reservoir, respectively, Q_{in} and Q_{out} are the flowrates (L/month), \forall is the monthly reservoir volume, and time (t) was taken at monthly increments. A positive R_F value indicates MIB production, and a negative value indicates MIB loss.

Laboratory Methods. Water samples from Saguaro Lake were collected at 5 m vertical depth increments, transported to the lab, and immediately filtered (ashed Whatman GF/F). Batch MIB and Geosmin degradation experiments were conducted in 125 mL amber glass bottles incubated at 22°C in the dark for up to 35 days. Abiotic controls were obtained by adding a biocide (100 mg/L sodium azide) to the samples; results were consistent with abiotic controls held in the dark at 4°C. Geosmin (Waco Ind., Japan) was added in select experiments. Additional experiments using a "biological seed" were conducted to simulate the effects of increased bacterial and nutrient levels on algae metabolite degradation. The biological seed consisted of hypolimnetic water collected from Saguaro Lake 7 days prior to initiation of the above degradation experiments into which 100 mg/L each of sodium nitrate, sodium phosphate, and sodium acetate was added. The bacterial population was not enumerated but the culture was visually milky-cloudy. One mL of the biological seed was added to 125 mL of sample in select experiments. Sample bottles were sacrificed at days ca. 10, 20, 26, and 38; at least 15% of the bottles were duplicated.

Results. All three reservoirs were thermally stratified at depths of 5 to 20 m, typically from April through September or October. Surface temperatures ranged from 10 to 30° C throughout the year. The maximum temperature differentials between the epi- and hypolimnion ranged from 12-14°C for Bartlett and Pleasant reservoirs and 5° C or less for Sagauro Reservoir, respectively (Figure 5.13B). Figure 5.14 shows a representative vertical profile for several water quality parameters. The dissolved oxygen (DO) profile reveals stratification more clearly than temperature.

The shallowest Secchi disk (SD) transparencies were observed in November and December (0.6 to 1.5 m)(Figure 5.13A). The deepest SD transparencies occurred between January and June. Lake Pleasant generally had higher transparencies (5 to 9 m) than Bartlett or Saguaro Lakes (4 to 6 m). Chlorophyll-a concentrations were typically less than 10 μ g/L, but varied seasonally. Chlorophyll-a was detected in the hypolimnion of some reservoirs, indicating cell settling from the epilimnion. Planktonic algae counts typically ranged from < 20 to a maximum of 5000 cells/mL, but were typically 200/mL to 500/mL. Diatoms dominated the epilimnetic algal counts; blue-green counts were always < 300/mL (Figure 5.13C). Only a few algae blooms were observed during the two year study of the reservoirs, based upon visual observation and/or high cell counts (>1000 cells/mL). Chlorophyll-a was not correlated with cyanophyte counts.

MIB and Geosmin followed similar spatial and temporal trends. MIB concentrations were higher than Geosmin concentrations for > 95% of the samples (n = 132) from the epi- and hypolimnions of the three reservoirs, so this paper focuses on MIB. During the sampling event illustrated by Figure 5.14, MIB and Geosmin samples were only collected to a depth of 20m, but

showed maximum concentrations at a depth of 5m. Other, deeper, vertical profiles indicated a gradual decline in MIB/Geosmin concentrations to the reservoir bottom. After thermal destratification MIB concentrations were uniform throughout the water column.

Temporal trends of MIB concentrations are shown for Bartlett Lake (Figure 5.15). Saguaro Lake and Lake Pleasant had similar trends. MIB concentrations generally increased from April through September or October of each year, with higher concentrations in the epilimnion than the hypolimnion. Stratification periods (temperature differential from top to bottom > 4° C) are indicated. Epilimnetic MIB concentrations declined around the time of thermal destratification due to mixing with the lower-MIB hypolimnetic water. The total MIB masses in the reservoirs declined to essentially zero within three months after thermal destratification (Figure 5.15).

Results of laboratory degradation experiments are shown in Figure 5.16. Initial ambient MIB concentrations varied, since the water samples were collected from different depths (corresponding to vertical profile shown in Figure 5.14). Minimal loss of MIB was observed in the sodium-azide spiked controls or the 4° C controls over 36 days of the kinetic study. The results supported the conclusion that the observed losses in non-controls were due to biodegradation. A lag phase of about 10 days was observed for degradation in the epilimnetic samples (0 and 5 m), after which a nearly linear biodegradation rate was observed. Hypolimnetic samples (10, 15 and 20 m samples) did not exhibit a lag phase, and were characterized by an immediate onset of MIB biodegradation.

Addition of the "bioseed" to the 5m epilimnetic sample eliminated the lag phase for MIB degradation observed in the sample without the added "bioseed" (Figure 5.17A). Similar results were observed for Geosmin biodegradation (Figure 5.17B). Pseudo zero-order laboratory biodegradation rates (R_L , ng MIB/L/day) were calculated based upon a linear regression of metabolite concentration versus time for each experiment, using data after the onset of observable degradation (post lag phase for epilimnetic samples without the added bioseed). Linear regressions all had goodness of fit (R^2) values being greater than 0.97. Representative linear fits of data are presented in Figure 5.17B. Rates for MIB biodegradation ranged from 0.8 to 1.2 ng/L/d, with an average of 0.96±0.15 ng/L/d (n=7), and were statistically different (α <0.05) from the abiotic experiments (Table 5.3). Geosmin biodegradation rates were similar (Table 5.3). Over the naturally occurring concentration range considered, R_L values were statistically (α =0.05) independent of initial concentration, initial sampling depth, or initial addition of a bioseed.

Production of Algae Metabolites in Reservoirs. No statistical correlation was observed between MIB concentrations and total biomass measurements (total algae counts or chlorophyll-a) or blue-green algae counts. There are three possible reasons for this. First, MIB was produced by a few specific algae that sometimes produced prodigious quantities of MIB. Geosmin production for a cyanophyte (*Anabaena sp.*) was on the order of 10 to 150 ng Geosmin / ng Chlorophyll-a (Saadoun et al., 2001). Similar results have been observed in the authors laboratories for MIB and MIB producing cyanophytes. Therefore, based upon a median value of 25 ng Geosmin / ng Chl-a, a chlorophyll-a concentration of only 0.002 μ g/L would be required to produce a culture with 50 ng/L of Geosmin. Chlorophyll-a levels in the reservoirs ranged from 0.3 to >10 μ g/L. Thus, it is unlikely, except during the case of a significant bloom of a dominant MIB producing algae that algae biomass indicators (chlorophyll-a, cell counts) would be viable indicators of MIB.

Second, periphyton rather than phytoplankton may be the source of MIB. For example,

sampling in a reservoir (Lake Mathews, CA- maximum storage ~ 2x10⁸ m³) with divers indicated MIB concentrations greater than 1000 ng/L directly above a periphytic bloom of *Oscillatoria* in a single lake cove in 2 to 11 m water depth was probably the source of MIB concentrations of 10 to 20 ng/L throughout the water column in the entire lake (McGuire et al., 1981; McGuire et al., 1984). However, intensive sampling in Saguaro Lake was not successful in identifying benthic producers of MIB and MIB concentrations were fairly uniform spatially and vertically within the epilimion. Elevated MIB levels can therefore occur in reservoirs with very low concentrations of phytoplanktic chlorophyll-a where benthic algae produce MIB instead, a common situation in several California reservoirs, but did not appear to the be case for the Arizona reservoir studied herein.

Third, MIB degrades fairly slowly, so at any given time the MIB in the water column may have originated from an algal bloom that occurred several weeks prior to sampling (Means and McGuire, 1986), obscuring the relationship between MIB levels and measures of algal abundance. Blooms of blue-green algae in the three semi-arid reservoirs were infrequent and not very intense (maximum blue-green counts have been < 500/ml), and it appears that MIB is generated more-or-less continuously. Under this scenario MIB levels increase as long as production exceeds degradation.

MIB accumulation in the epilimnion of the reservoirs were correlated with temperature, consistent with results from previous laboratory experiments that indicated a relationship between extracellular MIB and Geosmin production by different pure algae cultures and temperature (Saadoun et al., 2001; Izaguirre and Taylor, 1998; Izaguirre et al., 1999). An exponential function (MIB (ng/L)= $z \cdot e^{x \cdot Temp(C)}$) was observed to fit season epilimnion MIB concentration in Saguaro Lake (z = 0.15; x=0.21; $R^2=0.64$; n=18) and Bartlett Lake (z = 0.0013; x=0.35; $R^2=0.80$; n=15), but was not statistically significant ($R^2<0.5$) for Lake Pleasant.

MIB accumulation in the hypolimnion of deep reservoirs could be due to a number of different processes (Vanbreemen et al., 1992). Firstly, benthic algae in clear water, or actinomycetes, could produce the metabolites directly in the hypolimnion. However the highest MIB concentrations have always been observed in the epilimnion, and discounted the relative importance of hypolimnetic production. Secondly, settling cyanophyte cells from the epilimnion, as evident by chlorophyll-a detection in the hypolimnion, could lyse upon prolonged darkness, releasing intracellular metabolites in the hypolimnion. Thirdly, metabolites could diffuse across the metalimnion. The thermal gradient across the metalimnion is not as sharp in these reservoirs as is typically found in many natural lakes, so the diffusional barrier associated with the thermal barrier is not as strong. Finally, plunging inflows from upstream reservoirs may transport some MIB to the hypolimnia of downstream reservoirs. This mechanism would likely be most important in Saguaro Reservoir, which continuously receives large inflows throughout the summer. Ongoing work is currently underway to determine the relative importance of these processes.

Net Rates of Metabolite Production / Loss in Reservoirs. The mass of MIB in each of the three reservoirs and timing of thermal destratification was presented in Figure 5.15. Calculated monthly rates of MIB reaction in the reservoir is presented in Table 5.4. These rates are net rates, representing the difference between gross MIB production by algae or actinimycetes and gross losses from biodegradation and other processes (possibly volatilization or photolysis). For Bartlett and Saguaro reservoirs, R_F values were positive during the late spring and summer, reflecting MIB production by culprit algae in the reservoirs. R_F values became negative soon after thermal destratification, with maximum loss rates ($R_{F,max}$) occurring between September

and November and averaged 0.40±0.17 ng/L/d (n=9).

For Bartlett and Pleasant reservoirs, internal reaction was generally the predominant mass flux during periods when MIB mass was changing. For the fall period (September-November), the mass of MIB lost by net internal reaction exceeded mass inflows by 2-30 times and exceeded mass outflows by 2-45 times. Because Saguaro is operated as a pumped storage reservoir with substantial inflows and outflows throughout much of the year, mass fluxes from inflow and outflow are often large and contribute substantially to the change in overall MIB mass. The high MIB influx during the summer reflects MIB production in upstream reservoirs.

In situ R_F values during the fall period were approximately half the value of lab-based R_L values, indicating simultaneous production and loss in the reservoir (Tables 5.3 and 5.4). During the laboratory experiments biodegradation was probably the dominant mechanism occurring since other potential mechanisms were minimized. Filtration of samples minimized production of MIB by lysis of algae cells; new algae growth was minimized by filtration and dark incubation; and volatilization losses were minimized by use of closed vessels. $R_{F,max}$ represents MIB losses due to biodegradation, volatilization, photolysis, and other potential losses.

 $R_{F,max}$ lagged by one to two months after thermal destratification, and corresponded to the fallseason month with the highest chlorophyll-a concentrations. The observed lag period in the field may have similar origins as the lag period observed in the laboratory experiments with the epilimnetic waters. In the lab bioseeding increased bacteria and nutrient levels, and biostimulated the onset of MIB biodegradation. In the field, turnover was accompanied by decreased SD transparencies (Figure 5.13) and increasing TN and chlorophyll concentrations, all indicative of higher biological activity.

The increased biomass present at the time of the maximum calculated MIB loss rate (R_{Emax}), as indicated by elevated chlorophyll-a levels and SD transparencies, could provide carbon primary substrate material for bacterial growth. MIB is a probably degraded as a secondary substrate in fixed-biofilms (Rittmann et al., 1995). A secondary substrate may yield no energy to the cell (i.e., co-metabolism) or negligible energy due to its low concentration. For secondary substrate utilization the Monod relationship can be simplified to a mixed second-order relationship: $r_{\text{utilization}}$ = -K₂S_sX; where K₂ is the mixed second order rate coefficient (~ 1 to 2 cm³(mg_xhr)⁻¹ for MIB and Geosmin), S_s is the secondary substrate concentration and X is active biomass density Biodegradation of MIB & Geosmin occurs and will be a function of (Rittmann et al., 1995). retention time with active biofilms, and presence of a primary substrate. Higher bacterial activity would occur with elevated primary substrate and nutrient levels, increasing the rate of MIB utilization. If MIB were degraded as a secondary substrate, R_i in lab experiments would have increased with addition of primary substrate. This did occur in our experiments (e.g., bioseeded experiments), although we investigated only one level of nutrient addition. Izaquirre et al. (1988) observed a lag period prior to degradation of MIB by natural lake bacteria, and postulated it represented the time for growth of MIB degraders. Limited bacterial counting was done in that work and showed higher bacterial counts when MIB was used as a sole carbon substrate (initial MIB = 23 mg/L) compared cultures without MIB, and concluded that other unidentified organic or inorganic nutrients were required for MIB degradation at environmentally relevant concentrations. Extrapolation of the results reported herein to other systems could be limited to similar semi-arid region reservoirs with comparable algae biomass densities. Higher biomass densities would probably biostimulate natural lake bacteria to a higher extent, and potentially increase the rate of MIB biodegradation as a secondary substrate. Bacteria in the hypolimnion may already have been acclimated to MIB, whereas bacteria in the epilimnion were

not.

Bacteria appear to be responsible for MIB degradation in the lakes. This is supported by observations of population cycles of gram positive heterotrophic bacilli that appear in greatest numbers at a time corresponding with the highest levels of earthy-musty odors (Hoehn, 1965). The cyclic patterns were characterized by a disappearance of the earthy-musty odors and increasing populations of bacillus. Natural bacterial populations in lake water were hypothesized to be the mechanism for MIB and Geosmin degradation, after observations of rapid (3-5 weeks) degradation for high Geosmin (> 150 ng/L) and MIB (inoculated at 1000 ng/L) concentrations (Means and McGuire, 1986). Loss rates in these systems were estimated to be between 5 and 50 ng/L/d for MIB and Geosmin, respectively. The 5 ng/L/d Geosmin loss rate occurred in a lake and may have been due to a number of factors combined: dilution after reservoir destratification, hydraulic flushing with imported transbasin water, and / or biodegradation. Separately, a rate of nearly 50 ng/L/d for MIB removal was estimated from MIB inoculated lake water, and may have been impacted by a primary carbon source present in the MIB solvent. Bacillus cereus has been suggested as the key bacilli species responsible for degradation of earthy-musty odors in lakes and sand filters (Hoehn, 1965; Oikawa et al., 1995; Danglot et al., 1983: Saadount and El-Migdadi, 1998: Ishida and Miyaji, 1992: Macdonald et al., 1987).

During the period of maximum MIB loss ($R_{F,max}$) the primary substrate for heterotrophic bacteria probably is organic matter released during algae growth or lysis. Roughly 40% to 50% of the dissolved organic carbon (DOC) obtained from laboratory cultures of green algae is biodegradable in bioacclimated sand reactors (Allgeier et al., 1996).

Implications for Drinking Water Supply Lake Management. This study quantified the accumulation and degradation of MIB in the three study reservoirs. MIB accumulates in the epilimnion during the warm summer months. Following overturn, MIB concentrations decline for two to three months, to near zero levels. In two of the reservoirs, internal reaction was the predominant mass flux term. In all three reservoirs, R_L during this period was 0.3 to 1.0 ng/L-day, with an average of 0.4 ng/L-day. Observed $R_{F,max}$ values in the reservoirs were on the same order of magnitude as laboratory biodegradation rates (R_L) using reservoir water.

Lake managers can utilize this knowledge to predict MIB loss rates. These predictions could be used to warn downstream utilities of imminent MIB episodes, allowing them time to start withinplant treatment (e.g., addition of powdered activated carbon) before elevated concentrations reach their plants. In some situations, water could be held in the lakes for a few months while the metabolites degrade, while downstream water treatment plants used alternative water sources (e.g., lower MIB/Geosmin containing surface waters, groundwaters). This strategy has been adopted by the CAWCD in its operation of Lake Pleasant. In 1999, MIB levels built up in the epilimnion. During turnover, elevated MIB levels were found throughout the water column. The outflow was turned off, and water was routed directly from the Colorado River to downstream customers, bypassing Lake Pleasant. When the episode subsided, water was again released from the reservoir (Baker et al., 2000).

Heterotrophic bacteria present in reservoirs (e.g, bacilli) appear responsible for degradation of two algae metabolites studied (MIB and Geosmin). Thermal destratification and maximal chlorophyll-a productivity provide bacteria with inorganic nutrients and primary carbon substrate (biodegradable cellular material) and create conditions conducive for microbial growth, and subsequent co-metabolism of ng/L concentrations of MIB and Geosmin. Hoehn (1965) applied

this in-situ degradation concept a step further by validating the feasibility of bioseeding a reservoir (10 km²) with mass cultures (9 m³ lots) of Bacillus cereus applied to the lakes surface and shoreline (Hoehn, 1965; Silvey et al., 1964). The bioseeding, or bioaugmentation, successfully decreased the threshold number for earthy-musty odors, but a "decaying vegetation" odor was detected. Developing a better understanding of the factors controlling bacterial degradation of MIB may lead to management practices (e.g., short-term nutrient enrichment or bioseeding) to accelerate the process.

Approximately 75% of surface waters containing T&O compounds (e.g., MIB or Geosmin) had detectable levels of microcystins in one survey (Carmichael et al., 2000). Although the same cyanophytes species do not produce both T&O and biotoxin metabolites, these results imply that conditions that favor cyanophyte growth can lead to the production of both metabolites in a water supply. Conclusions based upon the loss of MIB and Geosmin are consistent with observations for other cyanophyte extracellular metabolites (e.g., cyanotoxins). Some studies report prolonged persistence of cyanotoxins in aquatic systems (Jones and Orr, 1994; Ressom et al., 1994). However, most aquatic systems contain bacteria capable of biodegrading the cyanotoxins to forms of low health concern (Yoo et al., 1995; Bourne et al., 1996; Lam et al., 1995). However rates of cyanotoxin biodegradation range from a few days in the laboratory (generally high cyanotoxin concentrations used) to weeks in the field (presumably cyanotoxins used as a secondary substrate), where a lag phase occurs after the peak cyanotoxin concentrations prior to the onset of cyanotoxin degradation. The approaches used here to study MIB and Geosmin degradation could readily be extended to other algal metabolites.

Soil Leaching of MIB and Geosmin

Background. In March 2000, levels of MIB were approximately an order of magnitude higher in the SRP canals than in February 2000 or April 2000. Furthermore during March 2000, MIB concentrations in Bartlett or Saguaro Lakes were largely unchanged from previous months. This observation suggests a rapid, but short-duration pulse of MIB into the system downstream of Bartlett and/or Saguaro Lakes, and upstream of the head of the Arizona and South Canals. A significant rainfall event (3.21 inches over 4 days) occurred between March 5th and 8th, 2000. This observation and subsequent data lead to development of the following hypotheses:

- <u>Primary hypothesis</u>: Rainfall mobilizes MIB and Geosmin produced by soil bacteria into surface waters.
- <u>Alternative hypothesis</u>: Rainfall transports nutrients into surface water that results in stimulation of blue-green algae growth, resulting in MIB/Geosmin production.
- <u>Alternative hypothesis</u>: Rainfall transports particulate material into surface waters that increase shading, causing blue-green algae to release MIB/Geosmin.

During March 2000, the flow below the lowest elevation lake (Bartlett Lake) on the Verde River was 100 to 150 cfs and only 8 cfs on the Salt River. Therefore, the Verde River provided nearly the entire flow into the Granite Reef Diversion "lake", from which water flows into the Arizona and South Canals. Figure 5.18 shows stream flow in the Verde River below Bartlett Lake and downstream at the USGS station near Scottsdale, AZ. Typically, the flow decreases along the Verde River due to Indian-related agriculture withdrawals. However, in early March flows downstream on the Verde River at Scottsdale were higher than released flows from Bartlett Lake. This occurred during a period of rainfall were daily precipitation amounts at Bartlett Lake

were recorded to be 0.47", 1.94", 0.77", and 0.06" between March 5th and 8th.

Routine baseline sampling was conducted on March 16th for sites located at the head of the Arizona and South Canals. During this sampling, the MIB concentration below Bartlett Dam was 2.4 ng/L whereas the concentration at the head of the Arizona Canal (above the CAP input) was 21.5 ng/L. CAP enters the SRP canals downstream of Granite Reef Dam. The percentage of CAP water entering the Arizona Canal (44%) was similar to that entering the South Canal (43%). CAP water had a MIB concentration of 2.7 ng/L. In the Arizona Canal below the CAP input, the MIB concentration was 15.1 ng/L which roughly corresponds to the dilution of Verde River water by CAP water. Therefore, the MIB concentration at the head of the Arizona canal was considered "valid". A similar analysis was conducted on the South Canal. Therefore, MIB concentrations increased between the outlet of Bartlett Lake and the head of the SRP canal.

Based upon data from the March 16th baseline sampling, an intensive sample collection effort was undertaken along Verde River on March 27th, 2000. MIB concentrations at several sites along the Verde River below Bartlett Lake (R7, at Green Valley, at Beeline Highway) only had MIB concentrations of 2 to 3 ng/L. The Arizona Canal (above CAP input) had a MIB concentration of 5 ng/L. Therefore, the elevated MIB levels observed nearly 2 weeks earlier were no longer present. The March 2000 MIB elevated MIB event was termed a "rapid short-duration" event, and contrasts with several months of increasing MIB concentrations that typically occur between August and October.

Soil microorganisms are well known producers of MIB. We hypothesize that rainfall saturated the soil, which solubilized and transported MIB into the nearest surface water (e.g., Verde River). Elevated stream flows in the Verde River between Bartlett Lake and Scottsdale confirmed that rainfall affected stream flow. The mobilization of soil-derived MIB decreased after stream flow levels returned to "normal" (i.e., no overland or subsurface flow contributions). In review of MIB data collected by the University of Arizona for a previous SRP project (3/97 – 7/98), rapid short-duration spikes of MIB also occurred in the Verde River (at Beeline Highway) and Saguaro River (at Bush Highway) (Figure 5.19). Based upon historic data, many of these rapid short-duration spikes occurred shortly after rainfall events, as evident by high turbidity events at Val Vista WTP.

Methods. Using soils collected from different locations, irrigated (S4) and non-irrigated (S1-S3), experiments were conducted to mobilize MIB or Geosmin. A fixed amount of soil was placed in a batch reactor with water and agitated for 40 hours. Samples were centrifuged and filtered prior to analysis for MIB and Geosmin.

Results. The results are presented in Figure 5.20. The results indicate that soil can leach MIB and Geosmin, and well-irrigated soils have a slightly higher tendency than non-irrigated soils.

Over the course of the current 3-year ASU study rainfall amounts have been below normal, and large MIB spikes have not been observed. It could be hypothesized that during wetter years, soil bacteria generate more MIB and Geosmin that could be mobilized during subsequent rainfall events.

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IN-LAB GROWTH OF MIB PRODUCING ALGAE

During this study, there have been several cases of organisms ceasing production of MIB or Geosmin. This trend has confounded the identification and investigation of producers isolated from the various water systems. However a potential suitable medium for triggering production of MIB and Geosmin by these algae was identified.

Isolate 506, a *Pseudanabaena sp.*, was confirmed to produce MIB soon after being isolated from the Verde River (Figure 5.21). However, it later stopped producing MIB. Then when grown in media made from Verde River water, the alga again began producing MIB. Media with three different treatments of Verde River water were utilized: 1) raw Verde River water, 2) water filtered thorugh a 0.2 μ m pore-size membrane and 3) autoclaved. The *Pseudanabaena sp.* produced MIB in all three media treatments (Figure 5.22)

Production of MIB or Geosmin could be triggered by nutrients or other factors within the water of the water systems. Therefore the transport of a producing organism from one water system to another could trigger production, as well as production being turned off/on by mixing water from different systems.

Linear regression of data from monthly baseline monitoring of algae and water quality parameters in Saguaro Lake indicated there is no linear relationship between algae and MIB production (Table 5.5). There does, however, appear to be a correlation between temperature and MIB production, with the temperature taken at a 10 m depth having strongest correlation. Using the Pearson Correlation, the significance for 10 m temperature and MIB concentration is .000 with a high Pearson Correlation of .669 (Table 5.6).

Linear regression analysis of nitrogen, phosphorus and conductance in the epilimnion of Saguaro Lake shows a significant linear relationship with total nitrogen and dissolved nitrogen (Table 5.7). A regression analysis of temperature multiplied by total nitrogen with MIB has a significance of .000 with r^2 of .779 (Table 5.8). Together, total nitrogen and temperature at 10 m depth, are strong predictive tools for the production of MIB in the epilimnion of Saguaro Lake (Figure 5.23).

ISOLATION AND CHARACTERIZATION OF CULPRIT CYANOBACTERIA UNDER LABORATORY CONDITIONS

Objectives

The objectives of this task were to identify the culprit taste and odor-causing organism(s) and the associated environmental and physiological conditions that lead to their becoming a nuisance, and to provide the biological basis on which effective mitigation measures could be determined to prevent or reduce the production of taste and odor compounds in the field.

Background

MIB and Geosmin are produced as secondary metabolites by a number of cyanobacteria, as well as by actinomycetes and certain species of fungi. Most MIB and Geosmin produced in cyanobacteria are retained in the cells, whereas a minor portion is released into water under normal physiological conditions. Subcellular thylakoid and cytoplasmic membranes are the major binding sites for most of MIB and Geosmin in the cyanobacteria. Therefore, a spike of MIB and/or Geosmin in a water body is likely due either to occurrence of a high density of producing organism(s) or to massive release of the secondary metabolites from the cells upon lysis and decomposition of MIB- and Geosmin-containing biomass.

MIB and Geosmin are thought to be derived from monoterpene and sesquiterpene precursors, respectively, and their synthesis is linked to chlorophyll and carotenoid synthesis in cyanobacteria. However, the biosynthetic pathway of MIB and Geosmin remains speculative, as no genes or enzymes directly involved in MIB and Geosmin production has been identified and characterized. The cellular functions of MIB and Geosmin are not known.

Environmental factors may exert a profound influence on cyanobacterial growth and production and release of MIB and Geosmin. The factors include, but are not limited to, light intensity, temperature, and nutrient concentration. Controlled laboratory studies of isolated MIB- and Geosmin-producing cyanobacteria is an essential approach to understand how the production may be influenced by biotic and environmental factors. Data obtained from the laboratory studies will be discussed in relation to their ecological significance and will serve as guide for future field-scale studies of various control and operational measures on MIB- and Geosminproducing organisms.

Methods

The isolation of planktonic and periphytic algae commenced during the first reporting period as a necessary precursor to controlled laboratory experiments. Unialgal cultures are required before an organism may be conclusively labeled an MIB or geosmin-producer. For this effort, collected planktonic and periphytic algae were transferred to several standard culture media including Alga-Gro freshwater medium, BG 11 medium and Bold's Basic medium enriched with soil-water medium (Carolina Biological Supply Company, 1978) (Figure 5.24). These transfers were made to both agar and liquid medium. Almost thirteen hundred (1292) algal cultures were isolated between August 1999 and October 2001 (Figure 5.25). In addition, 16 actinomycetes were isolated during the same period (Table 5.11). Raw water samples and laboratory cultures were constantly evaluated for odors in an attempt to detect the presence of earthy-musty odors.

All experiments were carried out in a batch mode, using either test tubes (10 ml culture volume) or flasks (40 ml culture volume). Cultures were incubated without agitation in a Percival illuminated growth chamber (model: 135LLVL, Boone, Iowa) (Figure 5.26A). Unless stated otherwise, a growth temperature of 26 °C and light intensity of 20 μ mol m⁻² s⁻¹ was used.

Temperature experiments were conducted on a custom-designed thermal gradient device (Figure 5.26B). A stable temperature gradient was established along an aluminum plate by heating one end of the plate with a heating element and cooling the opposite end with a refrigeration evaporator. Light intensity experiment was conducted in growth chamber in which culture tubes were placed at different distances from the light source.

Samples were taken from each culture at designated time intervals. Algal biomass from each culture vessel was extracted in 100% methanol at 4 °C in the dark for 24 hours. Absorbance at 664 nm for chlorophyll *a* was determined on an aliquot of the methanol extract using a spectrophotometer (model DU-64, Beckman Instruments Inc. Fullerton, CA). Increases in chlorophyll *a* concentration between consecutive samplings during the exponential growth phase were used to calculate the specific growth rate (μ ?d⁻¹) using the equation μ @⁻¹) = (LnX₂-LnX₁)/(t_2 - t_1), where X_1 and X_2 are the chlorophyll *a* concentrations at times t_1 and t_2 , respectively.

MIB and Geosmin recovered from growth medium and algal biomass were analyzed using GC/MS method, as described in Task 1.

Results

Isolation of MIB/Geosmin Producers

A review of the baseline monitoring data for MIB and geosmin from August 1999 through October 2001 revealed that several areas in the system appeared to be potential "hot spots" for the production of taste and odor-causing compounds. During intensive monitoring, additional samples were collected from the "hot spots" in an effort to isolate and identify species that produce MIB and/or geosmin. Table 5.9 shows the number of algal isolates obtained from each site during the project. Intensive monitoring efforts were undertaken at the following sites because high MIB and/or geosmin concentrations were reported: Waddell Canal site (R3), Squaw Peak and Deer Valley Water Treatment Plants (R14-R17), the epilimnion sample from Lake Pleasant (R2A), Saguaro Lake (R9A and R9B), and the Verde River above Bartlett Lake (R5). During intensive monitoring, additional samples were collected from these "hot spots" in an effort to isolate species that produce MIB and/or geosmin.

The production of taste and odor causing compounds was confirmed using GC/MS in ten algae isolates collected from six baseline-monitoring sites, three Arizona Canal intensive-monitoring sites and one Saguaro Lake intensive-monitoring site between August 1999 and June 2002 (Table 5.10). MIB production was confirmed in one Phormidium *sp.* isolated from the Verde River between Horseshoe and Bartlett Lakes (R5) and three different *Pseudanabaena spp. Pseudanabaena* sp. #1 was isolated from three different intensive-monitoring sites along the Arizona Canal. *Pseudanabaena* sp. #2 was isolated from one intensive-monitoring site on Saguaro Lake (SS4). *Pseudanabaena* sp. #3 was isolated from the Arizona Canal above the Cross-Connect (R12). Geosmin production was confirmed in *Oscillatoria splendida* isolated from the CAP Canal above Waddell Canal (R1), the CAP Canal at 7th Street (R4) and the Deer Valley WTP Inlet (R16), and *Oscillatoria agardhii* isolated from the Verde River below Bartlett Lake (R7). Over 120 presumptive isolates were analyzed using GC/MS to confirm whether MIB and/or geosmin were produced. All of the presumptive producers tested negative for MIB and/or geosmin production.

Geosmin production was confirmed for 16 actinomycete strains (two confirmed using GC/MS and 14 based on similar odor to GC/MS tested isolates) isolated from Sites R1, R6A, R7, R9B, R11, R12, R13, R14, R16 and R20 during the same period (Table 5.11). There was no indication that actinomycetes were responsible for the production of MIB throughout the project.

MIB Producer Pseudanabaena sp.

Effect of temperature. Four temperatures (12, 20, 25 and 35 °C) were evaluated and the results are shown in Figure 5.27. The *Pseudanabaena* cells exhibited little growth at 12 °C. A significant increase in growth was observed at 20-22 °C, with the growth further enhanced as temperature increased to 35 °C. Similar to growth, little production and release of MIB was detected in cultures maintained at 12 °C. Increased production and release of MIB occurred at the higher temperatures, exhibiting a trend that the higher the temperature the higher the production of MIB. At 12 °C, up to 38% of MIB produced by the cells was released into the growth medium. When temperature increased from 20 to 35 °C, the percentage of released MIB to produced MIB was similar: it increased slightly from 5 to 8% over the culture period.

Within the temperature range, the production and release of MIB occurred during all growth phases, with the maximum values occurring during the exponential phase, and leveling off or declined thereafter when the culture entered the deceleration, stationary and death phases (Figure 5.27B and C). The decrease in production and release of MIB during stationary and death phases was more pronounced in cultures grown at higher temperatures (25 and 35 °C). It was during this period that the odors from the culture shifted from earthy/musty to a more complex foul/rotten odor, perhaps indicative of a changing cellular secondary metabolism.

Effect of light intensity. The effect of four light intensities of 5, 25, 50 and 100 μ fnol m⁻² s⁻¹ on growth and MIB production were studied and the results are shown in Figure 5.28. A lag phase of ca. 6 days was evident in the cultures at 5 μ fnol m⁻² s⁻¹ before notable growth occurred. As cell numbers increased, the production of MIB increased. The production and release of MIB appeared to be somewhat proportional to the increase in cell numbers in the exponential phase. On average, ca. 8 % of produced MIB was released into the growth medium (Figure 5.28C). With increasing light intensity, cells underwent the acceleration and exponential growth phases without a significant lag phase. The optimal light intensity range (25 to 50 μ fnol m⁻² s⁻¹) resulted in the highest biomass production. A further increase in light intensity to 100 μ fnol m⁻² s⁻¹ resulted in decreased growth and a shorter time for the cultures to enter into the stationary and death phases. At a light intensity of 25 and 50 μ fnol m⁻² s⁻¹, the production of MIB paralleled the growth in the exponential phase (Figure 5.28A). Thereafter the production of MIB leveled off and/or declined. At 100 μ fnol m⁻² s⁻¹, a similar positive correlation was evident only in early exponential phase. Both production and release of MIB decreased in the stationary phase (Figure 5.28B).

Effect of light intensity on production and release of MIB was compared on a per chlorophyll *a* basis (Figure 5.29). The cellular production and release of MIB remained low and constant in cultures at 5 μ mol m⁻² s⁻¹. At higher light intensities of 25, 50, and 100 μ mol m⁻² s⁻¹, enhanced production of MIB occurred in early exponential phase and then declined during deceleration, stationary and death phases. On a per chlorophyll *a* basis, low release of MIB was associated with the lowest light intensity and high release of MIB was associated with the highest light intensity. Under the optimal light intensity range of 25 to 50 μ mol m⁻² s⁻¹, released MIB fell between the two extremes.

Effect of extended dark incubation. Prior to the dark treatment, all cultures were maintained at 30 μ mol m⁻² s⁻¹ for 7 days to ensure that the cells were in the exponential growth phase for the maximal production of MIB. Following the transfer of the cultures into dark conditions, the biomass concentration decreased rapidly over time (Figure 5.30). The cell-bound MIB decreased from 800 ug L¹ to below 10 ug L¹ within 18 days, and remained low for the

remainder of the experiment (Figure 5.30). On the other hand, MIB concentration in the growth medium increased two-fold (from 65 ug L⁻¹ at day one to 165 ug L⁻¹ at day 18) during the first 18 days in the dark period. The concentration of MIB in the growth medium decreased gradually thereafter. No induction of MIB by extended dark period was observed in this organism. The increase in MIB concentration in the growth medium was the result of release of this compound from the cells due to cell lysis and decomposition during the extended dark period. The ecological significance of this finding is that even a small portion of a MIB-producing population transferred from photic zone into the dark zone of a water body could potentially contribute to a large increase or pulse in MIB concentration in the water column and may last for an extended period.

Geosmin Producer-Phormidium sp.

Effect of temperature. Three temperatures were tested: 12, 20 and 25 °C. Like the *pseudanabaena* sp., the *Phormidium* did not grow well at a temperature of 12 °C and below. When temperature was increased from 12 to 25 °C, algal biomass increased substantially (Figure 5.31A), as did the production and release of Geosmin (Figure 5.31B and C). On the other hand, a low temperature of 12 °C seemed to enhance the production of Geosmin, on a per chlorophyll *a* basis, whereas higher temperatures of 20 and 25 °C resulted in low and somewhat constant production of Geosmin (Figure 5.32A). A general trend was evident that the release of Geosmin into the growth medium increases over the culture period, however, growth temperature exerts little effect on this trend (Figure 5.32B). On average, ca. 2 % of Geosmin produced by the cells was released into the growth medium at 12 °C, whereas up to 9 % of Geosmin releasing was observed in cultures grown at higher temperatures (Figure 5.32C).

Effect of light intensity. The effect of four light intensities (5, 25, 50 and 100 µ/hol m⁻² s⁻¹) on Geosmin production was evaluated. An inverse relationship was evident between light intensity and chlorophyll *a* concentration (Figure 5.33A). However, a direct positive correlation between light intensity and cell bound- and released-Geosmin was also observed (Figure 5.33A and B). For instance, a high light intensity (100 µ/hol m⁻² s⁻¹) resulted in a medium production of Geosmin, although at this light intensity the biomass production was low. As a result, on a per chlorophyll *a* basis, the higher the light intensity the higher the production and release of Geosmin (Figure 5.34B). The percentage of released Geosmin to Geosmin produced by the cells was also affected by light intensity. Roughly, 10 % of cellular produced Geosmin was released into the growth medium under the light intensity of 5 to 50 µ/hol m⁻² s⁻¹. High light intensities may also stimulate the release of Geosmin, and up to 35 % of released Geosmin was observed in cultures exposed to 100 µ/hol m⁻² s⁻¹ (Figure 5.34C).

Effect of extended dark incubation. *Phormidium* cultures were initially maintained at 30 **m**² s⁻¹ for two weeks to allow cultures to reach the linear growth phase. Then, the culture tubes were transferred into a black box to begin the dark incubation for additional 20 days. Vigorous growth occurred with a concomitant increase in cell bound Geosmin during the first two weeks in light, and at the same time a slow increase in Geosmin concentration in the growth medium was also detected (Figure 5.35A). In the following dark period, no significant changes in chlorophyll *a* and cell bound Geosmin were observed for the first four days. However, a notable increase in Geosmin concentration in the growth medium was detected during this period (Figure 5.35B). Thereafter, rapid decline in both chlorophyll *a* and cell bound Geosmin occurred, and the cells lost about 80 % of their chlorophyll *a* and cell bound Geosmin within five days and continued to decrease over time. Along with these changes, Geosmin concentration in the
medium increased three-fold and then declined gradually. Again, this experiment demonstrated that under certain circumstances a spike in Geosmin concentration could be attributed to cellular lysis and decomposition of producers that encounter an extended dark period either in the lower part of the reservoirs or in canal.

It becomes clear that although the growth rate of *Phormidium* cells was only about one-fifth of that of *O. splendida* under optimal culture conditions, *Phormidium* cells may release at least 10 to 100-fold more Geosmin into the surrounding medium than *O. splendida*. This indicates that there is great variation in the production potential of different cyanobacterial strains.

Geosmin Producer-Oscillatoria splendida.

Effect of growth phase. In batch experiments, the growth of O. splendida, as indicated by chlorophyll a concentration, followed a typical trend: growth proceeded through a lag-, exponential-, linear-, stationary- and decay phases (Figure 5.36). The amount of Geosmin released from the cells was generally biomass-dependent: the higher the biomass concentration (chlorophyll a), the higher the Geosmin concentration in the medium (Figure 5.36A). There was about three orders of magnitude more Geosmin found within cells than there was released in the medium. At peak biomass (day 21) the ratio of cell-bound Geosmin to Geosmin in the medium was about 5,000. Cellular content of Geosmin followed essentially the same pattern as the growth in biomass. However, cell-bound Geosmin per chlorophyll a was the highest when the cells were in the exponential growth phase. Less cell-bound Geosmin per amount of chlorophyll a was found in cells in lag or stationary growth phases (Figure 5.36B). Clearly, Geosmin production is constitutive in O. splendida, and the higher the specific growth rate the higher the cellular Geosmin content. From the literature, the cellular content of Geosmin can vary by three orders of magnitude among different cyanobacterial species (0.025 to 97.4 ug Geosmin ug⁻¹ chlorophyll a). Our isolate of O. splendida appears to be a comparatively strong Geosmin producer (Table 5.12).

Effect of temperature. Effects of temperature on growth and production of Geosmin were studied at three temperatures, 12, 20 and 26 °C, to reflect winter/early spring, late spring/fall and summer conditions in the Arizona Canal. The specific growth rate of *O. splendida* increased steadily from 0.04d⁻¹ at 12 °C to 0.22 d⁻¹ at 26 °C (Figure 5.37A). As temperature increased, the concentration of cell-bound Geosmin increased with increasing algal biomass. However, cell-bound Geosmin per amount of chlorophyll a was significantly higher at lower temperatures (Figure 5.37B). On a volumetric basis, the amount of Geosmin released into the medium was similar at all three temperatures. When released Geosmin was normalized on a per-chlorophyll a basis, more Geosmin was released from the cells at lower temperatures (Figure 5.37C).

Effect of light intensity. An inverse relationship between light intensity and the specific growth rate was evident in *O. splendida* cultures (Figure 5.38A). The highest specific growth rate of 0.26 d¹ was obtained in cultures at the lowest light intensity of 6 μ mol m⁻² s⁻¹. The specific growth rate decreased as light intensity increased to 100 μ mol m⁻² s⁻¹. Higher concentrations of Geosmin in the medium were associated with cultures grown at lower light intensities (or with higher biomass concentrations) (Figure 5.38B). On the other hand, a positive correlation between light intensity and cell-bound Geosmin was evident (Figure 5.38C). Cell-bound Geosmin in *O. splendida* was three times as much per amount of chlorophyll *a* at 100 μ mol m⁻² s⁻¹.

Effect of dark incubation. The *O. splendida* cultures were first illuminated at 20 μ mol m⁻² s⁻¹ and 20 °C for one week to reach the exponential growth phase and then transferred to a dark chamber at the same temperature for 25 days. Algal biomass and water samples were taken at several time intervals for analysis of chlorophyll *a* and Geosmin concentrations. As shown in Figure 5.39A, the chlorophyll *a* concentration of the cultures remained stable for the first 14 days, and thereafter declined gradually. By day 25, chlorophyll *a* in the cultures was almost undetectable as the cells were decomposing.

During this period, both cellular Geosmin content and Geosmin in the medium underwent dramatic changes. The content of cell-bound Geosmin increased by 50% over the first 7 days, and decreased gradually for the following 7 days. A considerable loss of cellular Geosmin was observed 14 days after initiating the dark treatment, and continued to decrease through the 25 days. Geosmin in the medium was low for the first 14 days, and then increased dramatically in the following 7 days. After a peak of 13 ug L^{-1} , Geosmin in the medium decreased rapidly by day 25 (Figure 5.39B).

Effect of nitrate and phosphate. Small increases in chlorophyll *a* concentration were observed in laboratory cultures of *O. splendida* grown in raw canal water, but cell division ceased after four days of incubation. Likewise, cultures with canal water enriched with 1.0 mgL⁻¹ of PO₄³⁻ (P as phosphorus) resulted in similar growth. In contrast, an extended growth period and a considerably higher chlorophyll a concentration were obtained in cultures in which 5 mg N L⁻¹ of nitrate (N as nitrogen) was added. A further increase in chlorophyll a concentration was observed in cultures enriched with 20 mg N L⁻¹ of nitrate and 1.0 mg P L⁻¹ of PO₄³⁻ (Figure 5.40, curved line). Following the growth pattern, Geosmin concentrations in the culture media were low in both the control and the phosphate-enriched cultures. A higher concentration of Geosmin occurred in the medium when cultures had additional nitrate or nitrate together with phosphate (Figure 5.40, bars). However, cell-bound Geosmin per chlorophyll *a* was similar across these treatments.

Discussion

Numerous taste and odor incidents associated with formation of MIB and Geosmin in drinking water supplies have been reported worldwide. The concentration of MIB and Geosmin may differ by two orders of magnitude (several hundred ng per liter) among different aquatic environments. This may be attributed to differences in species composition of algal communities. Since algae-based production of MIB and Geosmin is restricted to certain cyanobacteria, a water body in which cyanobacteria are the dominant species and/or in high population density may have greater probability of producing more MIB and/or Geosmin and other off-flavor compounds. Furthermore, cyanobacterial composition is largely influenced by water chemistry. High nitrogen and phosphorus loads in water, which may stimulate algal blooms, have often been linked to odor- and taste-incidents. Interestingly, it was observed that Geosmin appeared to be more common in soft water with total alkalinity and hardness below 50 mg L⁻¹ as CaCO₃ whereas MIB is typical for hard water. The comparatively high MIB, but low Geosmin concentrations occurring in the metropolitan Phoenix water supply source may be related to the hard water properties (over 150 mg L⁻¹ CaCO₃) of the water supply.

The three culprit organisms isolated from the Phoenix water supply system that have undergone laboratory study are representative of the periphyton, making up part of microbial mats along the submerged canal walls and littorals of lakes and rivers. Historically, studies were focused on the planktonic cyanobacteria as the major taste and odor producers. In recent years, however,

periphytic species have begun to receive more attention. Although these three species appeared only in moderate population densities in the system, they have been shown to be significant producers of MIB and Geosmin.

Laboratory studies demonstrated that MIB and Geosmin production may occur throughout the growth stages of three culprit organisms, with the highest production usually in the exponential growth phase. A decline in cell-bound MIB or Geosmin during the stationary growth phase was likely due to increased secretion or leakage of the compound into the culture medium. Therefore, the production of MIB or Geosmin must be constitutive in these species. Considering that only a small portion of cellular synthesized MIB or Geosmin was released into the growth environment under normal culture conditions, a spike of MIB and/or Geosmin production in aquatic environments must primarily be a result of increasing biomass of producer organisms under favorable growth conditions, and/or followed by large release of these odorous compounds upon lysis and degradation of the cells during the stationary and decay phases.

Our laboratory study of these three MIB/Geosmin producers has confirmed the phenomenon observed in the water system: no significant production of MIB and Geosmin occur until water temperature increase to above 20 °C. The temperature dependent growth, production and release of MIB and Geosmin of these organisms contributes to the frequent episodes of MIB and Geosmin production during the summer and fall seasons in the Phoenix water supply sources.

In conclusion, we have extensively characterized one MIB- and two Geosmin-producing cyanobacteria isolated from the metropolitan Phoenix water supply that exhibit high intracellular concentrations and comparatively low extracellular release of MIB or Geosmin, except upon cell lysis. Our results also illustrate that MIB and Geosmin production is constitutive, but variable and influenced by environmental conditions.

SUMMARY

Experiments were conducted in the laboratory to (1) screen parameters important for implementation at field- or full-scale and (2) gain insights into a biological process or mechanism. Powder activated carbon (PAC) tests demonstrated PACs ability to remove MIB and Geosmin from surface waters in Arizona. Performance of PAC brands varied, were lower in surface water than distilled water, and the kinetics of MIB adsorption requires at least one hour of contact time. Ozone and advanced oxidation processes that produce hydroxyl radicals can oxidize MIB and Geosmin, and are more effective than chlorine dioxide; chlorine did not oxidize MIB or Geosmin. Copper biocides can kill MIB-producing algae, but organically complexed copper products should be avoided since they react with free chlorine to form organic chloramines. Inorganically complexed copper products are recommended. Coating concrete canal walls with biocides or photo-reactive paints offer potential to reduce periphytic biomass and reduce in-canal T&O production.

Environmental factors (temperature, light intensity, growth phase, and nutrient conditions) affected culprit algae growth and production and release of MIB and Geosmin into water. Approximately 8 to 10 culprit algae were isolated from the water supply system which produced MIB or Geosmin, from over 1000 cultures. MIB and Geosmin biodegrade in reservoirs between the months of November and January at rates on the order of 0.5 to 5 ng/L/day. MIB and Geosmin degradation in the lower parts of the canal system have also been observed. Soils,

especially irrigated and vegetated soils, can leach MIB and Geosmin during rainfall and runoff events. This may be a significant factor for "pulses" of T&O compounds that occurs shortly after precipitation events.

This study also provides direct physiological evidence that an extended period of darkness (several days or weeks) may affect the cellular production and release of MIB and Geosmin. In case of O. splendida, over 50% increase in cellular content of Geosmin in the dark for the first 7 days suggests a dark-triggered active metabolic partitioning of carbon sources toward the synthesis of Geosmin. On the other hand, the remarkable increase in MIB or Geosmin in the medium and concomitant decrease in cellular MIB and Geosmin content during the extended dark period indicates the onset of lyses and decomposition of the cyanobacterial biomass. Note that during cell lysis the increase in MIB or Geosmin concentration in the growth medium was just a small portion of cellular content of these compounds, suggesting that the majority of MIB or Geosmin released from the cells were degraded and volatilized under our experimental conditions. In the field, however, MIB and Geosmin released from lysed cells could immediately be carried away by the large volume of flowing water, thereby leaving degradation and volatilization of Geosmin to a minimum level. For instance, it may be predicted that if all cellular MIB and Geosmin entered a water body without the possibility of degradation and volatilization. cellular lysis of one liter of *O. splendida* culture that contains 800 ug L¹ of cellular Geosmin could impart a notable earthy/musty odor (10 ng L¹ Geosmin) to as many as 80,000 liters of water. Our results suggest that under certain circumstances the lysis of dead cells at bottom of the canals and lakes may contribute a significant amount of MIB and Geosmin to the water column.

SECTION 5 TABLES AND FIGURES

Table	5.1.	PAC	brands	and	characteristic	parameters	PAC	characteristics	obtained	from
manuf	acture	er liter	ature an	d rep	resent typical va	alues.				

PAC Brand	Company				Location	Acronym		
WPL	Cal	Calgon Carbon Corp.			ittsburgh Pa	W	WPL	
WPH	Cal	gon Carbor	n Corp.	P	ittsburgh Pa	W	'PH	
WPM	Cal	gon Carbor	n Corp.	P	ittsburgh Pa	W	PM	
PAC 20B	N	orit America	as Inc		Atlanta Ga	2	0B	
Hydrodarco-B	N	orit America	as Inc		Atlanta Ga	H	DB	
Hydrodarco-O	N	Norit Americas Inc			Atlanta Ga	Н	DO	
Watercarb		Acticarb			Dunnellon Fl	WCARB		
Picatif PCO		Pica			France	Pica1		
Picazine		Pica			France	Pi	Pica2	
AC900		Acticarb			Dunnellon Fl	AC	C900	
Properties	WPL	WPH	20B		HDB	WCARB	AC900	
Iodine # (mg/g)	530	800	800		540	550	800	
Molasses #	120	160	190	500		110	n/a	
Material type	coal	coal	bituminou	S	lignite	wood	coal	
		coal			coal	bark		
Tannin value	1420	930	900		220	1110	NA	
(mg/L)								

Table 5.2. Removal of MIB by PAC addition (15 mg/L) from ultrapure water (DOC < 0.2 mg/L) and natural water (DOC = 2.5 mg/L from the Arizona Canal) (contact time 3 hours).

PAC Type Added	MIB Remaining (ng/L) in Ultrapure water	MIB Remaining (ng/L) in SRP water
Control – No PAC added	30 ± 2	30 ± 2
Pica1	0	24
HDB	0	16
WCARB	3	16
Pica2	10	13
HDO	0	13
WPH	0	13
WPL	0	7
AC900	0	6
20B	0	5
WPM	0	6

Table 5.3. Calculated pseudo zero-order loss rates (ng/L/d) for MIB and Geosmin from laboratory experiments (R_L), and annual maximum pseudo zero-order loss rates (ng/L/d) of MIB from three reservoirs ($R_{F,max}$) for Fall 1999 (†), Fall 2000 (††) and Fall 2001 (††). NA = not available due to lack of data above Geosmin detection limits.

Source of data	MIB loss rate	Geosmin loss rate
Batch Experiments (R _L values)		
Abiotic	0.11	0.10
0 m	0.79	NA
5 m (5 m duplicate)	0.95 (0.90)	0.81
5 m + bioseed	1.1	0.90
10 m	0.80	NA
15 m	1.2	NA
20 m	1.0	NA
Field Reservoirs (R _{F,max} values)		
Bartlett Lake	0.35*, 0.47**, 0.22 ***	NA
Saguaro Lake	0.64*, 0.41**, 0.44 ***	NA
Lake Pleasant	0.60*, 0.45**, 0.10 ***	NA

Year	Months	Saguaro Lk.	Bartlett Lk.	Lk. Pleasant
	August-September	0.07	0.25	0.94
1000	September-October	0.21	0.10	(0.42)
1999	October-November	(0.23)	(0.35)	(0.60)
	November-December	(0.64)	0.00	0.05
	December-January	0.24	0.00	(0.22)
	January-February	(0.17)	0.00	(0.19)
	February-March	0.16	0.01	0.17
	March-April	0.08	0.06	(0.01)
	April-May	0.30	0.01	0.15
2000	May-June	0.20	0.11	(0.20)
2000	June-July	0.26	0.27	0.15
	July-August	(0.01)	0.85	0.16
	August-September	(0.33)	(0.29)	(0.45)
	September-October	(0.41)	(0.32)	(0.35)
	October-November	(0.23)	(0.47)	(0.05)
	November-December	(0.11)	0.12	0.06
	December-January	0.02	(0.06)	(0.09)
	January-February	(0.19)	0.00	0.00
	February-March	(0.13)	0.00	0.00
	March-April	(0.02)	0.00	0.00
	April-May	0.24	0.19	0.00
2001	May-June	0.24	0.27	(0.01)
	June-July	0.00	0.12	0.03
	July-August	0.38	(0.22)	0.12
	August-September	0.45	(0.10)	0.38
	September-October	(0.27)	(0.22)	(0.10)
	October-November	(0.44)	0.18	0.17

Table 5.4. Net reaction rates (R_f , ng/L-day) for all three reservoirs. Values in parentheses indicate loss of MIB while values without parentheses indication production of MIB.

Table 5.5. R9-A linear regression for algae and MIB concentration.

Coefficients	Significance
R9A total bluegreen algae	0.292
R9A total algae count	0.451
R9A total chlorophyll a	0.840
Dependent Variable: R9A_MIB	3

r²: 0.052

Table 5.6. R9-A Pearson Correlation: MIB and Temp at each level.

Depth	Pearson Correlation	Significance at 0.05 level
0 m	0.630	.000
5 m	0.654	.000
10 m	0.669	.000
15 m	0.648	.000
20 m	0.639	.000
25 m	0.635	.000
30 m	0.631	.000

Table 5.7. R9-A Linear regression N, P and conductance to MIB.

Coefficients	Significance at 0.05 level
Total nitrogen	0.000
Dissolved Nitrogen	0.001
Conductance	0.907
Total Phosphorus	0.158
Dissolved Phosphorus	0.160
Dependent Variable: MIR	POA

Dependent Variable: MIB_R9A r²: 0.821

Table 5.8. R9-A Linear regression T x DN to MIB.

Coefficients			Significance at 0.05 level
Temperature Nitrogen	х	Dissolved	0.000
Dependent Var r ² : 0.779	iable	: MIB_R9A	N Contraction of the second seco

Table 5.9. Number of algal isolates from the baseline monitoring sites (August 1999 - June 2002).

Site	R1	R2	R3	R4	R5	R6	R7	R8	R9
Isolates	51*	32	56	68*	82*	50	82*	19	241*
Site	R10	R11	R12	R13	R14	R16	R17	R18	R20
Isolates	77	60	88	61	68	74*	11	75	28

*MIB/Geosmin production confirmed using GC/MS

Table 5.10. Baseline-monitoring sites and intensive-monitoring locations of confirmed algae producers of mig and Geosmin (August 1999 - June 2002).

Algae	T & O Compound	Site/Location
Oscillatoria splendida	geosmin	CAP Canal above Waddell Canal (R1)
Oscillatoria splendida	geosmin	CAP Canal at 7 th Street (R4)
Oscillatoria splendida	geosmin	Deer Valley WTP Inlet (R16)
Oscillatoria agardhii	geosmin	Verde River below Bartlett Lake (R7)
Phormidium sp	MIB	Verde River between Horseshoe and Bartlett Lakes (R5)
Pseudanabaena sp.#1	MIB	AZ Canal Intensive-Monitoring Sites (Scottsdale Rd., Central Ave & DVWTP)
Pseudanabaena sp.#2	MIB	Saguaro Lake Intensive-Monitoring Site (SS4)
Pseudanabaena sp.#3	MIB	AZ Canal above Cross-Connect (R12)

Table 5.11. Sites of confirmed Actinomycete producers of Geosmin (August 1999 - June 2002)

Site	R1	R2	R3	R4	R5	R6A	R7	R8	R9B
Isolates	1	0	0	0	0	1	1	0	1
Site	R10	R11	R12*	R13	R14	R16*	R17	R18	R20
Isolates	0	1	3	1	1	4	0	0	2

* Geosmin production confirmed using GC/MS

Table 5.12. Comparison of cell-bound Geosmin and released Geosmin among different cyanobacterial taxa.

Species	Maximum cell-bound Geosmin per chl <i>a</i> (ug/ug)	Reference
Anabaena viguieri	0.025	Wu et al. (1991)
Anabaena sp.	97.4	Blevins et al. (1995)
Anabaena sp.	135	Saadoun et al. 2001
Fischerella muscicola	0.44	Wu and Juttner (1988a)
Oscillatoria tenuis	0.15	Wu and Juttner (1988b)
Oscillatorai brevis	0.07	Haes et al. (1989)
Oscillatoria splendida	0.3-2.1	This study
Phormidium sp.	0.13	This study

Figure 5.1. Adsorption kinetics for MIB and Geosmin using Norit 20B (upper) and MIB using Norit HDB (lower).



Figure 5.2. Dose response curves for Hydrodarco B (Norit Americas), 20B (Norit Americas), and WPM (Calgon) for MIB (solid lines) and Geosmin (dashed lines) remaining in solution (SRP canal water; Contact time = 240 minutes, Initial MIB and Geosmin concentrations varied between 25 and 150 ng/L).



Figure 5.3. Raw water MIB concentration (ng/L) in the (\blacklozenge) morning and (\blacksquare) afternoon on several sample dates, along with average PAC doses applied to the East (\circ mg/L of Norit 20B) and West (\triangle mg/L of Norit HDB) treatment trains at Val Vista WTP.



Figure 5.4. Percentage MIB removed during full-scale implementation at Val Vista WTP for morning (\blacklozenge , \diamondsuit) and afternoon (\blacktriangle , \triangle) samples from the East (Norit 20B; solid symbols) and West (Norit HDB; open symbols) treatment trains.



Figure 5.5. PAC Implementation guide for Norit 20B at Val Vista WTP; based upon field PAC slurry and raw water. Values indicated on graph near each curve represent raw water MIB concentrations (MIB_{raw}) and the y-axis indicates finished water MIB concentrations (MIB_{finished}). To achieve MIB_{finished}=10 ng/L the following equation can be used to estimate PAC dose: PAC Dose = $12.7 \ln(\text{MIB}_{\text{raw}}) - 28.5$.



Figure 5.6. Approximate costs versus % removal for PAC types.



Figure 5.7. Ozone decay (insert) and oxidation of MIB and Geosmin in Arizona Canal Water (Ozone dose = 3 mg/L; initial MIB and Geosmin concentrations indicated in legend).







Figure 5.9. Effect of biocide coatings (Alphacoat and EP2000) on algal biomass (chlorophyll-a) attached to 6cmx6cm clay tiles after 3 and 4 weeks of incubation in a recycle photobioreactor (BG11 liquid media).





Figure 5.10. Chlorine demand by copper-based biocides in Super-Q and Arizona Canal water.

Figure 5.11. Free and chloramine chlorine residuals in the presence of A) Cutrine-Plus, B) Earthtec, C) copper sulfate, D) super-Q water.



Figure 5.12. Change in MIB concentration in distilled and CAP water in the presence of 1 mgCu/L. Solid symbols indicate initial MIB concentrations with error bars indicating one standard deviation.



Figure 5.13. Temporal patterns in physical and biological indicators for Bartlett Lake (\Box), Saguaro Lake (\triangle), and Lake Pleasant (\diamondsuit).



Figure 5.14. Vertical profiles for MIB (\blacklozenge ng/L), Geosmin (\blacksquare ng/L), dissolved oxygen (\triangle mg/L), and temperature (\diamondsuit °C) in Saguaro Lake (September 2000).



Figure 5.15. Temporal trends in MIB concentrations at upstream (\triangle), epilimnion (\blacksquare), hypolimnion (\blacktriangle), and downstream (\diamondsuit) sampling sites for Bartlett Lake. Total MIB mass in the reservoir (\ast) is also indicated.



Figure 5.16. Kinetic degradation of MIB in batch experiments for samples collected from Saguaro Lake (9/00; corresponding to samples presented in Figure 1) from the surface (\diamond 0 m) and at several depths (\triangle 5 m; \Box 10 m; \bigcirc 15 m; * 20 m). Duplicate samples at 5 m (error bars show 1 std.dev.) and abiotic control sample (\blacksquare) were split from the epilimnetic sample collected at a 5 m depth.



Figure 5.17. Kinetic degradation MIB (A) and Geosmin (B) experiments with water collected at a depth of 5 m from Saguaro Lake (9/00; corresponding to samples presented in Figure 1). Abiotic control sample (\blacksquare) has negligible degradation compared against the 5 m sample without the added bioseed (\triangle) or with the added bioseed (\diamondsuit). Geosmin samples were spiked to 23 ng/L. Error bars show one standard deviation. Lines represent fitted laboratory pseudo zero-order rates (R_L).



Figure 5.18. Stream flow in the Verde River below Bartlett Dam and at the USGS gauging station near Scottsdale, AZ for February-March, 2000. MIB concentrations below Granite Reef dam where: 2.4 ng/L (Feb. 24), 21 ng/L (Mar. 14), and 5.6 ng/L (Mar. 24).



Figure 5.19. Historic MIB data (lines) and periods of elevated turbidity at Val Vista WTP (indicated by grey arrows) (source: University of Arizona- David Walker).



Figure 5.20. MIB or Geosmin leached into solution from soil samples collected near the Salt River (S1), CAP Canal (S2), Arizona Canal (S3), and grass at ASU (S4). Samples were agitated for 40 hours; an abiotic sample contained sodium azide.



Figure 5.21. Isolate 506, a *Pseudanabaena sp.*, was confirmed to produce MIB soon after being isolated from the Verde River site R-5 in October, 1999. However, laboratory cultures later stopped producing MIB.



Figure 5.22. Isolate 506 stopped producing MIB in laboratory cultures when grown in a standard BG-11 medium. However, when the culture was grown in three different treatements of Verde River water, 1) raw Verde River water, 2) filtered with a 0.2 um pore-size membrane, and 3) autoclaved, the cultures again produced MIB.



Figure 5.23. Total Nitrogen (TN) multiplied by temperature (T) have a strong linear relationship with MIB concentration. Together, TN and T can be a strong predictive indicator for the production of MIB in the epilimnion of Saguaro Lake.







Figure 5.25. Total algal isolates from Baseline Monitoring sites.



Figure 5.26. (A) A *Percival* light-gradient growth chamber (model: 1-35LLVL, Boone, Iowa) in which culture tubes can be placed at different distances from the light source to affect light intensity. (B) A custom-designed thermal gradient device for temperature experiments. A stable temperature gradient can be established along an aluminum plate by heating one end of the plate with a heating element and cooling the opposite end with a refrigeration evaporator.



B)

Figure 5.27. Effect of temperature on growth (A), production (B) and release (C) of MIB in cultures of *Pseudanabaena* sp. Light intensity: $30 \mu \text{ mol m}^{-2} \text{ s}^{-1}$.



Figure 5.28. Effect of light intensity on growth (A), production (B) and release of MIB (C) in cultures of *Pseudanabaena* sp. Temperature: 20 °C.





Figure 5.29. Effect of light intensity on production (A) and release of MIB (B) in cultures of *Pseudanabaena* sp. on a per chlorophyll *a* basis.



Figure 5.30. Effect of dark incubation on chlorophyll *a* concentration (A) and cell-bound MIB concentration and MIB released into the medium (B) of *Pseudanabaena* sp. cultures. Temperature: 20 °C; Light intensity for phototrophic growth: $30 \mu \text{ mol m}^{-2} \text{ s}^{-1}$.


Figure 5.31. Effect of temperature on growth (A), cell bound (B) and released Geosmin (C) from cultures of *Phormidium* sp. Light intensity: $30 \mu \text{ mol m}^{-2} \text{ s}^{-1}$.



Figure 5.32. Effect of temperature on cell-bound (A) and released Geosmin (B) in cultures of *Phormidium* cells on a per chlorophyll *a* basis. Effect of temperature on the percentage of released Geosmin to the Geosmin produced by *Phormidium* cultures during the growth phases (C).



Figure 5.33. Effect of light intensity on growth (A), cell-bound (B) and released Geosmin (C) in cultures of *Phormidium* sp. Temperature: 20 $^{\circ}$ C.



Figure 5.34. Effect of light intensity on cell-bound (A) and released Geosmin (B) in *Phormidium* cultures on a per chlorophyll *a* basis. Effect of light intensity on percentage of released Geosmin relative to cell-bound Geosmin in *Phormidium* cells as a function of time.



Figure 5.35. Effect of dark incubation on chlorophyll *a* concentration (A) and Geosmin concentration in cells and in the growth medium (B) of *Phormidium* sp. cultures. Temperature: 20 °C; Light intensity for phototrophic growth: $30 \mu \text{ mol m}^{-2} \text{ s}^{-1}$.



Figure 5.36. Changes in chlorophyll *a* concentration (A, bar graph) and Geosmin concentration in medium (A, curved line), and cell-bound Geosmin (B, bar graph) and the ratio of cell-bound Geosmin concentration to chlorophyll *a* (B, curved line) as a function of time. Light intensity: 20 μ mol m⁻² s⁻¹; temperature: 26 °C. Bars represent standard deviation of 3 replicates.



Figure 5.37. Effect of temperature on the specific growth rate (A) cellular content (B, bar graph), cell-bound Geosmin per chlorophyll a (B, curved line), and release of Geosmin to the medium (C, bar graphs) and released Geosmin per chlorophyll a (C, curved line) by *O. splendida*. Samples taken on day 5 and 7 were used for calculation of the specific growth rate and on day 7 for analysis of Geosmin concentration. Error bars indicate standard deviation of 3 replicate cultures.



Figure 5.38. Effect of light intensity on the specific growth rate (A), Geosmin in medium (B) and cell-bound Geosmin to chlorophyll *a* ratio (C). Samples taken on day 6 were used for analysis of Geosmin and on day 4 and 6 were used for calculation of the specific growth rate. Error bars indicate standard deviation of 3 replicate cultures.



Figure 5.39. Changes in chlorophyll *a* content (A) and cell-bound (B, line with closed circles) and released Geosmin to the medium (B, line with closed squares) as a function of time during dark incubation. Culture conditions: *O. splendida* cells were first maintained in BG-11 growth medium at 20 μ mol m⁻² s⁻¹ and 20 °C for one week, then transferred to a dark chamber. Samples were taken at selected time intervals for chlorophyll *a* and Geosmin analysis. Each value represents the mean of four replicates.



Figure 5.40. Effect of nitrate and phosphate concentrations on chlorophyll *a* concentration (solid line) and release of Geosmin to the medium (bar graph). Treatment 1: Control = filtered raw water from the Arizona Canal; Treatment 2: +P = filtered raw water enriched with 1mg/L of PO₄⁻³ (as P); Treatment 3: +N = filtered raw water enriched with 5 mg/L of NO₃⁻ (as N); Treatment 4: +P/+N = filtered raw water enriched with 1mg/L of PO₄⁻³ and 20 mg/L of NO₃⁻ (as N). Temperature = 20 °C; light intensity = 25 μ mol m⁻² s⁻¹. Samples were taken on day 6 and 10 of the experiment. Data are means of four replicates with bars denoting standard deviation.



Treatments

SECTION 6: STUDIES OF DOC SOURCE, CHARACTERIZATION, AND TREATABILITY (TASK 5)

The purpose of this task was to understand the source dependent factors that influence the amount, sources/sinks, chemical structure, and treatability of dissolved organic carbon (DOC). DOC may be related to algae production, but also serves as a primary substrate that affects reservoir biogeochemistry.

Baseline monthly data collected since August 1999 includes DOC concentration, source characterization (FI), and DBP reactivity (SUVA). In addition, seven quarterly samples for all study sites had been analyzed for THM and HAA formation (SDS) and aluminum oxides adsorption tests (September 1999; January, April, July, October 2000; January and April 2001). Large quantities of water from the Verde River were collected, filtered/isolated (XAD-8) for further characterization of DOC sources (using FI and C/N ratio), structure (C¹³-NMR, MW fractionation) and reactivity (DBP formation and biological degradation, BDOC). In addition, DOC characterization of three water supplies (CAP, Verde, Salt) in April 2001, and molecular weight fractionations from February 2001 were performed.

In-lab algae growth experiments are continuing. We have previously shown that algae growth produces DOC and that it is chlorine reactive. Large quantities (40-L) of algae-produced DOC (by the green algae: *Scenedesmus quadricauda*) was grown in the lab in order to characterize the structure (using C¹³-NMR, C/N ratio), reactivity (forming DBP), as well as its degradability in comparison to in-situ DOC.

TRENDS IN DOC & SDS-DBPS

Tables 6.1 to 6.4 summarize the spatial variability of DOC in the 4 sampling clusters (CAP/Pleasant, Verde, Salt, SRP canals) from August 1999 to April 2001. DOC is slightly higher in the reservoirs (epilimnion), indicating that algae probably produce DOC. The average DOC concentrations in the CAP and Salt systems are similar and relatively constant (2.96 \pm 0.43 mg/L and 2.93 \pm 0.49 mg/L, respectively) (Tables 6.1 and 6.3).

In general, DOC concentrations in the Verde cluster are lower than in the Salt and CAP clusters, but more variable spatially and temporally. The average DOC concentration in this system is 2.02 \pm 0.73 mg/L (ranging from 0.6 mg/L during low flow to 3.7 mg/L during surface runoff at R20). There were two relatively small runoff events (October 2000 and March 2001) in the upper Verde River (R20) that appeared to affect DOC concentrations/characteristics (allochthonous source) (Figure 6.1). DOC concentrations at Site R20 were elevated during these events (2.6 to 3.7 mg/L). SUVA values also increased to 0.033 and .026 (mg/L⁻¹cm⁻¹) in October 2000 and March 2001, respectively. It is also important to point out that although runoff increases DOC concentrations in the Verde River; these runoff events that occurred during this period of study are far smaller than those observed in previous studies (spring runoffs in 1995 and 1998). Peak flow during spring runoff of 1995 (2/15/95) was 70200 cubic feet per second (cfs) (DOC ~ 4.5 mg/L), approximately 25 times higher than 2001 peak spring runoff (3/15/01) of 2760 cfs (DOC ~ 3.7 mg/L). Peak spring runoff of 15290 cfs (DOC ~ 6.6 mg/L) in the 1995 study is almost 5.6 times higher than occurred during the current year.

SUVA and FI values, which are potential indicators of algal-derived DOC were largely unchanged with the exception of the Verde River system. DOC in the CAP and Salt systems

has lower SUVA values (0.015 and 0.018 (mg/L⁻¹cm⁻¹) (Figure 6.3) than the Verde River system (>0.02 (mg/L)⁻¹cm⁻¹) (Figure 6.2). This finding suggests that DOC from the Verde system is more reactive to DBP formation (per unit DOC concentration) than the CAP and Salt systems. Higher variability in SUVA and FI values was expected on the Verde cluster since it has fewer upstream impoundments than the Salt (four upstream reservoirs on Salt River) or CAP (Lake Powell and Lake Havasu on the Colorado River) clusters.

THM and HAA Formation (SDS)

DBP formation (SDS) was analyzed quarterly since September 1999 on raw/untreated water. The results show that DBP formation in the Phoenix Metropolitan source waters varied spatially and temporally. In general, the Salt River and the Arizona canal waters had higher DBP formation (THM > 112 \pm 26 µg/L, HAA₉ = 53 \pm 13 µg/L) compared to the CAP canal water (THM= 70 \pm 17 µg/L, HAA₉ = 39 \pm 9 µg/L) (Figures 6.4 and 6.5). Saguaro Lake epilimnion (R9A) and hypolimnion (R9B) had higher DBP formation than those measured in Bartlett Reservoir and Lake Pleasant. THM and HAA₉ concentrations increased slightly at the downstream end for both CAP and SRP canals (R11 and R16, respectively).

Although the average DOC concentration in the Verde cluster was lower than the CAP and Salt clusters, the average THM and HAA concentrations in the Verde cluster (THM = 89 \pm 36µg/L, HAA₉ = 42 \pm 12 µg/L, n = 6) were higher than in the CAP cluster. The reactivity of DOC in forming DBPs was calculated for each water source by taking the ratio of DBPs to DOC (THM/DOC and HAA/DOC). DOC from the Verde system was more reactive to THM and HAA formation (THM/DOC = 42 \pm 10 µg/mg; HAA₅/DOC = 15 \pm 2 µg/mg; n =6) than the Salt system (THM/DOC = 33 \pm 2 µg/mg; HAA₅/DOC = 9 \pm 0 µg/mg; n =6) and the CAP system (THM/DOC = 21 \pm 2 µg/mg; HAA₅/DOC = 7 \pm 1 µg/mg; n = 6). The potential of DOC in forming THM upon chlorination is more than 2 times the HAA₅ formation. DBP formation in the SRP canals are mixed and intermediate between the ranges in the other clusters (THM/DOC = 91 \pm 31 µg/mg; HAA₅/DOC = 40 \pm 9 µg/mg).

DOC Treatability

In addition to THM and HAA (SDS) formation experiments, quarterly samples were subjected to aluminum oxide sorption tests, used as a measure of DOC sorption to metal oxides during treatment. In general, 30 to 60% of the DOC was removed. However, higher percentage of DOC removal was observed in the spring, summer and fall than in winter when there is little input of terrestrial or aquatic DOC. This observation suggests that long-term reservoir storage (e.g., winter: following algae bloom and before spring runoff) could remove the more sorbable fraction of DOC. Coagulant addition during water treatment removes a small portion of adsorptive DOC (~10%). The UV absorbing (UVA₂₅₄) fraction of DOC is more preferentially removed than the non-UV absorbing fraction (40-80 % UVA₂₅₄ removal). This leads to a small reduction in specific UV absorbance, or aromatic carbon content, which is a surrogate measure of DBP formation potential.

DOC ISOLATION AND CHARACTERIZATION

DOC isolation / fractionation was accomplished by adsorption chromatography using XAD-8 and XAD-4 resins. DOC was fractionated into hydrophobic and hydrophilic portions. The

procedure involved passing 30-Liters of filtered/acidified (pH 2.0) samples through a column containing XAD-8 resins (500 mL) at flow rate of 95 mL/min. The premeate (effluent from the column) is functionally defined as the hydrophilic fraction. The retentate in the column was eluted with 0.1 NaOH; the eluent represents the hydrophobic fraction (functionally defined as hydrophobic acids or fulvic acids). Figure 6.6 also shows the fractionation of hydrophilic materials (XAD-4 retentate and its 0.1 NaOH eluent) from ultrahydrophilic materials (XAD-4 retentate and its 0.1 NaOH eluent) from ultrahydrophilic materials (XAD-4 retentate).

Samples from Lake Pleasant (R2), Bartlett Reservoir release (R7) and Saguaro Lake release (R10) were collected in April 2001 in order to isolate and determine the difference in DOC sources, structures and characteristics. In order to obtain sufficient amount of isolates, large quantities of samples (150-L each) were collected and concentrated using reverse osmosis (RO); greater than 90% DOC recovery was achieved. DOC fractions were isolated according to the schematic in Figure 6.6. Hydrophobic (XAD-8 isolates) and hydrophilic (XAD-4 isolates) acids from each of the reservoir systems are being further characterized for source/structure and DBP reactivity. Figure 6.7 shows the fractions of DOC for each reservoir. The Verde system has the highest fraction of hydrophobic materials (with 40% hydrophobic acids). Saguaro Lake has the lowest hydrophobic fraction (22.3% hydrophobic acids), which is similar to algal-produced DOC (22.2 % hydrophobic acids).

On seven occasions, October 1999 (R20 and R7), April 2000 (R20, R5, R7), and July 2000 (R20, R6A, R6B), September 2000 (R5), December 2000 (R5, R6A), March 2001 (R20, R5), and April 2001 (R6A, R7) large quantities of water were collected from the Verde system, filtered/isolated (using XAD-8 only) for further characterization of DOC sources (using FI and C/N ratio), structure (C¹³-NMR, MW fractionation) and reactivity (DBP formation and biological degradation, BDOC). Analyses for these isolated materials are ongoing. The majority of the isolates (fulvic acids) had been analyzed by C¹³-NMR to determine carbon structures (% aromatic vs. aliphatic carbons) and CHN to determine the carbon and nitrogen content of isolates. In general, terrestrial-derived DOC has higher aromatic and lower nitrogen contents in comparison to algal-derived (aquatic) DOC. Therefore, aquatic (i.e. algal-produced) fulvic acids have lower Cto-N ratios (C/N) and Aromatic Carbon-to-Aliphatic Carbon ratios (Ar-C/AI-C) in comparison to terrestrial-derived fulvic acids (i.e. Suwannee River Fulvic Acids, or SRFA).

Table 6.7 shows the characteristics of DOC in the Verde River-Reservoir system. The characteristics of these samples were shown in comparison to fulvic acids derived from different sources, algae (ALG6) and terrestrial source (SFRA) in order to understand the source and structural characteristics of DOC in the reservoirs. Suwannee River fulvic acid was obtained from the International Humic Substances Society (IHSS). Assuming a continuum between terrestrial- and algal-derived DOC on C-to-N ratios vs. Aromatic Carbon-to-Aliphatic Carbon ratios (Ar-C/AI-C), Figure 6.8 shows that fulvic acids from the Verde cluster are closer to algal derived DOC than terrestrial DOC. Upon closer examination, fulvic acids affected by surface runoff tends to shift slightly to the terrestrial end. Figure 6.8 shows examples of sites affected by runoff loading of DOC. Site R20 represents an example from the beginning of spring runoff (3/05/01). Site R5 (12/12/00) represents the release of October-November 2000 runoff (10/22/00-11/14/00: peak flow 2390 cfs at R20) following storage (10/19/00-11/28/00: ~ 10 cfs released at R5). From June 03, 2000 to August 15, 2000, there was no water released from Horseshoe Reservoir because of a maintenance problem (broken pipe). During this time, water input to Bartlett Lake was low (avg. 138 cfs at R20). Sample collected at R5 (9/01/01) is representative of reservoir production (2.5 months storage of low DOC input). This is represented by a decrease in C/N and Ar-C/Al-C ratios (closer to algal-source). In addition,

variation in C/N ratio is more pronounced than the Ar-C/AI-C ratio.

Molecular Weight Fractions of DOC

In February 2001, samples were collected from the Verde, CAP and Salt systems to determine the molecular weight distributions and transformation in surface water supplies. Apparent molecular weight (MW) fractionation of DOC was accomplished by ultrafiltration (UF). MW distributions were determined by using pressurized stirred-cells with membranes characterized by nominal MW cutoffs of 1000 and 10,000 Daltons (YM1 and YM10, respectively). The MW distributions of DOC in natural water varied from source to source. The transformation of DOC in the river-reservoir system could be observed based on the changes in MW distribution. Figure 6.9 shows MW distributions for water from three different surface water sources (Verde, CAP, and Salt). In general, the Verde river-reservoir system tends to have larger proportion of high MW (31% >10, 000D). DOC within the resevoirs exhibited a decrease in low MW (25%< 1000D) and an increase in intermediate MW (1000D < 42-52% < 10,000D) fractions in comparison to the inflow (upstream) sites, suggesting some mechanisms of bacterial degradation/transformation of low MW DOC.

Biodegradation of DOC

In addition to isolation and MW fractionation of DOC, biodegradability of DOC plays an important role in understanding the fate of DOC in the river-reservoir system. Degradation of DOC was performed using the BDOC₅ method. Biodegradable DOC (BDOC) was subjected to removal in batch culture of bacterially adapted sand (silica sand) for five days. Figure 6.10 show the average amount of biodegradable DOC (BDOC₅) for the Verde river-reservoir system from December 2000 to February 2001. The amount of biodegradable DOC in the system is relatively low, ranging from 5 to 20% DOC. Higher degradation occurred before spring runoff (prior to March 2001), ranging from 15 to 20% DOC. A statistically significant reduction in biodegradable DOC was observed at R5 (Horseshoe reservoir release) in comparison to R20 (Horseshoe reservoir input), suggesting removal of biodegradable DOC occurred during storage. BDOC in the reservoir (R6A: Bartlett epilimnion) increases in comparison to R5, indicating production of biodegradable DOC within the reservoir. Contribution from algalproduced DOC may be responsible for causing the increase in the biodegradable fraction within the reservoir. DOC produced from algae growth is more labile. This observation is supported by the degradation of algae produced DOC conducted in the laboratory. Figure 6.11 shows that the majority (62 \pm 6 %) of the DOC produced by algae is biodegradable after five days of exposure to bacterially acclimated sand. These results further indicated that a large fraction of the new algal-produced DOC in the reservoirs was guickly degraded.

RESERVOIR DOC BUDGETS

With the previous knowledge of spatial and temporal variability of DOC concentrations and characteristics, this section will address the role of hydrology and hydrologic control on DOC production/transformation. Analyses of water and DOC budgets were performed for Lake Pleasant, Saguaro Lake, Horseshoe Reservoir, and Bartlett Lake in order to understand the role of reservoir storage on the fate and transport of DOC in surface water supplies.

Table 6.5 shows the water budgets for the four reservoirs from June 1999 to May 2001.

Hydrologic operation of Lake Pleasant is most unique. The majority (95%) of the water input was from the CAP canal; the Agua Fria River accounted for only 5% of total input. Water input to Lake Pleasant from the CAP canal occurred mainly from November to March of each year. Water release (96% of total input) from Lake Pleasant (to the CAP canal) generally occurred in the summer and fall periods (June to October). Less than 1% of the input was unaccounted for in Lake Pleasant. In contrast, the Horseshoe reservoir and Bartlett Lake on the Verde River show a loss of 5.6% and gain of 19% of total input, respectively. If we consider the loss in the Horseshoe Reservoir as underground seepage into Bartlett Lake downstream, there is still 13% of the total water input not accounted for in the water balance. We estimate that the extra water gained in Bartlett Lake was the result of ephemeral inputs of ungauged creeks in the smaller watershed below Horseshoe Reservoir. This portion would play an important role in estimating DOC loading and mass balance for the reservoir system.

Table 6.6 shows DOC budgets for the four reservoirs from June 1999 to May 2001. Saguaro Lake has the highest DOC loading (~ 2.5 x 10^6 kg) of the four reservoirs, although Lake Pleasant has more water input. DOC load to Horseshoe Reservoir is small in comparison to Approximately 19 to 20% of DOC load is produced within Horseshoe other reservoirs. Reservoir. Production of DOC within Bartlett Lake is less than 1% of DOC load. This is a significant underestimation of DOC production since 19% of the water input was unaccounted for in the water budget. We would expect that DOC production in Bartlett Lake is similar to, or higher than that in Horseshoe Reservoir based on longer hydraulic retention time (HRT). Bartlett had 144 days, compared to Horseshoe with 39 days. Previous results in 1995 and 1998 showed Bartlett Lake had a low DOC loss (when there is a net loss in the upstream Horseshoe Reservoir, 1998) and higher net gain (when there was a net gain in the upstream reservoir, 1995). Lake Pleasant had the largest percentage of DOC production of the four reservoirs (~30% of total DOC load). However, this number would be an overestimation of DOC production because DOC input from Agua Fria River (which accounted for 5% of total water input to Lake Pleasant) was unaccounted for (DOC concentrations were not measured). Saguaro Lake exhibited a small percentage of DOC loss (3 to 4 % of total DOC load). Hydraulic operations at Saguaro Lake have significant impact on DOC load estimation. The inflow to Saguaro Lake was not measured. The amount of water input was estimated using the water balance equation that assumes inflow from the Salt River (below Canyon Lake at R8) as the only source of water input. A further assumption was made to set inflow to equal the measured net outflow (at R10). There is a negative inflow, which results from the pump back of water released from Saguaro Lake to the inflow to Canyon Lake. This results in an increase in the amount of water delivered and released from the reservoir.

Overall, Horseshoe Reservoir has the highest net rate of DOC production (0.011 mg/L-day), which is one to two orders of magnitude higher than those from Lake Pleasant and Bartlett Lake, respectively.

In an attempt to establish a relationship in DOC load to DOC production or degradation, monthly net rates of DOC gain or loss were plotted against cumulative DOC load (DOC_{in}) and DOC release (DOC_{out}). Figures 6.12, 6.13, and 6.14 show such trends for Lake Pleasant, Horseshoe Reservoir, and Bartlett Lake, respectively. There was no established temporal trend in DOC production/degradation for both Lake Pleasant and Horseshoe Reservoir. Bartlett Lake shows some temporal variation in DOC production/loss during the study period from August 1999 to June 2001. The reservoir exhibits net DOC production from late fall to early spring (November to February), and net DOC loss occurred in late summer and early fall (June to October).

ORGANIC NITROGEN REMOVAL AT WTPS

Natural organic matter (NOM) is usually quantified by dissolved organic carbon (DOC) measurements, but NOM contain carbon (~45% by wt.), oxygen (~40%), hydrogen (~ 5%), nitrogen (~5%), sulfur and other elements. Recent concerns in the drinking water industry related to production of nitrosamines (e.g., NDMA) has given rise to interest in monitoring DON concentrations in drinking water. One possible mechanism for NDMA production is associated with DON as precursor material. DON concentrations in the Arizona and South Canals ranged from 0.1 to 0.2 mgN/L, and represent DOC/DON ratios on the order of 10-15. The C/N ratios of the hydrophobic acid isolates (Table 6.7) were higher than 10 to 15, and were on the order of 20-30 on a mass basis (25-35 on a molar basis). It is well documented that the hydrophobic acid fraction contains the highest C/N ratio, and other organic matter fractions (hydrophilics, neutrals, and bases) are nitrogen enriched (lower C/N ratio). Therefore, the observed DOC/DON ratio of 10 to 15 makes sense.

Approximately 20% to 40% of the DON was removed by conventional treatment (with PAC addition) at Squaw Peak (21% and 38% removal on 10/4/01 and 11/1/01, respectively) and Val Vista (30%, 34%, 52% on 10/4/01, 11/1/01, and 2/14/02, respectively) WTPs. A slighter larger fraction of the DOC and DON is present in Arizona Canal water as higher molecular weight material (> 1000 dalton) (Figure 6.15). Low molecular weight DON may be present as free amino acids, but based upon literature free amino acids account for less than 30% of the total amino acid content of NOM. The remaining amino acids are combined, or hydrolysable amino acids. In general DON contains roughly 50% amino acid nitrogen, with the remaining organic nitrogen comprised of amide or heterocyclic organic nitrogen.

Controlled batch coagulation tests (jar tests) were conducted with CAP water, plus a NF/XAD4 fraction isolated from CAP water (Figure 6.16). The observed rank order of decreasing removal efficiency in jar tests, and full scale WTPs, was: UVA > DOC > DON. All three parameters decreased up to an alum dose of roughly 20 mg Alum per mg DOC. The results of the DON studies indicated that DON is present in raw and finished drinking water, and DOC removal could be used to roughly estimate DON removal.

DOC REMOVAL AT WTPS

Figures 6.17 and 6.18 present the removal of DOC and UVA_{254nm} by the three WTPs monitored during the project. DOC removal ranged from 5% to 55%, but a median value of 15% was observed for all three WTPs. In general DOC removal higher during warm water temperature conditions and probably reflects the change in aluminum hydroxide solubility and improved kinetics of flocculation. UVA material is removed during coagulation and chlorine can oxidize UVA material. UVA material at 254nm measures carbon-carbon double bonds. UVA removal was higher than DOC removal. The change in SUVA (UVA₂₅₄/DOC) is presented in Figure 6.19, and is consistent with above observations. SUVA is important since it is a parameter that impacts whether or not a WTP must practice Enhanced Coagulation.

SUMMARY

The DOC component of this study provided a linkage between regulatory issues (DBPs formed

during disinfection) and aesthetic issues (T&O from algae). The study clearly shows an impact of algae on the production and structure of DOC in the reservoirs, and ultimately in raw and finished water at the WTPs. Additional details of this work are published in a PhD dissertation (My-Linh Nguyen, ASU May 2002). The following points summarize the DOC study:

- DOC concentrations and characteristics of the source water vary temporally and spatially. Mean DOC concentrations within each cluster were 2.85, 2.85, 2.35, and 1.93 mg/L in the CAP, Salt River, SRP canal, and Verde River clusters, respectively.
- DOC concentrations increase during runoff (upper reservoir systems). Although the study was conducted during three years of below average rainfall or watershed snowpack, historic data suggests that DOC concentrations increase during wetter than normal years.
- DOC from the CAP system (65/35) is less reactive to DBP formation than from the Salt (115/50) or Verde (85/40) Rivers. Values in parentheses indicate mean (µg/L) THM-SDS/HAA₉-SDS concentrations. Verde River system has the lowest DOC concentrations, but most reactive (to DBP formation) DOC compared to the lower Salt and CAP system.
- The effect of algal-derived DOC in reservoir system maybe small in comparison to terrestrial DOC load during high runoff periods. This resulted from the rapid degradation of the more labile algal-produced DOC.
- However, algal-produced DOC can be significant during summer storage (low in put from upstream runoff). Fulvic acids isolated from the Verde cluster were more closely related to algal-derived fulvic acids, especially during storage (no release from Horseshoe Reservoir) and low flow in the Verde River (~ 100 cfs upstream of Horseshoe Reservoir) during the summer (6/03/00 to 8/15/00).
- Mass balances on the reservoir systems show significant DOC production in upstream reservoirs (Horseshoe Lake).
- There is no significant temporal trend in the net rate of production or degradation; although Bartlett Lake exhibits net DOC production during late fall and winter and net degradation in the late summer-early fall.
- The results of the DON studies indicated that DON is present in raw and finished drinking water (0.1 to 0.3 mgN/L), and DOC removal across the COP WTPs could be used to roughly estimate DON removal.
- DOC removal ranged from 5% to 55%, but a median value of 15% was observed for all three WTPs

SECTION 6 TABLES AND FIGURES

CAP- Pleasant	Average	Max	Min	Median	Stdev	n
R1	2.861	4.168	2.477	2.775	0.371	21
R2A	3.213	5.769	2.642	3.068	0.645	21
R2B	3.031	3.704	2.622	3.006	0.275	21
R3	2.821	3.295	2.444	2.739	0.245	21
R4	2.873	4.082	2.449	2.744	0.398	21
R11	2.840	3.484	2.329	2.778	0.289	21

Table 6.1. Dissolved organic carbon (DOC) concentrations in the cap cluster.

Table 6.2. Dissolved organic carbon (DOC) concentrations in the Verde cluster.

Verde River	Average	Max	Min	Median	Stdev	n
R20	1.940	6.649	0.558	1.484	1.415	43
R5	2.420	4.706	0.773	2.128	1.158	37
R6A	2.746	4.393	1.454	2.200	1.035	32
R6B	2.527	2.716	1.222	1.921	1.010	32
R7	2.532	3.08	1.291	1.902	1.048	41

Table 6.3. Dissolved organic carbon (DOC) concentrations in the Salt cluster.

Salt-Saguaro	Average	Max	Min	Median	Stdev	n
R8	2.946	4.248	2.638	2.890	0.356	21
R9A	3.113	4.1	2.811	3.048	0.291	21
R9B	3.168	5.442	2.636	3.020	0.567	21
R10	2.483	3.109	1.863	2.451	0.381	21

AZ Canal- WTPs	Average	Мах	Min	Median	Stdev	n
R12	2.231	3.299	1.179	2.173	0.493	21
R13	2.416	3.078	1.894	2.441	0.358	19
R14	2.579	3.902	1.890	2.569	0.482	19
R15	2.245	2.972	1.710	2.243	0.400	16
R16	2.535	3.518	1.967	2.558	0.446	19
R17	2.298	2.848	1.672	2.294	0.365	16
R18	2.408	3.420	1.432	2.384	0.471	21
R19	2.099	3.042	1.044	2.136	0.433	21

Table 6.4. Dissolved organic carbon (DOC) concentrations in the SRP canal cluster and selected Phoenix WTPs (R15, R17, R19).

Table 6.5. Water budgets for four arid-region reservoirs in Metropolitan Phoenix from June 1999 to May 2000.

	Horseshoe Res.	Bartlett Res.	Saguaro Lake	Lake Pleasant
D Storage				
$x 10^6 m^3$	(15.03)	105.77	(0.97)	(51.70)
Runoff Input				
$x \ 10^6 \ m^3$	542.14	510.95		68.49
Other Input			745.00	1 010 00
x 10° m°			715.98	1,212.93
Evaporation				
$x 10^{6} m^{3}$	16.03	22.05	14.36	111.30
Seepage				
$x \ 10^6 \ m^3$				1.73
Output				
$x 10^6 m^3$	510.95	480.52	738.59	1,225.65
Gain/loss				
$x 10^6 m^3$	(30.19)	97.40		5.57
Mean HRT,				
days	39	144	75	401

Table 6.6. DOC budgets for four arid-region reservoir systems (Metropolitan Phoenix, AZ) from August 1999 to May 2001.

	Total Load, x 10 ⁶ Kg	Total Release, x 10 ⁶ Kg	Storage change, x 10 ⁶ Kg	Net DOC gain/loss, x 10 ⁶ Kg (%)	Reaction rate, mg/L-d
Horseshoe	1.147	1.436	-0.059	0.217 (18.7)	0.01097
Reservoir	1.160	1.437		0.231 (20.1)	0.01164
Bartlett Reservoir	1.436 1.437	1.047	0.562	0.011 (0.75) 0.012 (0.84)	0.00015 0.00017
Lake	1.695	1.063	1.150	0.503 (29.4)	0.00114
Pleasant	1.710	1.064		0.519 (30.6)	0.00117
Saguaro	2.455	2.294	0.055	-0.075 (-3.0)	-0.00133
Lake	2.476	2.347		-0.106 (-4.3)	-0.00188

Table 6.7. Characteristics of isolated fulvic acids from the Verde river reservoir system.

	Fulvic acids %	SUVA, (mg/L)- 1cm-1	Ar-C/AI-C mol/mol	Aromaticity	C/N mol/mol
R20 (Oct 99)	41.5	0.026	0.25	0.160	34.3
R20 (Apr 00)	31.9	0.024	0.21	0.142	40.8
R20 (Jul 00)	33.1	0.034	0.30	0.176	19.6
R20 (Mar 01)	47.7	0.031	0.31	0.173	37.8
R5 (Apr 00)	40.3	0.034	0.22	0.134	30.6
R5 (Sept 00)	37.0	0.037	0.30	0.178	26.1
R5 (Dec 00)	60.0	0.031	0.31	0.182	44.8
R5 (Mar 01)	63.6	0.032	0.28	0.172	37.4
R6A (Dec 00)	43.1	0.021	0.26	0.162	36.9
R7 (Oct 00)	48.5	0.023	0.26	0.158	31.3
R7 (Apr 00)	32.4	0.020	0.21	0.133	38.9
ALG6 (Feb 01)	22.2	0.016	0.19	0.124	10.1
SRFA Standard		0.044	0.64	0.240	93.9

Figure 6.1. Influence of hydrology on DOC concentrations in the Verde River above Horseshoe Reservoir (R20).



Figure 6.2. Variations in DOC reactivity (SUVA values) in the Verde cluster.



Figure 6.3. DOC reactivity to DBP formation (SUVA values) in the SRP canal cluster (raw water) and Phoenix WTPs (treated water).



Figure 6.4. Spatial distribution of THM formation (SDS) for the different source waters: CAP cluster (R1- R4&R11); Verde cluster (R20 &R5-R7); Salt cluster (R8 - R10); n =6.



Figure 6.5. Spatial distribution of HAA_9 formation (SDS) for the different source waters: CAP cluster (R1- R4&R11); Verde cluster (R20 &R5-R7); Salt cluster (R8 - R10); n =6.



Figure 6.6. Schematic of DOC fractionation by adsorption chromatography using XAD-8 and XAD-4 resins.



Figure 6.7. Fractions of DOC from 3 arid region reservoirs (Lake Pleasant, Bartlett Lake, Saguaro Lake) in Spring 2001 (April).



Figure 6.8. Characteristics of isolated fulvic acids from the Verde cluster in comparison to terrestrial- and algal-derived fulvic acids (SRFA and ALG6, respectively).



Figure 6.9. Spatial distribution of apparent molecular weight fractions (MWFs) for the three reservoirs system in February 2001 (before the impact of spring runoff)







Figure 6.11. Biodegradability (BDOC₅) of algal-produced DOC (Scenedesmus quadricauda).





Figure 6.12. Trend in DOC loading and net rate of DOC reaction in Lake Pleasant.

Figure 6.13. Trend in DOC load and net reaction rate in Horseshoe Reservoir.





Figure 6.14. Trend in DOC load and net reaction rate in Bartlett Reservoir.

Figure 6.15. Molecular weight of DOC and DON for Squaw Peak (SP) WTP in the raw (In) and finished (out) water on October 4, 2001.



Figure 6.16. DON removal in jar tests conducted with CAP water plus a NF/XAD4 acid fraction isolated from CAP water (Initial conditions: DOC = 5 mg/L, DON = xx mg//L, $UVA = \text{m}^{-1}$).



Figure 6.17. Removal of DOC by three City of Phoenix WTPs.



Figure 6.18. Removal of UVA₂₅₄ by three City of Phoenix WTPs.



Figure 6.19. Change in $SUVA_{254}$ by three City of Phoenix WTPs.



SECTION 7: MIDCOURSE EVALUATION (TASK 6)

PURPOSE OF THE MIDCOURSE EVALUATION

From its inception, the major goal of this project was to implement and validate measures for reducing the taste and odor of water for consumers in Phoenix. The goal of the midcourse evaluation was to evaluate potential T&O mitigation practices identified in the original proposal (plus a few others), and to develop an overall T&O mitigation strategy. The midcourse evaluation consists of five parts:

- 1. A discussion of evaluation tools and a proposed metric for evaluating success of the T&O mitigation program in the implementation phase.
- Examination of operations of the source water supply system (reservoirs and canals) and water treatment plants. Knowledge of the water supply system will set the stage for the discussion of individual T&O mitigation practices.
- 3. An analysis of the spatial and temporal aspects of the T&O problem in Phoenix, with an emphasis on causative factors.
- 4. An analysis of individual T&O mitigation practices, including technical, economic, and legal/institutional issues.
- 5. Development of a multiple barrier strategy for T&O mitigation, based on a suite of the most successful individual practices, and an approach for continuation of a T&O management program beyond the end of this project (2002).

EVALUATION TOOLS

The evaluation of T&O control practices was based on the following:

- 1. Literature review. An extensive body of literature on T&O mitigation was used to identify and evaluate potential T&O control practices.
- Knowledge of the spatial and temporal aspects of the T&O problem. Results from the monitoring program (Task 1) were used to determine where and when potential T&O mitigation strategies would be most effective. The monitoring program has also been used to evaluate the success of early implementation measures.
- 3. Lab experiments. Lab experiments were used to isolate "culprit" algae and actinomycetes, study their environmental preferences, and evaluate control measures.
- 4. Field-scale experiments. These were experiments conducted in the field, to achieve realism, but were done at a scale that would not likely result in the delivery of better-tasting water to consumers.
- 5. Full-scale implementation of T&O mitigation practices. These are "experiments" in one sense treatments are done in a controlled fashion and data are collected that result in defensible conclusions regarding the treatment effectiveness, but have been done at a

scale has led to discernible improvement in the quality of water delivered to consumers.

Evaluation of individual control measures has typically expanded in time and space. Early in the evaluation process experiments might be done in laboratory beakers over the period of hours to several days. Measures that appear to be successful at this scale sometimes are evaluated in field-scale experiments that have greater realism but are still restricted in either spatial scale or duration. For example, in the fall of 1999 we conducted field-scale experiments with canal brushing. This experiment consisted of nine treatment patches along the side of the Arizona Canal, each 30 m long, which were subjected to brushing treatments (no brushing, one time brushing, and brushing every two weeks for three months). This experiment was useful in determining optimum brushing intervals but because the patches were small, it had little or no effect on T&O compounds in the canal. In September, 2000, brushing was conducted along a one mile stretch of canal in which MIB concentrations had increased significantly, resulting in lower concentrations of MIB and Geosmin in water delivered to the Deer Valley Water Treatment Plant. However, mechanical brushing could be improved because algae were also growing on the bottom of the canal – an area that could not be reached by the current brushing machinery. SRP may soon build a maintenance barge that will be able to brush the bottom of the canal as well as the sides. Use of this barge would probably further improve control of T&O culprit algae.

EVALUATION METRIC

As we move into the implementation phase of a T&O mitigation strategy, a metric is needed to evaluate the success of individual control measures and the overall mitigation strategy. The ideal metric would integrate several aspects of the T&O problem:

- 1. Concentrations of MIB and Geosmin in water delivered to consumers.
- 2. The *number of people affected* by control measures.
- 3. The duration of effectiveness.

We propose a metric that meets these criteria: *consumer days below threshold* (CDBT). The "threshold" is a concentration of MIB and Geosmin deemed acceptable. For example, for most people 10 ng/L is considered a taste threshold for both MIB and Geosmin. Consumer days below threshold must therefore be referenced to a specific MIB or Geosmin level. For a 10 ng/L threshold, the acronym would be CDBT-10. Because consumer complaints generally do not start until MIB and Geosmin levels exceed 20 ng/L (W. Alsmadi, per. comm.) and because it will probably be difficult to consistently achieve 10 ng/L concentrations in this system, we have also enumerated "CDBT-20s", consumer days below a 20 ng/L threshold. In either case, CDBTs are calculated as the product of the *service population* times the *duration* for which MIB or Geosmin is below the threshold concentration.

The CDBT concept integrates the effect of service population with that of duration and is therefore a good overall measure of the impact of T&O on consumers. The concept can be used in several ways. First, the effectiveness of most T&O control measures could be evaluated by computing reductions in CDBTs, compared to a non-treatment option. For example, if 500,000 people were drinking water that had a MIB concentration of 20 ng/L for one month (30 days), there would be 0 CDBT-10s. If powered activated carbon (PAC) were added

to the treatment plant, reducing the MIB level to 7 ng/L (below threshold), the service population would experience 15 million CDBT-10s (500,000 people x 30 days). PAC treatment therefore increased the number of CDBT-10s from 0 to 15 million. Over the period of a full year, untreated water would often have < 10 ng/L MIB, so PAC treatment would not always reduce the CDBT values.

The CDBT concept could also be used to compare treatments. For example, one treatment may reduce MIB to < 10 ng/L for a service population of 50,000 for fifteen days. Another treatment might also reduce MIB to < 10 ng/L for a service population of 25,000 for a full month. Judged by the CDBT criteria, both treatments would be considered equivalent (50,000 x 15 days = 25,000 x 30 days = 750,000).

The concept could also be used to evaluate cost-effectiveness of T&O mitigation efforts when the costs are clearly defined. Ultimately, most measures can be evaluated on the basis of dollars spent per CDBT (\$/CDBT).

Finally, the CDBT concept could be used to evaluate overall changes in consumer satisfaction over the period of several years. For three Phoenix water treatment plants (Deer Valley, Squaw Peak, and Val Vista) we will be able to evaluate annual CDBTs from 1998 through the end of this program (2002), except for part of 1999.

RESERVOIR SYSTEM AND OPERATIONS

Morphologic and hydrologic characteristics of the study reservoirs are shown in Table 7.1. Although the three reservoirs vary in size, they are all over 100 feet deep and have similar hipsographic characteristics (Table 7.2). For example, the percentage of total area below a depth of 25 feet varies by only 7% among the three reservoirs, and the area below a depth of 50' varies by only 6%.

CAP System and Lake Pleasant

Lake Pleasant is by far the largest of the three reservoirs in this study. It is also the only dam with multiple outlets – located at 1506 feet and 1610 feet – and is the only pumped storage reservoir. Prior to 1999, normal operation was to pump water from the Colorado River during the late fall to fill Lake Pleasant. Filling was completed before May and from then on water was released from Lake Pleasant to the CAP Canal downstream throughout the summer. This operation was modified in 1999 to ameliorate T&O problems. In 1999, water from the Colorado was pumped past Lake Pleasant (pass-through pumping) during the months of July through November. Water was also released from the lower gate (in the hypolimnion during the summer) rather than the upper gate (Figure 7.1). The impact of these operational modifications will be discussed below (Source Water Selection).

CAP water is used by Phoenix's Union Hills Water Treatment Plant. CAP water can also be pumped into the Arizona and South Canals at the Granite Reef Interconnect Facility. CAP water has been a minor fraction of total water delivered via the Arizona Canal: 18% in 1997 and 5% in 1998. CAP water demands are typically "programmed" in the fall for the following year and deliveries during any single month are usually limited to eleven percent of the annual water allocation.

SRP Reservoirs

Water is supplied to downstream SRP users "on demand". Four of the reservoirs on the Salt Reservoir system, including Saguaro, are used for hydroelectric operation. In general, SRP deliveries during the summer are predominately from the Salt River side of the system, whereas winter deliveries are obtained primarily from the Verde side. The Salt River side is preferentially used in the summer to take advantage of the relatively high value of electricity during the summer. Since the Verde River reservoirs are not equipped with hydroelectric generation capacity, water from this system is used mainly during the winter months. The switchover from Salt to Verde River water is abrupt, occurring on October 25 (1996), October 25 (1997), October 23 (1998), October 24 (1998), October 2 (1999), and October 3 (2000). After the initial shut down, varying amounts of Salt River water are used throughout the winter. Per agreement with the Arizona Fish and Game Department, a minimum flow of 100 cfs is maintained in the Salt River below Stewart Mountain Dam throughout the winter. All of the reservoirs in the SRP system have a single outlet near the bottom. During the summer stratification period, water released from these reservoirs comes from the hypolimnion.

Stream flow in this region is extremely variable. Although reservoirs buffer hydrologic variations to some extent, water releases from the reservoirs also varies significantly from year to year (Table 7.3). From 1996 to 1999, releases from Horseshoe and Bartlett varied by a factor of three. Outflows from Saguaro Reservoir are more stable but even so outflow in 1996 was 50% higher than outflow in 1998 (Table 7.3). Because water inputs to Saguaro Reservoir are controlled by a series of upstream reservoirs, water is maintained at near-constant elevation, around 1525' (Figure 7.2). By contrast, elevation of the Verde River reservoirs varies by as much as 100' (Figure 7.2). The considerable variability in annual hydrology imposes constraints but also creates opportunities with respect to T&O mitigation from year to year.

Canals

Water is conveyed to COP's drinking water plants by canals. Hydraulic characteristics of the AZ Canal have some bearing on the T&O problem. As water moves down the AZ Canal, diversions reduce the flow (Figure 7.3). From the upper end of the canal to the lower end, velocities drop from ~ 3 fps to 1 fps. The Arizona Canal is shallowest at the upper end and lower end (ca 4 ft), with greater depths in the mid-section (up to 8 ft). The lower flows and shallower depths found at the lower end of the AZ Canal are conductive to the growth of algae (see Temporal and Spatial Dimensions of the T&O Problem, below).

Phoenix Water Treatment Plants

Phoenix operates five water treatment plants, which cumulatively deliver 98,100 million gallons per year to consumers. The plants and their percentage of total production are: Deer Valley (18%), Squaw Peak (20%), Val Vista (23%), Union Hills (28%), and Verde (7%). A small amount of groundwater (4% of total) that does not go through the treatment plants brings total water production up to 102,280 million gallons per year (280 MGD). For a total service population of 1.3 million, average daily consumption is 220 gallons/person-day. Water production and consumption varies among seasons, from 158 gallons/capita-day in January to 291 gallons/capita-day in June (Table 7.4). The main reason for higher summer consumption is landscape irrigation. To evaluate CDBTs values in subsequent sections of this report,
values from Table 7.4 were used in conjunction with monthly production data from individual water treatment plants to estimate the number of consumers served during a particular month. This approach was necessary because the water distribution system is interconnected among water treatment plants, making it impossible to determine a discrete service population for each treatment plant.

All the water treatment plants in Phoenix except for Union Hills employ conventional treatment with a treatment train consisting of pre-sedimentation, coagulation/flocculation, sedimentation, and mixed bed depth filtration. Union Hills is a direct filtration plant. None of the plants are equipped with membrane filters, carbon beds, or ozonation. Most plants have some algae problems and employ various methods of pretreatment to control algae. All plants can and have used powered activated carbon (PAC) to remove T&O compounds. In-plant algae and T&O control options are discussed in other sections.

TEMPORAL AND SPATIAL DIMENSIONS OF THE T&O PROBLEM

The development of a multiple barrier approach for T&O control depends upon a thorough knowledge of the spatial and temporal dimensions of the T&O problem. In developing the midcourse evaluation we used three sets of data:

- A U of A study conducted from 1997-1998.
- An ASU study conducted from early 1998 to early 1999.
- The current project, with data from August 1999 to October 2000.

Questions that can be addressed by these data sets are:

- 1. What are the general temporal and spatial patterns of MIB and Geosmin concentrations?
- 2. What environmental conditions (temperature, nutrients, etc.) are associated with high levels of MIB and Geosmin?
- 3. What organisms are associated with elevated MIB and Geosmin levels?
- 4. What is the frequency of episodes above criteria levels?

Reservoirs

Bartlett Reservoir

Data from 1998 (SRP study) and the current study (1999-2000) show MIB concentrations in Bartlett Reservoir peak in the late summer or early fall (Figure 7.4). Over the three-year period, peak MIB levels in the epilimnion were 22 ng/L (October 1998), 12 ng/L (October 1999), and 54 ng/L (August 2000). High MIB levels in August 2000 were preceded by elevated counts of bluegreen algae (144/mL) in July. Peak MIB levels in the Verde River below Bartlett Reservoir were 23 ng/L (October 1998), 12 ng/L (October 1999), and 14 ng/L (October 2000). MIB concentrations in water released from Bartlett Reservoir during the summer stratification period were generally lower than concentrations in the epilmnion because MIB produced in the epilmnion is prevented from diffusing to the hypolimnion by a thermal barrier (the thermocline). For example, the MIB concentration in the water exiting Bartlett Reservoir during August 2000 was only 7 ng/L, even though MIB in the epilimnion was 54 ng/L.

Geosmin levels have generally been much lower than MIB levels in Bartlett Reservoir, with one exception: a concentration of 118 ng/L reported for the bottom on August 26 1998. Otherwise, concentrations have consistently remained below 10 ng/L. Peak Geosmin concentrations in the Verde River below Bartlett Reservoir were 18 ng/L on August 29, 1998 and 17 ng/L on September 26, 1998. Geosmin levels have otherwise remained below 10 ng/L at this site.

Saguaro Reservoir

No MIB or Geosmin data had been collected from Sagauro Reservoir prior to this study. Peak MIB levels were observed in September 1999 (28 ng/L) and August 2000 (44 ng/L)(Figure 7.5). The August 2000 peak was preceded by a minor blue-green bloom (252/mL) comprised largely of *Anabaena sp.*, but MIB concentrations had been increasing gradually since April in the apparent absence of major blue-green blooms. During late summer water is released from the hypolimnion, where concentrations are generally lower. During August 2000 for example, the MIB concentration in the Salt River below Saguaro Reservoir was only 14 ng/L. Peak MIB levels in the Salt River occurred following turnover in October 1999 (15 ng/L) and October 2000 (24 ng/L).

Lake Pleasant

MIB and Geosmin data were collected during the U of A study (1996-1997) and in the current study. In the current study, peak epilimnetic MIB concentrations were 45 ng/L (September 1999) and 14 ng/L (August 2000)(Figure 7.6). As with the other reservoirs, MIB levels were generally lower in the hypolimnion than in the epilimnion. MIB levels at site R4, about 10 miles downstream from Lake Pleasant on the CAP Canal, were consistently below 10 ng/L as the result of modified reservoir operations. This point will be discussed later (Source Water Selection).

Summary

MIB concentrations were not well correlated with overall algae abundance (as indicated by chlorophyll concentrations; Figure 7.7). MIB concentrations in water released from the reservoirs accounts for the majority of MIB observed in WTP influents. MIB levels do appear to be related to blue-green algae counts, but the relationship is not very precise (Figure 7.8). On at least two occasions, blue-green blooms were associated with spikes in epilimnetic MIB levels. The best single predictor of high MIB levels is temperature (Figure 7.9). The relationship between MIB and temperature is not a simple linear relationship but shows a distinct threshold effect. There are two notable temperature thresholds: (1) when the water temperature is < 20°C, epilimnetic MIB levels were always < 20 ng/L and (2) MIB levels exceeded 30 ng/L only when the water temperature was > 25°C. MIB values > 20 ng/L did not occur during the winter or spring in 1999 or 2000, when water temperatures were < 20°C. MIB levels are not always high when the temperature exceeds 25°C; elevated temperature appears to be a necessary but not sufficient condition to cause an MIB episode. These rules of thumb, if they bear up under further scrutiny, may be useful for planning future T&O mitigation efforts.

Canals

T&O problems have consistently occurred at the lower end of the Arizona Canal. Since 1997, 25 samples had MIB > 10 ng/L and 15 samples had MIB > 20 (Table 7.5). The majority of episodes occurred from July onward, particularly in the July- October time frame. Fewer Geosmin

samples have exceeded 10 ng/L (10) and fewer yet have exceeded 20 ng/L (3). The most serious MIB episode occurred in September-October, 1997, during the U. of Arizona study, when MIB peaked at 170 ng/L. Peak MIB levels in subsequent years were 43 ng/L (October 1998), 28 ng/L (October 1999), and 64 ng/L (September 2000) (Figure 7.10). These peaks typically occur about a month later than MIB peaks in the reservoirs. MIB levels typically decline by November, when temperatures drop below 25°C. There is little doubt that MIB is produced within the canals. With earlier data, there was some question regarding the reliability of data during longitudinal data collection runs, but samples collected in August of this year clearly show an increase from ~ 30 ng/L to 64 ng/L in a one-mile stretch of canal between 19th and Central Ave. Laboratory experiments with blue-green algae isolated from canal walls in this vicinity confirm that several species produce MIB.

Water Treatment Plants

During our 1998-1999 study, there was some evidence of MIB production within the Squaw Peak and Deer Valley WTPs. However, the analytical method used during this study was subject to variable recovery rates and these data are suspect. Detailed measurements of MIB and Geosmin throughout the Deer Valley, Val Vista and Squaw Peak WTPs from August to November 1999 show that very little or no MIB is produced within the water treatment plants (Figure 7.17). From August 1999 to October 2000), the average change in MIB concentration between the inlet and outlet was Δ 1 ng/L at the Squaw Peak WTP and Δ 6 ng/L at the Deer Valley WTP, indicating that very little removal or production of MIB occurs in these WTPs. Average MIB in the outlet of the Val Vista WTP was somewhat lower than inlet concentrations because PAC was used during the fall of 2000. Intensive sampling throughout the entire treatment train of the Deer Valley WTP also indicated no MIB production at any point in the plant.

EVALUATION OF INDIVIDUAL T&O MANAGEMENT PRACTICES

This section examines nearly 20 potential T&O control practices outlined in the original proposal. Each was evaluated for technical, economic, and legal/institutional feasibility. Based on this evaluation, a few practices were selected for implementation.

Watershed Nutrient Control

Control of nutrient inputs from the watershed is the mainstay of lake eutrophication management [Cooke, 1993 #31]. Watershed nutrient control was therefore initially considered as a potential management strategy.

Technical evaluation

Two questions were addressed:

- 1. Are nutrient loadings from the watersheds above the three reservoir systems elevated, compared to regional reference levels?
- 2. Would reduced nutrient inputs reduce production of T&O compounds in the reservoirs?

The SRP system is supplied water from the Salt and Verde Rivers. The watershed of the Salt River above its confluence with the Verde is lightly populated (30,000), contains almost no agriculture and has no livestock operations. This river is a suitable reference site by which to evaluate possible nutrient impacts to the Verde River. The watershed of the Verde River above Horseshoe Reservoir has a population of 60,000. There is a small area of irrigated agriculture in the mid-Verde Valley which contributes irrigation return flow to the river, one fish hatchery that discharges water to a tributary, and several areas of intensive recreational activity (e.g., Oak Creek).

The CAP Canal receives water from the Colorado River at Lake Havasu. In most years the Colorado River is the major source of water to Lake Pleasant. During wet years, the Aqua Fria River contributes a significant fraction of the inflow. Because Lake Pleasant is an off-stream reservoir, inflows can be controlled at Lake Havasu or at the Waddell pump station.

Nitrogen (N) and Phosphorus (P) levels in the Saguaro Reservoir inlet (site R5) and the Verde River above Horseshoe Reservoir (site R20) are roughly comparable (Table 7.6). However, the Salt River has passed through four reservoirs before in reaches Saguaro Reservoir, whereas the Verde River above Horseshoe Reservoir is uncontrolled. Somewhat elevated P levels in both rivers reflects their geological setting with P-rich minerals. The Colorado River has lower TP than either the Salt or Verde rivers. All TP values were well below 0.1 mg/L. TN levels are similarly low, with means < 0.5 mg/L in all three inflows. Based on TN:TP ratios, the Verde River and the Salt River (at the inlet to Saguaro Reservoir) would be considered N-limited, whereas the Colorado River would be considered P-limited [Baker, 1996 #2].

N and P levels in the Verde River are comparable with those in the Salt River. Since the Salt River watershed is nearly pristine, it follows that there is little nutrient enrichment in the Verde River and therefore little opportunity to reduce nutrient inputs from human activities.

In some years, there may be an opportunity to reduce total P inputs to Lake Pleasant by controlling pumping from the Colorado River. The basis of this practice is that total P levels vary dramatically with flow, with TP generally increasing with increasing flow and suspended solids concentrations. For example, [Baker, 1981 #47] predicted that shifting pumping from May (peak flow, following snowmelt) to June would have reduced annual P input to a proposed reservoir in Colorado by 40%.

This strategy would be useful only in "flood years" with high turbidity. The Central Arizona Water Conservation District (CAWCD) temporarily halted pumping during a flood period in 1992. Although their goal was to prevent high-turbidity water from being delivered to water treatment plants, it probably had the effect of reducing TP loading to Lake Pleasant. The CAWCD can readily use its on-line turbidity monitoring in the CAP Canal at Lake Havasu to determine rapid increases in turbidity and make small adjustments in its pumping regime to reduce turbidity. In doing so, TP loading would also be reduced, with the probable effect of proportionally reducing total algae abundance in Lake Pleasant. This would be beneficial to water treatment plant operations because algae tend to clog filters and shorten filter runs, but would probably not have much effect on T&O production.

The second question is: would a reduction of nutrient inputs reduce the production of T&O compounds in the downstream reservoirs and canals? There is no question that nutrient reduction will, in most cases, reduce algae abundance in lakes [Cooke, 1993 #31]. Reducing

nutrient inputs is the cornerstone of most eutrophication management plans. However, it does not follow that there will be a reduction in formation of T&O compounds, because relatively few algae produce T&O compounds. We have found a weak relationship between algae abundance (as indicated by chlorophyll a) and concentrations of MIB (Figure 7.7). There was a weak relationship between TN and chlorophyll a and between TN and MIB (Figure 7.11A and B). For the two SRP reservoirs, the relationship between TN and chlorophyll a poor predictor of MIB (Figure 7.11C and D). Relationships between TP and chlorophyll and TP and MIB were not statistically significant (0.05 level).

Economic evaluation

Economic evaluation was not performed because the technical evaluation indicated that nutrient inputs to the reservoirs are not elevated and therefore not amenable to control.

Legal/institutional evaluation

Legal and institutional evaluation also was not conducted because no clear management strategy was indicated.

Summary

In summary: (1) nutrient inputs to the reservoirs were generally low and are not amenable to reduction, and (2) MIB was not closely correlated with algal abundance or nutrient concentrations. These data suggest that reducing nutrient inputs to the reservoirs, even if it was feasible, would not likely ameliorate the T&O problem.

Control of Nutrients in SRP canals

Technical evaluation

N concentrations in water entering the AZ Canal were low and fairly stable, averaging 0.3-0.4 mg/L. During this study, total and total dissolved N increased somewhat downstream, probably a result of an influx of nitrate-enriched well water (Figure 7.12). TN and TDN were somewhat higher in summer 2000 and then declined during the fall. Total and dissolved P concentrations were low and similar among sites. At all three sites, average concentrations were the same: 0.02 mg P/L for total P and 0.01 mg/L for total dissolved P. There was no apparent longitudinal trend in TP or TDP, indicating that phosphorus does not enter the AZ Canal as it passes through the urban core. The median ratio of total dissolved N: total dissolved P increased along the length of the canal, from 19:1 at site 13 to 27:1 and 43:1 at sites 14 and 16, respectively. There was no significant relationship between MIB and TN, TP, or TDN:TDN. The possible role of well pumping, which adds nitrate to the canal, warrants further scrutiny through the remainder of the project. In particular, several large production wells may be contributing to the proliferation of T&O-producing algae in the lower end of Arizona Canal. If further study indicates that these wells are contributing to the problem, one solution may be to utilize these wells at times of the year when growth of T&O-producing algae is less likely to occur. Based on observations to date, pumping in early to mid summer would likely cause less of a problem than pumping later in the season.

Economic evaluation

If further study shows that altering the pumping regime for a few wells would be a viable

strategy for reducing the growth of T&O producing algae in the Arizona Canal, the cost for implementation may be small, because the wells would be pumped anyway, but at a different time. The only cost would be the differential cost for electricity at one time of the year versus another.

Legal/institutional evaluation

The maximum contaminant limit (MCL) for nitrate is 10 mg NO₃-N/L.This level is never approached in the Arizona Canal under current operating conditions. Any change in well pumping regime would be constrained by the need to maintain NO₃-N well below the MCL. Because well pumping is always a small fraction of total flow throughout the year, this constraint should not be difficult to meet.

Summary

The potential for altering well pumping regimes should be studied further.

Reservoir Management: Control of P Cycle

Technical evaluation

Several reservoir management practices are commonly used to reduce availability of phosphorus to algae: these are (1) *destratification*, (2) *hypolimnetic aeration*, and (3) *alum treatment*. Destratification and hypolimnetic aeration may reduce P recycling in lakes and reservoirs where much of the phosphate is bound to iron hydroxides. An idealized scenario follows: adsorption to iron hydroxides removes phosphate from the water column. Under anaerobic conditions, which occur in the hypolimnia of all three reservoirs, iron hydroxide is reduced, releasing phosphate to the water column. Phosphate accumulates in the hypolimnion throughout the summer, and when fall turnover occurs, phosphate is circulated throughout the water column, causing an algae bloom [Wetzel, 1983 #60]. Both destratification and hypolimnetic aeration keep the water column oxic and thereby prevent release of iron-bound P.

Alum treatment works in a slightly different way: alum is added to bind soluble phosphate, forming an alum floc on the sediment surface. This floc then adsorbs phosphate released from sediments. This technique is most commonly used to control release of P from sediments in lakes where P inputs have been greatly reduced to control eutrophication. Under these circumstances, sediments that have been enriched with P over many years may continue to release P and maintain eutrophic conditions after external P loads are reduced [Garrison, 1984 #61].

Because these three techniques share a common mechanism, they were evaluated together. The broad question is: would reduced P recycling reduce T&O formation in the reservoirs? This question can be broken down into three more tractable questions:

- 1. Is P the limiting nutrient for algae growth?
- 2. Is the amount of phosphorus that is entrained from the hypolimnion to the whole water column large enough to stimulate an algae bloom?
- 3. Do such blooms occur, and, if so, are they composed of T&O-forming blue-green algae?

In most freshwaters, either N or P limits algae growth at low to moderate concentrations (at very high nutrient concentrations, light can be limiting). Based on the Redfield equation, the idealized N:P ratio is 7:1 (wt:wt). Thus, when the ratio of N:P is > 7, algae growth is P-liminted; when it is less than 7, it is N-limited. In practice, when N or P is added to natural waters in laboratory experiments and then seeded with algae, algae growth is stimulated by addition of N in waters with initial N:P ratios < 10:1 (wt:wt) and by addition of P in waters with initial N:P ratios > 20:1. In waters with intermediate N:P ratios, results were less clear [Chiaudani, 1974 #62].

Data collected during this study were used to compute three N:P ratios for the epilimnion of each reservoir: total N:total P(TN:TP), total dissolved N: total dissolved P (TDN:TDP), and particulate N: particulate P (PN:PP) (Table 7.7). On the basis of TN:TP ratios, Bartlett Reservoir (R6A) appears to be N-limited and the other two reservoirs are probably P-limited. Ratios of TDN:TDP in all three reservoirs are well above the 20:1. Ideally, this ratio would be a good indicator of nutrient availability, but we now hypothesize that much of the TDN occurs as refractory organic matter (associated with DOC) and is not available for algae growth. Thus, interpretation of ratios of TN:TP or TDN:TDP is suspect. The third ratio (PN:PP) reflects nutrient concentrations within algae cells. This ratio is lower for Bartlett Reservoir than the other two reservoirs appear to be P-limited. Thus, P levels should be correlated with algal abundance in Lakes Pleasant and Saguaro, but not in Bartlett.

The next two questions can be addressed by examining temporal patterns of TP, algae abundance, blue-green algae abundance, and MIB levels before and after turnover. If the hypothesis of P release and recycling is true, then P concentrations should increase in the uppper layer of the lake following turnover. This would trigger an algae bloom, resulting in increased chlorophyll, and perhaps a bloom of blue-green algae and a pulse of MIB. The postturnover sampling period was defined as the time at which the differential between the average temperature of the upper 15 m and the average temperature at all depths < 20 m was < 2° C. In both 1999 and 2000, turnover in Bartlett and Saguaro occurred in October and in Lake Pleasant it occurred in November. In 1999, TP in the upper layer of Bartlett reservoir increased from 0.006 mg/L in Sept. to 0027 mg/L in October, indicating entrainment of P during turnover. However, algae abundance and chlorophyll concentrations decreased (Table 7.8). Blue-green abundance increased somewhat, but MIB levels were nearly unchanged. For Saguaro Reservoir, TP increased slightly, but total algae counts decreased by half and chlorophyll concentrations changed little (Table 7.8). Blue-green counts decreased somewhat, but MIB concentrations were unchanged. Finally for Lake Pleasant, TP doubled following turnover, total algae abundance decreased, chlorophyll concentrations increased, and blue-green counts and MIB levels were essentially unchanged.

In summary, TP concentrations did increase following turnover in all three reservoirs, but total algae counts decreased. There was certainly no massive blue-green bloom following turnover, and very little change in MIB concentrations. These data, taken together, strongly suggest that measures to reduce recycling of phosphorus from the hypolimnia of these reservoirs would probably not reduce blue-green algal abundance or MIB levels. Data from October and November 2000 will be analyzed to confirm this conclusion.

Economic evaluation

The concentration of alum to be added depends upon alkalinity, to prevent severe pH drops. Based on a nomograph in [Cooke, 1993 #31], a 10 mg/L dose would be sufficient for local reservoirs. Alum treatment would be extremely expensive, with alum cost alone (not including application) running over \$1 million for each of the two smaller reservoirs and nearly \$10 million for L. Pleasant. One treatment would probably be effective for several years.

Legal/institutional evaluation

Alum is used in most water treatment plants, so adding alum to reservoirs would not impose a human health hazard. Although aluminum is toxic to fish in the Al³⁺ form, alum quickly results in a precipitate, and fish toxicity is not considered a major problem with alum treatment.

Hypolimnetic aeration probably would pose no legal or institutional problems. A side benefit would be a well-oxygenated, cool water refuge for cool water fish. Hypolimnetic aeration would also prevent accumulation of reduced chemical species such as sulfide, Fe²⁺ and Mn^{2+.} The latter is a minor problem in Lake Pleasant, because Mn²⁺ remains in water released from the hypolimnion as it flows to the Union Hills Plant.

Summary

The high cost of alum treatment and the lack of evidence implicating P recycling as a causal factor in stimulating blooms of MIB-producing algae indicate that this practice would probably not be a useful T&O mitigation practice. Hypolimnetic aeration and destratification may have other water quality benefits but it is unlikely that either would cause a reduction in T&O producing algae by the mechanism of controlling P recycling.

Reservoir Management: Destratification to Cool Surface Water

As noted above, destratification would probably not be successful in preventing post-turnover algae blooms, blue-green blooms, or MIB production by controlling P recycling. However, it may work by another mechanism. As noted earlier, elevated MIB levels occur only when water temperatures are elevated, with major episodes (MIB > 25 ng/L) occurring only when temperatures exceed 25° C (Figure 7.10). This observation suggests that destratification may reduce T&O episodes by cooling the epilimnion. The mechanism is simple: by mixing cooler hypolimnetic water with warmer epilimnetic water, the temperature of the epilimnion would decrease. The decrease can be predicted accurately by volume-weighting the observed temperatures of the epilimnion and hypolimnion. For example, in June 1999, the three study reservoirs all had surface temperatures to 17° C to 21° C (Table 7.10). The temperature of the water column would still increase throughout the summer, but the maximum temperature would always be lower than it would have been without destratification. Predicting water column temperatures throughout the season would require detailed thermal modeling.

Technical Evaluation

Observed effects of destratification are quite variable, and most destratification projects have involved lakes and reservoirs much smaller than the Phoenix area reservoirs, but this practice warrants further evaluation. It is possible that destratification could make the T&O problem worse. One possible response is that destratification would reduce the abundance of T&O producers with high temperature optima but promote growth of equally noxious T&O producers with lower temperature optima. Destratification would also eliminate the thermal barrier that now separates the epilimnion (which often has elevated MIB levels) from the hypolimion (which generally has lower MIB levels) and could possibly increase concentrations of MIB delivered to downstream customers during the summer. A side benefit of destratification is that it would

decrease evaporation by cooling the surface layer. Destratification, like hypolimnetic aeration, would also have benefits associated with an oxic water column: a deep refuge for coolwater fish, and decreased concentrations of reduced chemical species.

Lorenzen and Faust (1978) (in [Cooke, 1993 #31]) found, using empirical data for many destratification projects, that an air flow of 10 m³/km²-min is needed to achieve complete destratification. Air pumping requirements for each reservoir were computed using this design parameter (Table 7.11).

Economic evaluation

The USBR estimated that it would cost \$350,000 to install aeration equipment in Lake Pleasant and \$50,000/year to operate the aerator (1989 dollars; [USBR, 1989 #17]. The design was intended to aerate the hypolimnion, not destratify the reservoir and provided only 18 m³/min air. SRP is developing a preliminary cost estimate for destratification of Bartlett and Saguaro reservoirs based on air flow requirements in Table 7.11.

Legal/institutional evaluation

Destratification would certainly require permits from Arizona Fish and Game and the Department of Environmental Quality. By entraining oxygen throughout the water column, destratification could potentially improve the fisheries, particularly for coldwater species. By cooling surface water, destratification would also reduce evaporation rates and conserve water.

Summary

At this time it is not possible to fully evaluate the potential of destratification on the T&O problem. Continued monitoring and lab experiments may reveal insights regarding temperature optima of T&O-producing algae. Accurate predictions of air pumping requirements and thermal regimes following destratification require detailed thermal modeling, well outside the scope of this study.

Copper Sulfate Treatment

Technical evaluation

Copper sulfate has been widely used to control T&O episodes, with varying results. Until fairly recently, copper sulfate was used indiscriminately – often applied regularly throughout the summer or at the onset of every T&O episode. Several water management agencies, including the St. Paul Regional Water District (Dave Schueler, per. comm.) and the Metropolitan Water District of Southern California (Bill Taylor, per. comm.), have quit this practice over the past decade or two, because this approach is not cost effective. Although copper sulfate is effective at killing algae, the effect is short-lived, and nutrients released during one treatment are readily available for subsequent blooms within a few weeks [Swain, 1986 #19]. Used over long periods, copper sulfate becomes expensive, algae gain resistance to copper toxicity, and copper accumulates in sediments.[Hanson, 1984 #20][Izaguirre, 1992 #7].

Targeted copper sulfate remains an effective treatment for T&O control [Taylor, 1994 #10]. "Targeting" is accomplished by intensive monitoring, so copper is applied during the early phase of a bloom of T&O-producing algae. MWD has also used copper sulfate effectively in killing T&O-producing periphyton by applying copper sulfate in specific areas of the reservoir bottom covered by periphyton, using divers to guide the application (Bill Taylor, per. comm.). The key technical question regarding the use of copper sulfate is: where and when do T&O producing algae occur?

<u>Phytoplankton</u>. Blue-green counts for the three reservoirs show that blue-green phytoplankton tend to persist at low concentrations, with few blooms. MIB levels typically increase slowly throughout the mid- to late summer period even when blue-green counts remain well below 100/mL and comprise < 30% of the total phytoplankton counts (Figure 7.13A and B). Throughout the study period to date, only two minor blue-green blooms have occurred. The first occurred in Bartlett Reservoir in July, 2000. At this time, the chlorophyll concentration was only 3 ug/L but the blue-green count was 143/mL, comprising 59% of the total phytoplankton count. The MIB concentration increased from 17 ng/L in June to 40 ng/L in July, peaking at 54 ng/L in August (Figure 7.4). The other bloom was in Lake Pleasant, also in July 2000 (Figure 7.6). The blue-green count in July was 252/mL but blue-greens comprise only 17% of the total phytoplankton count. The chlorophyll concentration was 10 ug/L. MIB increased from 25 ng/L in June to 38 ng/L in July and peaking at 44 ng/L in August.

In summary, two minor blue-green blooms occurred in the study reservoirs and both appear to be associated with increases in MIB. However, because the reservoirs are stratified, high epilimnetic MIB concentrations are not necessarily a problem, because water is released from the hypolimnion of these reservoirs during the summer. MIB concentrations are generally lower in the hypolimnion. The problem arises during fall turnover, when MIB becomes entrained throughout the water column and is discharged to the outflows. MIB produced in early or mid summer may degrade before turnover, so it would not be judicious to use copper sulfate to treat blooms occurring in early to mid summer. MIB degrades at a rate of 0.1 to 0.5 ng/L-day, or 3 to 15 ng/L-month, so some of the MIB produced in early summer would degrade by the time the reservoirs turn over in the fall. Blue-green blooms that occur late in the stratification period (mid-August onward) or after turnover would more likely contribute to T&O problems downstream. Thus, two criteria should guide the application of copper sulfate to the reservoirs:

- MIB levels are increasing rapidly from mid-August onward.
- Algae identification reveals a T&O-producing phytoplankton.

The amount of copper sulfate to be applied is a function of the dosage and the volume of the epilimnion. Dosages of 0.25 mg/L, added as Cutrine, a chelated form of copper, have been used by SRP to control algae in the canals (Brian Moorehead, SRP, per. comm.), and this is a common application rate for many lakes. Dosages were calculated using both copper sulfate and Cutrine. Given the strong tendency of copper to precipitate in hard water, field experiments would be desirable to optimize the form and dosage of copper used for treatment before copper treatment is implemented. Table 7.12is therefore a preliminary guide.

For the two smaller reservoirs, total dosages of copper sulfate were 13,000 kg to 41,000 kg per application – roughly 14 to 20 tons. Treating the epilimnion of Lake Pleasant would require over 300 tons of copper sulfate and would probably be infeasible. Application of copper as Cutrine would require about 8,000 gallons for Saguaro, 13,000 to 26,000 gallons for Bartlett, and nearly 180,000 gallons for Pleasant

Copper sulfate could be applied from a large boat or from a fire fighting plane. A cost estimate for delivering copper sulfate by fire fighting planes based at Mesa's Falcon Field has been requested but not received.

Periphyton. In September 2000, the ASU team conducted an intensive monitoring to determine MIB spatial patterns in Saguaro Lake, with the goal of elucidating areas with MIB-producing periphyton. This reservoir was selected because it has the most stable water levels (5 m range) and was therefore the most likely of the three reservoirs in this study to have a stable periphyton community. In the other two reservoirs, water levels fluctuate by > 30 m during the summer. The rapid change in water level (downward through the summer) makes it less likely that stable periphyton communities would develop. This study failed to reveal "hot spots". For 10 sites sampled at depths of 3-5m throughout the length of the reservoir, MIB concentrations averaged 25 ng/L and varied within a narrow range: 21-32 ng/L. MIB concentrations generally declined with depth. The uniformity of MIB concentrations suggests that localized periphyton mats are not major sources of MIB. Although we cannot discount the possibility of MIB-producing periphyton in this or other the study reservoirs, the study to date has revealed no clear evidence of MIB-producing periphyton. Targeted application of solid copper sulfate chunks has been shown to be effective in controlling MIB-producing periphyton, but our study has not yet demonstrated that these organisms are a major source of MIB in the study reservoirs.

Economic evaluation

<u>Phytoplankton</u>. The cost of copper treatment for the epilimnia of the three reservoirs varies dramatically with the form of Cu used for treatment. For example, for Bartlett Reservoir, treatment with copper sulfate would cost \$29,000 to \$54,000, whereas treatment with Cutrine would cost \$237,000 to \$442,000. This difference further highlights the importance of conducting field trials before moving to full-scale implementation. If copper sulfate is as effective at controlling T&O-producing algae at the 0.25 mg/L dose, copper sulfate should be used because it is much cheaper.

<u>Periphyton.</u> The cost of treating periphyton patches cannot be estimated, because we have not found patches of T&O-producing periphyton. In MWD reservoirs, areas treated have often been a small fraction of the whole reservoir. The method of application, done by divers, is very labor intensive.

Legal/institutional evaluation

Copper sulfate is widely used for algae control and has been used by SRP to treat canals. The levels of copper sulfate used for algae treatment ~ 0.25 mg/L)are well below the drinking water MCL (1 mg/L). SRP occasionally applies Cutrine to the canals upon request of customers and has the necessary permits for conducting copper treatments.

Summary

To date, only two minor blue-green blooms have been sampled, and the extent to which these blooms contributed to the gradual upward rise in MIB concentrations is uncertain. Periphytic T&O producers have not been identified. Copper sulfate can be effective in controlling T&O-producing algae in reservoirs and should be considered when and if phytoplanktic or periphytic sources are clearly identified.

SOURCE WATER SELECTION

Source water selection encompasses a suite of activities including hypolimnetic withdrawal, pass-through pumping, blending between the SRP and CAP source waters, and treatment

system interchanges. Each will be defined and discussed below.

Selective Withdrawal and Pass-Through Pumping

These two practices are discussed together because they have both been used in the CAP system. Selective withdrawal means taking water from a reservoir via the outlet that yields the best water quality. In this area, Lake Pleasant is the only reservoir with dual outlets and is therefore the only reservoir in Phoenix's water supply system where selective withdrawal can be practiced. The CAP system also allows pass-through pumping. Pass-through pumping means pumping from the Colorado River through the CAP Canal directly to consumers, bypassing Lake Pleasant.

Technical evaluation

CAP implemented a modified reservoir release program using selective withdrawal and by-pass pumping in 1999 and 2000. By avoiding the use of epilimnetic water with very high levels of MIB (up to 45 ng/L) during the summer, and then hypolimnetic water in the early fall (near turnover), MIB levels were maintained below the 10 ng/L threshold throughout the year (see previous Periodic Report). The impact of this practice can now be evaluated with respect to water delivered to consumers (Table 7.13). This analysis considers only water delivered to customers from the Union Hills WTP, because this plant uses 100% CAP water. At no time from August to December did the Union Hills WTP receive water with MIB > 10 ng/L, resulting in 60 million CDBT-10s. Had Lake Pleasant been operated using epilimnetic release, as it had prior to 1998, MIB in water delivered to the Union Hills WTP would have remained above the 10 ng/L threshold for the entire period of analysis (last column of Table 7.13). Thus, the entire 60 million CDBT-10s can be attributed to operational modification of Lake Pleasant.

Economic evaluation

Pass-through pumping is not without costs. Although the same amount of water is pumped annually whether bypass pumping is used or not, the use of bypass pumping means that more water is pumped from the Colorado River in the late summer than during the winter. Because energy prices are higher in the late summer than in January, it costs more to deliver CAP water that has been bypass pumped during late summer than to drain the reservoir in late summer and fill it again in the winter. Although energy prices have been fluctuating wildly in the post-deregulation environment, making an exact analysis impossible, Tim Kacerek (CAWCD) has estimated that the differential in cost is about \$21/AF. This means that CAP water delivered directly from the Colorado River costs \$21/AF more if delivered in September than it would if it were delivered during the winter. To date, CAP has adsorbed this additional cost with no charge to the cities.

To be consistently effective, reservoir operations should be guided by an intensive monitoring program. The T&O "Blending Group" initiated a weekly T&O sampling program for the fall of 2000. Samples collected weekly by SRP and CAP sampling crews are being analyzed by the COP laboratory. Unfortunately, turn around times from sample collection to data availability were too long to be useful in a "rapid response" mode that would be needed to optimize reservoir operations (the data will nevertheless be valuable in conducting retrospective analysis).

Legal, institutional and political constraints

There do not appear to be any serious constraints to pass-through pumping or modified

operation of Lake Pleasant. To the extent that the public understands that these operations can improve water quality, these management practices would be looked upon favorably.

Source Water Selection at Union Hills

Technical evaluation

The Union Hills Water Treatment Plant is the only water treatment plant that receives water directly from the CAP Canal. Since CAP water often has lower concentrations of T&O compounds than SRP water, one management practice reduce to T&O problems in parts of Phoenix would be to produce more water at the Union Hills plant when there is a T&O problem at the SRP-supplied Deer Valley WTP. During T&O episodes on the Arizona Canal, Union Hills would increase its production, allowing the Deer Valley WTP to decrease production. This strategy would work only when concentrations of MIB and/or Geosmin are lower in CAP water than in SRP water. This practice is limited by the production capacity of the Union Hills WTP, currently 130 MGD.

Economic evaluation

The cost-effectiveness of this practice depends upon several factors, including (1) the cost differential between CAP and SRP water, (2) the price of energy to run pumps, (3) the cost of PAC treatment at the Deer Valley WTP, and (4) differences in alum and sulfuric acid requirements between the Union Hills and Deer Valley WTPs (M. Hymel, COP, per. comm.). The price differential between CAP water and SRP water varies depending upon a complex suite of factors, but can range from 5:1 to 2:1, with CAP water always being more expensive. The ratio was near 2:1 in 2000 because SRP was facing a drought and CAP had surplus water. Because the pressure zones in question are downhill from Union Hills but uphill from Deer Valley, delivering water from the Union Hills WTP requires no pumping. Thus, energy costs would always be lower for water delivered from Union Hills than from Deer Valley; the actual savings would vary depending upon energy prices, which have been fluctuating considerably as the result of deregulation. The cost of PAC treatment at Deer Valley would vary depending upon concentrations of MIB in the Arizona Canal. Finally, the cost of treating water at Deer Valley aside from PAC costs is higher because higher doses of alum and sulfuric acid are required at Deer Valley than at Union Hills (M. Hymel, per. comm.). The overall economics of this practice will vary depending upon these four factors.

Legal and institutional evaluation

The only limitation to this practice is the supply of CAP water available to the Union Hills WTP. Using Phoenix's original CAP allotment of 113,822 AF/yr and the "11% rule" which states that Phoenix can take only 11% of its annual delivery in any one month, the maximum amount of water that could be withdrawn at the Union Hills WTP is 131 MGD. Thus, if the Union Hills operated at capacity during the T&O season, it would use Phoenix's entire original CAP allotment. In most years, CAP users have been able to use more than 11% during a given year (up to 15-18% according to T. Buschatzke, COP, per. comm.). More CAP water is also available during "surplus" years.

Blending at the Granite Reef Cross-Connect Facility

Technical evaluation

In theory, water users on the Arizona or South Canals could order water from either CAP or SRP, using the source water with better water quality. Data from this study indicates that both water sources typically have low concentrations of T&O during the spring or summer and that the SRP water generally has higher concentrations of T&O compounds during the late summer and early fall. If this pattern persists, some degree of T&O mitigation might be achieved by managing water sources to minimize T&O problems. Assuming no change in annual deliveries from either source, the major modification would be to shift the timing of deliveries, using more SRP water in the summer (with a concomittent decrease in the fall) and using more CAP water in the fall (with a concomittent decrease in the summer). There are no technical obstacles to blending – concentrations of MIB in blended water can readily be predicted from flow-weighting of MIB concentrations measured at the inlet to the Arizona Canal (R12) and the CAP Canal at Granite Reef (R11).

In 2001 only, a 2-month CAP siphon outage next fall will eliminate any plans for exchanging CAP water to resolve T&O problems.

Economic evaluation

CAP water costs more than SRP water under any scenario, with cost differentials of 2:1 to 5:1. SRP also charges a transportation fee of \$8/AF to deliver CAP water through its canals. There are no other costs associated with this practice.

Legal/institutional evaluation

Water Exchange Agreements between SRP and CAP and between municipal users and CAP can be invoked to allow exchanges of water to improve quality. In essence, this means that in many cases, better quality water from one source can be exchanged for poorer quality water from another source. At a later time, when quality differences are minimal, the same amount of water is exchanged in the reverse direction. These agreements are well-suited for ameliorating the T&O problem, because the problem is largely seasonal.

There are a number of limitations on blending, some minor and some that would seriously limit blending.

- SRP must release enough water from its reservoirs during the later summer and fall to
 provide capacity for flood protection in the spring. This constraint applies primarily to the
 Verde River system, which has less storage capacity. The operating goal is to reduce
 the combined volume of Horseshoe and Bartlett reservoirs to 150,000 AF by the end of
 October. In most recent years, this constraint would not be significant because the
 combined volume of the reservoirs exceeded 150,000 only once in 1988 (Figure 7.14).
- Per the Municipal & Industrial Agreement between CAWCD and the cities, no city can
 order more than 11% of its annual CAP delivery in a single month. For Phoenix, with an
 original allotment of 113,822 AF/yr., this translates to a maximum allotment in a given
 month of 135 MGD. This constraint can be circumvented in many years because (a)
 Phoenix can obtain more CAP water during surplus years, and (b) the 11% rule is not
 rigidly enforced. In recent years, CAWCD has allowed Phoenix to obtain 15% to 18% of
 its CAP allotment in a given month.
- Downstream users share capacity in the "common" part of the CAP Interconnect Canal and in the Arizona and South Canals. The total capacity of the common section is 1,200

cfs; the gates to the South and Arizona Canals each has a capacity of 800 cfs. Phoenix owns 8.75% of the common canal (225 cfs), 31.25% (250 cfs) of the capacity in the turnout to the South Canal, and 60.75% (486 cfs) of the capacity in the turnout to the Arizona Canal. The limiting capacity is the leased capacity from the common portion of the CAP turnout, 225 cfs. During September-October, when T&O problems reach a peak, flows in the AZ Canal have ranged from about 500 to 800 cfs. Phoenix's 225 cfs capacity at the CAP turnout would therefore be about one-half to one-third of the typical flow of the Arizona Canal during this period. Typical MIB levels during this period are 25 ng/L on the SRP side and 5 ng/L on the CAP water would be 15 to 18 ng/L, a 28% to 40% reduction. Thus, while COP cannot blend its T&O problem away, it can reduce MIB levels substantially by blending at this point.

- Phoenix is obligated to pay for any loss of revenue incurred by SRP if it doesn't accept its water delivery. This could be a serious constraint up through the time (generally very early October) when SRP switches deliveries from the Salt River to the Verde River.
- SRP must drain 25,000 AF (833 AF/day, or 416 cfs) from Apache Lake in September. This is a considerable fraction of the flow in the Arizona and South Canals.
- SRP must maintain 100 cfs "plus orders" flow in the Verde River, per agreement with the Gila River Indian Community. This water enters the South or Arizona Canals.
- Flow across the fish barrier at the head of the AZ Canal must be maintained at 100 cfs. This is a small fraction of the late summer-fall flow (no more than 25%).
- Flow from Apache Lake must be maintained at 8 cfs (~ 475 AF/month) from Nov. 1 to May 1, per agreement with U.S. Fish and Game. This constraint is not important, because T&O problems generally occur in the late summer and fall.
- Pumping from SRP wells may be limited if it were to cause elevated nitrate or salt buildup. This is not likely, because very little well water is pumped into the Arizona Canal.

Physical/Chemical Treatment of Periphyton in Canals

Technical evaluation

Four lines of evidence indicate that MIB is produced within the Arizona Canal:

- Data collected in all three studies of taste and odor problems show that the number and severity of T&O episodes increases as one moves downstream along the Arizona Canal (Table 7.5).
- Intensive monitoring along the length of the Arizona Canal also shows that MIB (but not Geosmin) levels increase along the length of the canal on many occasions. On August 29, 2000, MIB increased from 9 ng/L to 68 ng/L in a one-mile section of canal between Central Avenue and 19th Avenue.

- 3. Analysis of MIB from several sources of water entering the canal (alum sludge discharge from water treatment plants; filter backwash; irrigation return flows from urban landscapes) along the Arizona Canal show that these sources cannot account for the observed increase in MIB.
- 4. Samples of periphyton collected from canal walls during routine monitoring often contain species that produce MIB when isolated in the lab (confirmed MIB producers; see Section 4). Furthermore, these species have been found at the lower end of the canal, where increases of MIB have been observed.

<u>Physical treatment (brushing).</u> Canal wall brushing was evaluated in a pilot-scale experiment in 1999. This experiment showed that it was necessary to repeat brushing every two weeks to control regrowth of algae. A brushing treatment was instigated following the observation of a massive increase in MIB concentrations between 19th Ave. and Central Ave. on August 29, 2000. Due to mechanical problems, brushing was not started until September 21. Brushing was repeated at roughly two week intervals (Sept. 21, Oct. 5, and Oct. 21). Because the Arizona Canal is unlined below 19th Ave, brushing was conducted only between Central and 19th avenues. MIB was measured weekly at eight locations between 19th Ave. and the Deer Valley Water Treatment Plant.

The major source of MIB in the one-mile section of canal between 19th Ave. and Central abated before brushing began, but brushing probably prevented regrowth of MIB-producing periphyton during September and October, as seen by the lack of increase in MIB in this section throughout the brushing period. Brushing therefore seems to have had a positive impact.

Mechanical removal of periphyton would be improved if the bottom of the canal could also be cleaned. SRP has designed a maintenance barge that would be able to clean both the sides and bottom of the canal (Figure 7.15), but has not yet planned to build it. This barge could also clean the bottom of the canal below 19th Avenue, where the Arizona Canal is unlined.

<u>Copper sulfate treatment.</u> SRP has treated several canals in the area with copper sulfate. In a typical application, a liquid mixture of Cutrine (chelated copper sulfate) is added by a small pump for around 8 hours, yielding a Cu concentration of 0.25 mg/L. Observations of such a treatment on the Consolidated Canal in early 2000 showed that the treatment was effective for less than a mile. Computer modeling showed that equilibrium copper concentrations were extremely low because copper would precipitate. Despite these limitations, copper treatment is probably an effective algicide over short distances. Copper sulfate treatment may also be effective in conjunction with mechanical cleaning.

Economic evaluation

In 1999, SRP was charging \$1,150 per mile for brushing. To repeat brushing every two weeks for two months would therefore cost \$4,600 per mile. Targeted brushing is therefore very economical if it prevents MIB increases in the AZ Canal.

A cost scenario for copper sulfate treatment is presented in Table 7.14. Costs are based on an 8-hour treatment with a dose of 0.25 mg Cu/L, with copper sulfate costing \$1200/ton and Cutrine costing \$17/gallon (Brian Moorehead, per. comm.). For perspective, average flows (1995-1998) in the Arizona Canal below Arizona Falls were: August = 946 cfs, Sept. = 397 cfs, October = 700 cfs. Not included is the cost of labor, currently \$60/hour. Setup, loading, and takedown require about two hours of labor per application. The scenario is based on a dosage

of 0.25 mg Cu/L for 8 hours of treatment. This treatment regime has not been optimized, so costs for improved treatment may be different. Using Cutrine (chelated copper), typical cost per application in late summer to early fall would be roughly \$4,000 to \$8,000 per application. With treatments repeated at two-week intervals for two months, the total would be \$16,000 to \$32,000. As noted above, the distance for which copper sulfate treatment is effective has not been well-documented.

SRP owns and operates the canals and is allowed to do routine maintenance such as brushing canal walls. Copper treatment is regulated, but SRP has done copper treatments in the canals on occasion and already has the necessary permits to do so. Brushing does cause briefly elevated turbidity, and downstream WTPs (Glendale's Cholla WTP) has asked that they be notified of brushing operations.

Summary

There are definitely hot spots of MIB production in the Arizona Canal that could be targeted for treatment. Brushing appears to be effective at removing algae from the canal walls, but with the current brushing device, the bottom of the Canal cannot be brushed. Copper treatment would probably be a useful ancillary treatment and may be the only treatment possible in the unlined section of the Arizona Canal immediately above the Deer Valley WTP.

PAC Treatment

Powdered activated carbon (PAC) is widely used to remove MIB and Geosmin from water supplies. As employed in Phoenix's water treatment plants, PAC is added to the presedimentation basin, then removed during sedimentation and sand filtration. Typical contract times are 2 to 4 hours. MIB and Geosmin are adsorbed to PAC. Treatment efficiencies depend upon PAC dosage, concentrations of dissolved organic carbon (DOC), temperature, and other factors. When MIB or Geosmin levels are high, PAC treatment may not reduce levels below the taste and odor threshold of 10 ng/L.

Technical evaluation

PAC treatment has been studied in the ASU laboratory. Results show that (1) removal efficiencies vary substantially among various brands of PAC and (2) treatment efficiency (C/Co) is independent of MIB or Geosmin concentration. These experiments were used to develop isotherm coefficients to describe the relationship between PAC dose and C/Co. During the fall 2000, ASU and COP compared T&O control at its Val Vista WTP using two brands of PAC: Norit HDB and Norit 20b. Norit HBD is the "low bid" PAC normally used by the city; Norit 20b was one of the better-performing PACs in lab experiments. Results showed that Norit 20b removed approximately 20% more MIB and Geosmin than did HDB. Results from the full-scale trial show that PAC treatment effects can be predicted reasonably well from lab experiments.

- One technical constraint on the use of PAC is the delivery systems now in place at the water treatment plants. Limitations on feed rates and hopper capacity mean that optimized PAC feed rates could not always be achieved.
- A second limitation for predicting PAC dosing is that adsorption isotherms were done with one type of canal water. Variations on the composition of canal water, particularly variations in DOC, would alter MIB and Geosmin adsorption efficiency.

Economic evaluation

To evaluate the potential cost of PAC, we "hindcast" the cost of PAC needed to maintain MIB levels at two thresholds, 10 ng/L (generally considered a taste threshold for both compounds) and 20 ng/L (a more conservative threshold suggested by COP) using MIB and Geosmin data collected at or near the inlet of Phoenix's four major water treatment plants in 1999. Freunlich isotherm data computed from the laboratory PAC experiments were used to compute PAC dosages for each month. The total cost of PAC was computed by multiplying total PAC usage for the year by the most recent bid price. Finally, the benefits were put in term of consumer days below threshold achieved, compared with the no-treatment option (e.g., consumers receiving water with MIB and Geosmin concentrations measured at the inlet to the water treatment plant). Three PACs were evaluated in this fashion: Norit 20b, Norit HDB, and Calgon WPM. Figure 7.16 shows PAC doses, total PAC use by month, and gain in consumer days below threshold for the hindcast model. Table 7.15 shows the costs of two types of PACs to maintain MIB concentrations in water produced by the WTPs at threshold concentrations of 10 ng/L and 20 ng/L. Simulation is based on monthly observed MIB concentrations at the inlet to each WTP for the period September 1999 to October 2000.

Results show that more Norit HDB than Norit 20b would be required to control MIB to a given threshold. However, because 20b is more expensive, the difference in purchasing cost between the two PACs would be modest (for all four plants, the difference in cost would be <\$100,000). It should be noted that costs used for this comparison were general estimates from the companies and do not represent actual bid prices. There are nevertheless two major advantages in using the best-adsorbing PAC: (1) lower PAC dose is required, overcoming to some extent limitations on feed capacity, and (2) sludge disposal costs decrease because less PAC is used and recovered.

Total PAC cost to maintain MIB < 10 would have been \$1.5 million and total cost to maintain MIB < 20 ng/L would have been \$0.6 million. Optimized use of PAC would have resulted in an additional 215 million CDBT-10s or 75 million CDBT-20s. For comparison, the total number of consumer days for the City of Phoenix is 475 million. No PAC was needed to keep MIB < 10 ng/L at the Union Hills WTP during the analysis period because the MIB concentration in CAP water delivered to this plant was always < 10 ng/L. About two-thirds of the total cost would have occurred at the Deer Valley WTP. Because of this, efforts to reduce MIB in the Arizona Canal upstream of the Deer Valley inlet are likely to be cost-effective.

In reality, fully optimized use of PAC would be difficult to achieve, for several reasons:

- 1. The model assumes that PAC doses are adjusted precisely to achieve target MIB levels. In reality, even with careful monitoring, one could never match actual PAC dosing with ambient MIB levels this precisely.
- 2. It may not be possible to achieve the dosing required to reduce MIB levels to target levels because hopper delivery systems may not be able to achieve the required dose.
- 3. None of the Phoenix WTPs can store dry PAC. PAC is therefore ordered when needed and made into a slurry in hoppers for dosing. Operators would therefore operate in one of two modes: (1) order PAC and start dosing before influent MIB hits target levels, or (2) wait until the target level is achieved, then order PAC and start dosing. Option (1) uses more PAC than is reflected in the model and option (2) would fail to control MIB levels

during the early part of an episode.

Nevertheless, optimizing PAC dosing makes economic sense. For contrast, feeding 20 mg/L PAC (20b) at the three treatment plants which experience T&O problems (not Union Hills) for three months (August to October) would have cost \$2.1 million and would not have kept MIB levels below the 10 ng/L threshold throughout the year.

Summary

The use of PAC must be part of an overall T&O mitigation strategy, but PAC cannot alone keep MIB levels below the 10 ng/L threshold. Optimized PAC dosing will likely improve MIB removal and/or reduce PAC costs.

Algae Control Within Treatment Plants

Technical Evaluation

In a previous study, there was some indication of MIB being produced in several Phoenix WTPs, but recovery in the analytical procedure was quite variable, putting these results in doubt. In the current study, with greatly improved methodology, monthly sampling at the inlet and outlet of three of Phoenix's WTPs revealed no production of Mbi or Geosmin (Figure 7.16). The averge change in MIB was Δ 1 ng/L at the Squaw Peak WTP and Δ 6 mg/L at Deer Valley. Average MIB in the outlet of the Val Vista WTP was lower because PAC was used in the fall of 2000.

Despite the lack of evidence for MIB production within the WTPs, algae, including several genuses that are known T&O producers, were observed at most of the WTPs. This indicates the potential for MIB production and suggests that algae control is warranted. Pulsed prechlorination, now used at several Phoenix WTPs, has been found to increase DBPs significantly. The alternative, injection of copper sulfate, eliminates algae and has little negative side effects. Val Vista has had considerable success with using 0.25 mg/L Cu as copper sulfate since May 1999 and has used copper sulfate in lieu of pulsed pre-chlorination with considerable success. The main technical limitation of continuous copper sulfate feed is that algae may become resistant to copper.

Economic evaluation

Using copper sulfate for algae pretreatment is inexpensive – about \$0.005/1000 gallons and would add little to overall chemical cost of treatment.

Legal/institutional evaluation

The only legal issue associated with the use of copper is the requirement to keep copper well below the MCL. The Cu dose normally used for algae control, 0.25 mg/L, is well below the Cu MCL of 1 mg/L. Furthermore, most of this copper precipitates out of solution.

IMPLEMENTATION OF A FULL-SCALE, MULTIPLE BARRIER TASTE AND ODOR MITIGATION PROGRAM

Based on results from this study to date, we recommend that the following T&O mitigation

practices be implemented and/or optimized to improve their efficiencies. These include:

PAC Treatment

PAC treatment to remove MIB and Geosmin within the treatment plants is practical and is often necessary to maintain MIB and Geosmin levels below the 10 ng/L threshold. However, the COP should shift from a constant dosing scheme to an optimized dosing scheme using realtime data (see "Process Control Monitoring and Evaluation", below). Optimized dosing would be more effective at keeping MIB and Geosmin levels below threshold and would keep PAC use to a minimum, saving on both PAC cost and sludge disposal costs.

Algae Control in Canals

There is little doubt the MIB is produced within the Arizona Canal, sometimes at prodigious rates, and that algae within the canal are the source. Algae control is therefore warranted. Field-scale implementation of brushing between 19th Ave. and Central Ave. showed that brushing at 2-week intervals was sufficient to prevent the regrowth of T&O-producing algae. Copper sulfate treatment would probably improve the effectiveness of algae control in stretches of the canal that are brushed and would be the primary method of algae control in unlined sections of the canal where brushing cannot be done (e.g., immediately above the Deer Valley WTP). This action also improved T&O at WTP intakes for other cities downstream of Deer Valley on the Arizona Canal (Glendale and Peoria). Algae control should be carefully targeted because T&O-producing algae are concentrated at specific locations along the canal and only at certain times of the year (see Process Control Monitoring, below).

Source Water Selection

CAWCD's operational modification of Lake Pleasant was highly successful, adding 60 million CDBT-10s during the summer and fall of 1999. The operational flexibility of Lake Pleasant makes it possible to select water from the epilimnion or the hypolimnion of Lake Pleasant, or to use water directly from the Colorado River at any given time. Intensive monitoring of T&O-producing compounds in late summer and fall would provide information to CAWCD managers to make operation management decisions with greater predictibility.

Increasing production at the Union Hills WTP takes advantage of the fact that water delivered from the CAP system generally has lower concentrations of T&O-causing compounds than water from the SRP system. Union Hills can supply water to parts of the system normally served by the Deer Valley WTP, which has the worst T&O problem among the Phoenix WTPs. Thus, during T&O episodes on the SRP side of the system, increasing production at Union Hills while simultaneously decreasing production at Deer Valley, would nearly always improve the quality of water delivered to consumers. The overall cost of doing this needs further evaluation, but it is likely that this option would cost less than using extensive PAC at Deer Valley.

Blending of CAP and SRP water at the Granite Reef Interconnect Facility is limited by various institutional and legal constraints but may be effective at the end of the irrigation season under certain circumstances, particularly during drier years.

Algae Control within Water Treatment Plants

Although this project has not identified production of T&O compounds within the Phoenix WTPs, there is extensive growth of algae within the WTPs, some belonging to genera that produce T&O compounds. Furthermore, algae growth within WTPs can shorten filter runs. Thus, it makes sense to refine algae control within the WTPs. Copper sulfate treatment at the inlet is effective at the Val Vista WTP. The only question regarding copper sulfate is whether algae will build up resistance.

Reservoir management

It would also be desirable to develop at least one T&O mitigation practice for the reservoirs. Extensive experience at MWD has shown that targeted copper sulfate treatment can be effective at reducing or eliminating T&O problems. However, analysis of extensive data on MIB and Geosmin, blue-green algae identification, and other limnological data do not yet indicate an approach for targeting. Of particular interest is production of MIB in the epilimnia of reservoirs from mid-summer onward, because this MIB is likely to become entrained throughout the water column during fall turnover. At this point MIB-laden water leaves the reservoir and becomes a problem downstream.

Intensive monitoring during 2001 should be conducted to target sources of T&O compounds. Weekly sampling of the reservoirs from July onward would identify T&O episodes associated with phytoplankton blooms. Extensive spatial sampling of periphyton on the bottom of the reservoirs should be continued to identify potential "hot spots" of MIB or Geosmin production associated with periphyton. If found, spot treatment using solid copper sulfate has been shown to be an effective method of control (Bill Taylor, MWD, per. comm.).

Process Control Monitoring and Evaluation

Data from this study shows that the T&O problem is highly variable in time and space. Although it may be possible to accurately forecast the occurrence of T&O episodes at some time in the future, it is unlikely that we will reach this point in the next year. It has also become clear that T&O problems can arise quickly (within days to weeks) and that mitigation efforts must be employed in a "rapid response" mode if they are to be effective at preventing T&O problems for consumers. Furthermore, T&O episodes in the canals and reservoirs may be caused by relatively small patches of periphyton. Thus, any T&O mitigation strategy must include *process control montitoring*. A weekly sampling program, with no more than a two-day analytical turnover time, is needed to make rapid decisions regarding PAC dosing, canal algae control, within-plant algae treatment, reservoir operations, and reservoir algae treatment.

Continuous evaluation of mitigation practices is also needed, for several reasons. First, mitigation practices can always be improved. This requires thorough evaluation of practices being employed, to determine where efficiencies might be gained. Second, the optimum mix of management practices changes with time. At a given time, flow management at Lake Pleasant might alone be sufficient to keep T&O problems to a minimum; at another, a mix of canal treatment, PAC treatment, and increased production at Union Hills might be the optimal mix. The CDBT concept, or a modification of this concept, would be employed to guide decision making. Overall programmatic goals could be set and evaluated using this concept or a modification of the concept. Finally, the cost of T&O mitigation practices should be evaluated in real time. This is important because costs

may change. For example, the economics of source water selection is sensitive to the cost differential between CAP and SRP water, the cost of canal treatment depends upon the spatial extent of T&O-producing algae within the canals, the cost of PAC will vary depending on sludge management practices (now being upgraded), and the cost of pumping water will vary in response to electrical power rates, which have been fluctuating widely following deregulation.

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SECTION 7 TABLES AND FIGURES

	System	Max.	Area at max.	Max.	Ave. depth at	Hydroelectric	Annual water
		volume, AF	volume, acres	depth, ft	full capacity,	generating	releases, AF/yr
					ft.	capacity, kw	
Saguaro	Salt	69,765	1,280	116	55	13,000	249512
Bartlett	Verde	178,186	2,700	188	66	None	154025
Pleasant	CAP	1,108,600	12,040	-	92	45000	

Table 7.2. Hipsographic data, showing % area as a function of depth at full volume.

Depth	Bartlett	Saguaro	Pleasant
25	78	76	83
50	58	56	62
75	42	35	>46
100	27	15	?

Table 7.3. Annual outflows from the SRP study reservoirs.

Year	Horseshoe	Bartlett	Saguaro
1996	70,350	104,275	319,980
1997	135,040	112,025	273,523
19986	266,985	284,600	199,825
1999	99,150	115,200	204,718
Average	142,881	154,025	249,512

Table 7.4. Average consumption	of municipal water in Phoenix.
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Month	Total consumption, gallons/capita-day
January	158
February	138
March	174
April	197
May	264
June	291
July	288
August	285
Sept.	238
Oct.	233
Nov.	192
Dec.	164
Average	219

Data source: Phoenix water production data files from Keith Larson, City of Phoenix

Table 7.5. Number of samples on the lower end of the Arizona Canal with MIB and Geosmin over criteria levels since 1997.

			٦	ИIB	Geosmin	
			# > 10	# > 10		
	# samples	# years	ng/L	# > 20 ng/L	ng/L	# > 20 ng/L
Jan-March	6	3	1	1	0	0
April-June	13	3	4	0	1	0
July-Sept.	14	4	13	6	4	2
OctDec.	10	4	7 8		5	1
Total	43	14	25	15	10	3

Table 7.6. Mean concentrations of total P and total N and the mean TN:TP rato in the inflows to the study reservoirs from October 1999 to September 2000 (mg/L).

	TP		TN		TN:TP
	Mean	Std. Dev.	Mean	Std. Dev.	ratio
Verde River (R20)	0.034	0.043	0.213	0.146	10
Saguaro inlet (R8)	0.022	0.005	0.302	0.089	12
Colorado R. (R1)	0.007	0.005	0.393	0.074	62

Table 7.7. Nutrient concentrations in the epilimnion of the three study reservoirs.

	TN, mg/L	TDN, mg/L	TP	TDP	TN:TP	TDN:TDP	PN:PP
Pleasant (R2A)	0.309	0.277	0.008	0.005	44.0	66.2	8.1
Bartlett (R6A)	0.250	0.202	0.018	0.015	13.3	30.6	5.2
Sagauro (R9A)	0.305	0.247	0.018	0.007	26.0	39.2	9.8

Values are averages for the period Sept. 1999 to August 2000.For concentrations below detection limits, one-half the detection limit was used. Ratios shown are medians.

Table 7.8. TP, total algae counts, chlorophyll a, blue-green counts, and MIB in the upper "A" layers of the three study reservoirs.

		TP	Total algae	Chlorophyll	Blue-greens	MIB
		mg/L	#/mL	ug/L	#/mL	ng/L
Pleasant	Oct.	0.003	136	2.3	28	30
	Nov.	0.008	87	4.8	26	27
Bartlett	Sept.	0.006	352	3.7	14	10
	Oct.	0.027	128	5.7	21	12
Saguaro	Sept.	0.006	274	7.7	72	22
	Oct.	0.010	135	9.0	43	20

Table 7.9. Cost of alum treatment of the study reservoirs, for a dose of 10 mg/L.

	Volume, AF ¹	Alum, tons	Cost ² , \$
Pleasant	439,822	73,426	9,618,827
Bartlett	61545	10,275	1,345,978
Saguaro	63386	10,582	1,386,240

¹ Volume on August 1, 2000. ²Based on the current cost of alum for the City of Phoenix is \$131/T (M. Hymel, per. comm.)

Table 7.10. Short-term effect of destratification in June, based on 1999 data.

Reservoir	Date	Elevation	Ave temp.	Ave temp.	T mixed, °C
		ft	Epilimnion, °C	hypolimion, ^o C	
Bartlett	06/01/00	1751	26	16	20
Saguaro	06/01/00	1526	26	20	22
Pleasant	06/01/00	1650	25	14	20

Average measured temperatures for the epilimnion and hypolimnion are shown, together with the average temperature that would have occurred immediately following destratification in June.

Table 7.11. Air requirements to destratify the study reservoirs, based on an air flow of 10 m^3/km^2 -min.

	Saguaro	Bartlett	Pleasant
Area, acres	1,224	2,700	12,040
Area, km ²	6	13	57
Rec. aeration rate, m ³ /min-km ²	9	9	9
Total air pumping, m ³ /min	53	117	521

Table 7.12. Copper treatment of the three study reservoirs.

Reservoir	Date	Volume of	CuSO4*5H2O		Cutrine, gallons	
		epilimnion, AF	Kg	\$	Gallons	\$
Bartlett	31-Aug-98	34,967	41,521	54,807	26,023	442,396
	31-Aug-99	20,035	23,790	31,403	14,911	253,479
	31-Aug-00	18,786	22,307	29,445	13,981	237,677
Saguaro	31-Aug-99	11,328	13,451	17,755	8,431	143,320
	31-Aug-00	11,347	13,474	17,785	8,445	143,560
Pleasant	31-Aug-99	239,822	284,770	375,897	178,481	3,034,184

Values are based on a dosage of 0.25 mg Cu/L in the epilimnion and costs of \$1200/T for copper sulfate and \$17/gallon for Cutrine. The volume of the epilimnion was computed as the difference between total volume (from elevation) and volume under the thermocline (surface elevation – depth to thermocline).

Table 7.13. Impact of operational modification of Lake Pleasant on Union Hills WTP, in consumer days below threshold.

	Union Hills	Water use,		MIB		MIB
Month	water prod., MGD	gal/capita-day	# consumers	CAP@7th	CDBT-10	R2A
Aug-99	101	285	353176	0	10595270	12
Sep-99	90	238	376835	0	11305053	45
Oct-99	94	233	400828	3	12024837	30
Nov-99	76	192	396652	0	11899547	27
Dec-99	77	164	473109	0	14193258	14
Total	438				60,017,966	

Table 7.14. Estimate cost of copper treatment in the Arizona Canal under varying flow regimes.

	CuSO ₄ *5H ₂ O		Cutrine	
Flow, cfs	kg	Cost, \$	gallons	Cost, \$
1,000	806	1,064	494	8,390
500	403	532	247	4,195
250	202	266	123	2,097
100	81	106	49	839

Table 7.15. PAC use and cost for the hindcast model at four Phoenix WTPs.

Deer Valley		20b			HDB	
	PAC, kg	PAC, \$	Increased	PAC, kg	PAC, \$	Increased
			CDBTs			CDBTs
10 ng/L threshold	789,906	921,030	94	1,026,775	903,562	94
20 ng/L threshold	413,518	482,162	40	613,820	540,162	40
Squaw Peak		20b			HDB	
	PAC, kg	PAC, \$	Increased	PAC, kg	PAC, \$	Increased
			CDBTs			CDBTs
10 ng/L threshold	199,612	232,747	71	259,469	228,333	71
20 ng/L threshold	8,304	9,683	19	12,327	10,848	19
Union Hills		20b			HDB	
	PAC, kg	PAC, \$	Increased	PAC, kg	PAC, \$	Increased
			CDBTs			CDBTs
10 ng/L threshold	0	0	0	0	0	0
20 ng/L threshold	0	0	0	0	0	0
Val Vista		20b			HDB	
	PAC, kg	PAC, \$	Increased	PAC, kg	PAC, \$	Increased
			CDBTs			CDBTs
10 ng/L threshold	295,323	344,347	49	383,882	337,816	49
20 ng/L threshold	93,699	109,253	16	139,086	122,395	16
Total cost						
10 ng/L		1,498,124	215		1,469,711	215
20 ng/L		601,098	76		673,405	76

Figure 7.1. Pumping to Lake Pleasant (top), releases from Lake Pleasant (middle), and pass-through pumping (bottom), 1998-2000.









Figure 7.2.b. Water outflows in Bartlett and Saguaro Reservoirs.



Outflows from Saguaro Reservoir













Bartlett - Blue-greens and MIB





Figure 7.5. Saguaro Reservoir, showing MIB and blue-greens (top) and temperature (bottom).



Saguaro- blue greens and MIB



Figure 7.6. Lake Pleasant, showing MIB and blue-greens (top) and temperature (bottom).



Lake Pleasant - blue-greens and MIB

Figure 7.7. Chlorophyll a versus MIB concentrations for all three reservoirs.



Figure 7.8. Blue green counts vs. MIB in the epilimnion of the three study reservoirs.



Blue-green count vs. MIB




Figure 7.10. MIB (top) and temperature (bottom) in the Arizona Canal during 1999-2000.



Temperature in the AZ Canal



Figure 7.11. For the three study reservoirs, A. TN vs. chlorophyll, B. TP vs. MIB and for Bartlett and Saguaro only, C. TN vs. MIB, and D. TN vs. chlorophyll.





Figure 7.13. Chlorophyll and total algae counts (top) and blue-greens, as fraction of total algae count (bottom) for Barlett, Saguaro, and Pleasant Reservoirs.



Figure 7.14. Combined volume of Horseshoe and Bartlett Reservoirs.



Combined volume of Horseshoe + Bartlett Reservoirs

Figure 7.15. Schematic of SRP maintenance barge, in development.



Figure 7.16. Optimized PAC dosing for the AZ Canal (A) observed MIB at the inlet and required PAC doses, (B) kg of PAC per month, and (C) CDBT-10s "generated" by PAC treatment.





Figure 7.17. MIB at the inlet and outlet of the Squaw Peak, Deer Valley, and Val Vista WTPs.

SECTION 8: IMPLEMENTATION CONTROLS (TASK 7)

INTRODUCTION

This section discusses implementation of the T&O control program. Formal implementation phase of the T&O Project did not start until July 2001.

The process of evaluating potential implementation measures is discussed in Task 6 the Midcourse Evaluation. This section focuses on actual implementation of measures that were excpected to cause a measureable decrease in T&O-causing compounds and and improvement in the taste of the water provided to consumers in a significant portion of Phoenix's water supply system. Five management practices were implemented at the operational scale: (1) modified operation of Lake Pleasant, (2) PAC treatment based on weekly monitoring and feedback (See Section 5), (3) source switching to avoid T&O episodes, (4) blending of SRP and CAP water at the head of the Arizona Canal, and (5) canal treatments to remove culprit algae (See Section 3). Extensive details on canal treatments are included in the fifth Periodic Report, and summarized in Section 3 of this Report. The first part of this section examines each of these treatment measures and their effectiveness. The second part examines the effectiveness of the entire program in quantitative terms.

IMPLEMENTED T&O CONTROL MEASURES

Modified Operation of Lake Pleasant

Among the three reservoirs. Lake Pleasant is most amenable to operational control of T&O in released water because it has the most flexible "plumbing" system. Water from the Colorado River can be pumped into Lake Pleasant to fill it or can be routed directly to the Phoenix area and points beyond via the CAP canal. Water can also be released from Lake Pleasant via two outlets, one at 1506' and one at 1610' above mean sea level. Water released from Lake Pleasant can be blended with varying amounts of Colorado River water in the CAP Canal. Prior to 1999. CAWCD's normal operation during the irrigation season was to release water from the upper outlet. This operational plan released water with elevated levels of MIB (see Figure 8.1), which were transmitted downstream. In the fall of 1999, CAWCD responded to consumer complaints and recommendations from a University of Arizona study by switching to hypolimnetic release (Figure 8.1). This kept MIB levels < 10 ng/L until turnover. After turnover, the average concentration of MIB increased to 20 ng/L (Figure 8.1 6, October). At this time, CAWCD stopped releasing water from the reservoir and routed water from the Colorado River directly to the Phoenix metro area (by-pass pumping). This operational strategy succeeded in keeping MIB concentrations in water delivered to the Phoenix area < 10 ng/L throughout the season. MIB levels in water delivered to customers would have reached 50 ng/l if CAWCD had not modified its operation. CAWCD continued its flexible release management strategy in 2000 and 20001. By operating flexibly, in response to weekly MIB measurements, CAWCD has succeeded in maintaining MIB levels at or below 10 ng/L, even when MIB levels in the epilimnion were much higher (Figure 8.1).

Since this operational strategy was implemented, MIB exceeded 10 ng/L only once (Figure 8.2) and has otherwise remained below 10 ng/L. This has made CAP a reliable source of low-MIB water for the City of Phoenix. Because the Union Hills WTP consistently receives low-MIB water, it can be used as the production side of source shifting (discussed below, "Source Selection"), making up production lost by shutting down the Deer Valley WTP.

Consistently low MIB also makes CAP water the desirable source of water during late summer and early fall, when SRP water generally has higher levels of MIB, making blending a technically feasible T&O control measure (discussed below, "Blending")

Blending

Throughout most of the T&O project, SRP water had higher MIB concentrations than CAP water (Figure 8.3). Blending of CAP and SRP waters at the Granite Reef Cross-Connect Facility reduced MIB concentration in water delivered via the Arizona Canal. For the period August 1999 to April 2002, average MIB in the SRP inflow was 14 ng/L, average MIB in the CAP water was 2 ng/L and the average MIB in the Arizona Canal at site R13 was 10 ng/L, 28% lower than in the SRP water. At some points, blending made a huge difference: during September 2000 MIB concentrations were 65 ng/L in the SRP inflow, 7.2 ng/L in the CAP inflow, and 9.1 ng/L in the mixture. During the peak of the T&O season, August-November (1999-2001) , MIB averaged 20.5 ng/L in SRP water, 4.5 ng/L in CAP water, and 14.3 ng/L in the blended water delivered to downstream customers. Thus, blending had a small but significant effect on water delivered via the Arizona Canal.

PAC Treatment

PAC was effective at reducing MIB and Geosmin concentrations in WTP effluent at all WTPs. Implementation of PAC activities began in fall 2000 at Val Vista WTP, and were fully implemented at all COPs WTPs starting in Fall 2001. Overall utilization of PAC (tons/year) increased in 2000 and 2001 (fiscal years 2001 and 2002 in Table 8.1) compared to the prior 2 years. In addition a shift from Norit HDB PAC to a better performing PAC product (Norit 20B) was made after fall 2000 lab-scale and field-scale testing at Val Vista WTP (see Task 4). In 2000, PAC doses at Squaw Peak WTP were extremely low and during 2001 PAC was added nearly continuously throughout the T&O fall season. This section summarizes key findings from the PAC implementation work.

Table 8.2 summarizes the frequency of MIB occurrence in raw and finished drinking water at Squaw Peak and Val Vista WTPs for Fall 2001. Deer Valley WTP was off-line most of Fall 2001 and is not shown. Squaw Peak raw water was always greater than 20 ng/L, due to in-canal production of MIB (see previous sections), but treated water always had lower MIB than raw water. MIB concentrations were less than 20 ng/L 33% of the time. Val Vista WTP also removed MIB, as indicated by a higher frequency of lower MIB concentrations. Although the target of achieving 10 ng/L in finished water throughout the fall was only partially met, the percentage of MIB removed by the WTPs were significantly improved this year over last year. Future improvements at the WTPs (e.g., higher PAC feed rates, lengthening contact times, and use of high performing PAC) will continue to allow WTPs to improve MIB removal. However, a maximum removal of about 75% is achievable at the WTPs. Therefore, raw water MIB levels must be maintained below 40 ng/L, through upstream T&O implementation activities in order to keep MIB below the desired threshold of 10 ng/L MIB.

During the summer and fall of 2001 ASU provided recommendations on PAC doses to the WTPs. The recommended PAC doses were selected to reach a finished water MIB concentration of 10 ng/L. The selected dosages worked moderately well for Val Vista WTP, but were less than satisfactory for Squaw Peak WTP. Table 8.3 presents actual MIB concentrations and percentage removed at Squaw Peak WTP during Fall 2001. The model used to determine

PAC doses during the Fall 2001 T&O season (Fall 2001 Predictive Model) overestimated MIB removal. A refined model based upon laboratory experiments and full-scale work at Val Vista (see Refined Model column in Table 8.3). The Refined Model MIB removal predictions track the observed removal better than the Fall 2001 Predictive Model. An attempt to develop a site-specific model for Squaw Peak WTP failed. It is our opinion that a number of factors affected the lack of agreement between models and field observations during the Fall 2001 period:

- Prechlorination activities concurrent with PAC application reduced the PAC effectiveness, which were in practice for part of the time of data collection with respect to Table 8.3.
- Residual Norit HDB rather than Norit 20B in the PAC slurry tanks; later in the fall the predictions more accurately predicted observed MIB removal trends. The switch from DHB to 20B was made in late September
- Periods of short PAC contact times. PAC was nearly removed 100% by mid-way through the sedimentation basins based upon grab samples and dry weight measurements. Therefore contact times in the presedimentation tanks and flocculation are critical. A 5% to 10% difference in MB removal in batch PAC kinetic studies was observed over contact times of 45 minutes to 90 minutes.
- PAC mixing/addition are important as is possible short-circuiting in the presedimentation basins. Hydraulic tracer tests should be used to confirm adequate flow hydraulics in the presedimentation basins.

The recommended model for predicting MIB removal based upon PAC dosage is

$$PACDose(mg/L) = \frac{-\ln\left[0.95 * \left(\frac{MIB_{finished}}{MIB_{raw}}\right)\right]}{0.079}$$
 Equation 8.1

or to achieve 10 ng/L MIB in finished water:

PAC Dose (mg/L) =
$$12.7xln(MIB_{raw}) - 28.5$$
 Equation 8.2

Where the raw (MIB_{raw}) and finished (MIB_{finished}) water MIB concentrations are in ng/L. For example, if the influent MIB concentration is 30 ng/L and the desired effluent MIB concentration is 10 ng/L, a 20B PAC dose of about 11.9 ng/L would be required. Practical operating curves were generated for future use of Norit 20B by all COP WTPs (Figure 8.4). The operating curves are easy to use nomographs what can be used in replacement of Equations 7.1 and 7.2, although the equations are more accurate than reading from the nomograph.

Screening PAC Suppliers Bid Submissions

This section summarizes the results from a blind laboratory batch test screening for the ability of six powder activated carbon (PAC) samples submitted to ASU from the City of Phoenix in May 2001. The purpose of these tests was to rank the relative performance of each PAC type to remove MIB from a local surface water (Arizona Canal water). Tests with different local water

sources have provided nearly identical results. In addition to the six PAC samples provided by the City of Phoenix, ASU analyzed three additional samples of PAC that were previously evaluated (Norit HDB, Norit 20B, and PACcarb plus). By chance the internal samples selected by ASU were some of the external samples provided by the City. The following Table 8.5 ranks the PAC types from Best performing (highest MIB removal capability) to lowest MIB removal capability.

After completion of the blind laboratory PAC performance testing (Table 8.5), the City of Phoenix provided cost and PAC characteristic data to ASU. An Index Value was computed as follows:

Index Value = [% MIB Remaining]x[Price per pound] Equation 8.3

The Index Value was computed for the 5 ppm and 15 ppm PAC doses. The PAC brand with the <u>lowest</u> Index Value represents the most cost effective supplier of PAC. PAC 1 (Norit 20B) had the lowest overall Index Value at a PAC dose of 15 ppm. At the lower PAC dose of 5 ppm PAC 1 and 2 (Norit HDB and 20B) had similar Index Values. Therefore at low PAC doses (< 5 ppm), the cost effectiveness of both PAC 1 and PAC 2 were comparable. However, PAC 1 was more cost effective as higher PAC doses are required. Furthermore, given that the City of Phoenix has a maximum PAC feed rate of ~ 15ppm then the PAC brand with the lowest %MIB Remaining would provide the best overall control of MIB at the WTPs. Based upon the information provided, ASU recommends purchasing PAC1 (Norit20B) as the PAC supply for all COP WTPs. Each year PAC suppliers may offer new products or change prices, so performance based testing should be repeated and update Index Values computed.

Laboratory Methods

Water Source. Water was collected on May 8, 2001 from the Arizona Canal at 56th Street. The water was filtered (Whatman GF/F). The filtered water had a DOC concentration of 2.8 mg/L and is representative of a "typical" surface water in Arizona. MIB was spiked to the sample to yield a final concentration of 80 ng/L, a value selected as an upper limit of values experienced over the past 2 years during an occurrence and monitoring project.

PAC Batch Experiments. Activated carbon adsorption studies with MIB were conducted in the laboratory with commercially available brands of PAC. PAC samples were obtained from a single batch from manufacturers in amounts sufficient to run all experiments. PAC doses were either 5 or 15 ppm (parts per million). PAC slurry of each PAC sample were prepared at a concentration of 2500 mg PAC/L ultra-pure water; the slurry was mixed and allowed to hydrate for 24 hours at room temperature. Centrifuge vials (50ml) were used for treatments and were shaken on a wrist shaker (Multi-wrist® shaker, Lab-Line, Melrose Park, IL) for 3 hours. Activated carbon was removed from the samples by syringe filtering with a 0.2 um nylon filter (Acrodisc® 32 Supor® 0.2 um syringe filters, Pall Corporation, Ann Arbor, MI). Control treatments contained MIB, but no PAC, and were shaken and filtered in a similar manner as the samples containing PAC. Experiments were conducted at room temperature.

Duplicate samples were performed at a PAC dose of 15 ppm. For PAC3 two different slurry mixtures were prepared for the experiments to determine if any significant error would occur simply due to preparation of the slurry. The statistical error was very small, and provided justification for comparison of MIB removals with different PAC brands.

Measurement of MIB and Geosmin. MIB and Geosmin were measured using Solid-Phase Microextraction/Gas Chromatography Mass Spectroscopy (SPME-GC/MS) (Watson et al., 2000; Lloyd et al., 1998). Twenty-five mI of sample is added to a 40 mI septum capped vial that contains 8 gm desiccated sodium chloride and a magnetic stir bar. An internal standard (10 ng/L IPMP, Aldrich Chemical Co., Milwaukee, WI) is added through the septum and the vial is placed in a water bath on a magnetic stir plate heated to 50 ± 1.5 °C. A SPME fiber (Supelco # 57348 U) is introduced into the head space gas through the septum and the sample is stirred for 30 minutes. The fiber is removed from the vial and inserted into the gas chromatograph injector at 250 °C for 5 minutes. The fiber was then retracted into the holder, removed from the GC inlet and reused for the next sample. Compounds are eluted from the column gas chromatograph to a mass spectrometer set for selective ion storage (selective *m/z* values: MIB = 95, Geosmin = 112 and IPMP = 124, 136). Calibration curves are generated using MIB and Geosmin standards (mixture standard: Supelco # 47525 U). Method detection limit for SPME is 2 ng/L. An MIB internal standard was run in triplicate, and had excellent reproducibility: 27.5±0.8 ng/L.

Results

Experimental results for the MIB concentration remaining after 3 hours of contact time are presented in Figure 8.10. The "No PAC" sample represents a control, and served as the basis for evaluating MIB percentage removal (Figure 8.11). Three replicate "No PAC" samples had an average concentration of 80.5±0.8 ng/L. At a PAC dose of 15 ppm duplicate samples were prepared and analyzed. Higher MIB removals were achieved at a PAC dose of 15 ppm than at a lower PAC dose of 5 ppm. The PAC brand with the highest MIB percentage removal at 15 ppm also had the highest MIB percentage removal at a PAC dose of 5 ppm. PAC1 and PAC6 had similar MIB removals at a PAC dose of 15 ppm. PAC1 and PAC6 had similar MIB removals at a PAC dose of 15 ppm. Table 8.6 summarizes the percentage of MIB remaining in each of the tests, and should be used in computation of the Index Value (equation 1).

Analysis

Although iodine numbers (mg/g) for each PAC source was provided, surface area was only provided for 4 of the 6 PAC sources. Neither iodine numbers nor surface areas alone were predictive of MIB removal by the PAC sources. The lack of an apparent correlation reinforced the necessity for the analysis presented above as a means of selecting the best performing PAC source.

Several water municipalities around the country employ an Index Value (equation 1) as a means of comparing the cost-effective performance of different PAC sources in selecting a bidding supplier. Table 8.7 summarizes the Index Values for the PAC sources evaluated. This approach accounts for both the removal capability and cost of a particular PAC source. PAC 1 (Norit 20B) had the lowest Index Value at the 15ppm dose of PAC, and was similar to PAC2 (Norit HDB) at a PAC dose of 5 ppm. Based upon this analysis PAC1 (Norit 20B) is recommended for selection as part of the City bidding process.

Several types of data analysis were subsequently performed to further evaluate the cost effectiveness of Norit20B versus Norit HDB, the two PAC types with the lowest Index Values. Historic data on MIB influent concentrations from three of the City water treatment plants (WTPs) were obtained from a monitoring program spanning from August 1999 through April 2001. A polynomial expression, calibrated from past and current work, was used to estimate the PAC dose required to achieve any set percentage MIB removal. It was assumed that the target MIB concentration in the WTP effluent should be either 5 or 10 ng/L. To meet these

goals Norit20B was cheaper than NoritHDB. Table 8.8 summarizes the results based upon estimates of PAC chemical costs (\$/1000 gal treated water). At a PAC dose of 15 ppm the cost of Norit20B (\$0.059/1000 gal) is 50% greater than Norit HDB (\$0.040/1000 gal), however less Norit20B material is required to meet the same set MIB concentration in finished water. Because of the higher removal efficiency of MIB by Norit 20B, Norit 20B is actually more cost effective and will save between 60% and 80% of the chemical costs if Norit HDB was used instead (based upon achieving a 5 ng/L MIB concentration in the finished water).

In addition to having a potential cost savings by using Norit 20B to reach set finished water MIB concentrations, there are other advantages of selecting the best performing PAC type. First, the frequency of feeding greater than 15 ppm of PAC is reduced by more than 50%. This is important for the City, since PAC feed equipment at the WTPs are limited to 15 ppm. Achieving higher PAC feed rates, as would be needed when using Norit HDB would require capital investments. Furthermore, reducing PAC feed rates reduces the amount of PAC used annually, allowing for on-site storage of PAC to last longer. Use of less PAC also results in less sludge production.

Source Switching

As used throughout this report, source switching means decreasing (or halting) water production at WTPs receiving high-MIB (low quality) water and increasing production at WTPs receiving low-MIB (high quality) water.

The T&O problem generally gets worse as water moves along the Arizona Canal, because algae in the canal contribute additional MIB and, to a lesser extent, Geosmin. Because of this, the Deer Valley WTP receives the highest concentration of MIB and Geosmin in the water among Phoenix's water treatment plants. The pattern of increasing MIB downstream is consistent from year-to-year, although the magnitude of the episodes varies. Adding PAC to the Deer Valley Plant would be expensive. Based on measured MIB at the inlet to the Deer Valley Plant and a target of 10 ng/L in production water, the cost of PAC treatment for August 1999 to September 2000 would have been \$921,000. Furthermore, the PAC feed system at the Deer Valley WTP was inadequate to supply required PAC doses. Because of these problems and construction plans, the City of Phoenix shut down the Deer Valley WTP during the 2001 T&O season, shifting production to plants that receive better quality water (Figure 8.5). During August-November 1999, Deer Valley produced 29% of Phoenix's total municipal water. For the same months, Deer Valley's contribution to total water production had decreased to 18% in 2000 and to 1% in 2001. Decreased production at Deer Valley was offset by increased production at the Val Vista and Squaw Peak WTPs. Shifting production to other treatment plants avoided several serious T&O episodes at the Deer Valley WTP.

OVERALL PROGRAM SUCCESS

Evaluating "Consumer Days Below Thresholds"

In the midcourse evaluation we proposed a metric for evaluating the overall success of the T&O implementation program, *consumer days below threshold*. This metric is simply the number of days consumers receive water with MIB and Geosmin levels below defined threshold levels. To evaluate this metric, we used threshold values of 10 ng/L and 20 ng/L. Ten ng/L is a lower taste and odor threshold for MIB and Geosmin for most individuals. Twenty ng/L is a "milestone"

standard by which to evaluate partial success of the implementation program. To estimate the total number of "consumer days" produced at each treatment plant, we first computed the average per-capita production by dividing the total production at all of Phoenix's water treatment plants by the service population (Figure 8.6).

Consumer days at each plant was then computed by dividing monthly water production by average monthly per capita water use to yield the number of consumer days. Monthly MIB and Geosmin values for product water was used to determine whether the plant accrued "consumer days below threshold".

The trend in percentage of CDBT-20s increases from August 1999 to December 2001 (Figure 8.7). The trend is particularly marked during the taste and odor season (late summer-fall), as seen in Figure 8.8.

For the main part of the T&O season, August-November, there has been a steady increase in the number of CDBT-20s, from 51% in 1999 to 74% in 2000 and 81% in 2001.

Impact of T&O Management on CDBTs

The impact of deliberate T&O control measures can be estimated for several measures: modified operation of Lake Pleasant, source switching, PAC treatment, and canal management. The starting point of this analysis is the observed CDBT-10s (and CDBT-20s for 2001 and the total number of consumer days for the year for all of the WTPs included in the monitoring program, about 446 million consumer days. Of the total number of consumer days, 93% were CDBT-20s and 73% were CDBT-10s.

Modified operation of Lake Pleasant

The impact of modified operation of Lake Pleasant can be estimated by comparing CDBT-10s and CDBT-20s observed during 2001 with CDBT-10s and CDBT-20s that would have occurred if water had been released from the epilimnion, the standard operating practice before 1999. This estimation is based on the assumption that water released from the epilmnion of Lake Pleasant would have had the same MIB levels as were actually observed at site R2A (Lake Pleasant epilimnion) from April to October of 2001 and the same MIB level as observed at site R3 for the rest of the year. In other words, epilimetic release would not have affected MIB levels in the epilimnion, a fairly reasonable assumption. In the epilimnetic release scenario, we assumed that MIB levels in water released from the epilimnion during the summer would be the same as MIB levels at the inlet to the Union Hills WTP. We also assumed that MIB levels actually measured in the CAP canal at 7th St. were representative of MIB at the inflow to the Union Hills WTP and that there would be no PAC treatment at Union Hills, so MIB in the inlet = MIB in the product water. Finally, we assumed that operational modification of Lake Pleasant affected only the Union Hills WTP. This is a conservative assumption, because some CAP water is also delivered to WTPs on the Arizona Canal.

The increase in CDBTs gained by operational modifications (e.g., hypolimnetic release and bypass pumping) was then computed by comparing real observation with the epilimnetic release scenario (Table 8.4). For 2001, epilimnetic MIB levels were consistently below 20 ng/L, so no gains in CDBT-20s accrued from modified operation of Lake Pleasant. However, modified operation probably increased the number of CDBT-10s by 30 million days. It other years with higher epilmnetic MIB levels, there would have been a greater gain in CDBT-20s. For example,

in 1999, operational modification probably added about 23 million CDBT-20s.

Source Switching

The impact of source switching can be estimated by assuming that all WTPs would have been operating at 1999 production levels in the absence of source switching. We also assumed that PAC treatment efficiencies for the WTPs operating throughout 2001 (except for the January shutdown) would have been the same MIB treatment efficiency as actually observed for 2001, based on measured MIB in the inlets and outlets of these plants. For the Deer Valley WTP, which was not operating for much of 2001, we assumed that the MIB removal efficiency would have been the same as observed at the Squaw Peak WTP in 2001, 24%. The gain in CDBTs was then computed by comparing actual observations (e.g., observations with source switching in place) with the modeled non-source switching scenario.

Source switching probably added 30 million CDBT-20s and 77 million CDBT-10s. For comparison, these gains represent 20% and 17%, respectively, of system-wide consumer days.

PAC Treatment

The impact of PAC treatment can be measured more directly. The sole assumption is that in the absence of PAC treatment, MIB in the inflow to the WTPs would be equal to MIB in the outflows, i.e., MIB would be neither removed nor added within the treatment plants. PAC treatment added about 41 million CDBT-20s and about 6 million CDBT-10s.

Canal Treatments

Canal treatments probably reduced MIB production in the Arizona Canal, but not enough to reduce MIB levels below 20 ng/L at the inlet to the Squaw Peak WTP. The analysis is also complicated by the fact that the Deer Valley WTP was off line for most of the summer and fall of 2001. This reduced flows in the Arizona Canal considerably, confounding an analysis of canal treatment. A reasonable conclusion regarding canal treatments is that they reduce MIB production in the Arizona Canal, but are not alone sufficient to keep MIB levels below 20 ng/L. Because of this, canal treatment, though useful, did not contribute to a gain in CDBT-20s or CDBT-10s, at least in 2001. Canal treatments are therefore an adjunct to PAC treatment, serving to reduce MIB levels at the inlet to the WTPs and decreasing required PAC dosages needed at WTPs downstream. See Section 3 for detailed results of implementation of canal treatments.

SRP-CAP Blending

The impact of blending is also difficult to evaluate, because the mixture of waters delivered to COP's WTPs depends upon many factors, not just water quality concerns. Although blending definitely reduced MIB in the Arizona Canal (see Figure 8.3), much of this blending would have occurred in the absence of a T&O control strategy. Therefore, the conservative assumption is that blending contributed little to the accrual of CDBT-20s and CDBT-10s.

No T&O Management Scenario

The impact of no T&O management program was estimated by assuming: (1) no PAC treatment, so no in-plant MIB removal, (2) no source switching, so all treatment plants produced

the same amount of water as they did in 1999, and (3) the CAP canal received water from Lake Pleasant's epilimnion, with 2001 MIB levels.

In the absence of T&O management, there would have been about 314 million CDBT-20s and 239 million CDBT-10s. This is about 70% and 54% of total consumer days, respectively.

Overall Impact of the T&O Management Program

The overall impact of the T&O management program for 2001 was computed two ways, first by subtracting "likely consumer days without management" from observed consumer days below the 10 and 20 ng/L thresholds, and second, by summing the impact of each T&O treatment measure. In theory, these two values should be the same, but because of slightly erroneous assumptions, they are somewhat different.

T&O management appears to have added between 102 million (by difference) to 132 million CDBT-20s (by summing terms) to Phoenix's water supply. This is 33% to 44% more CDBT-20s than would have occurred in the absence of the T&O management program. T&O management added 85 million to 113 million CDBT-10s, a gain of 36% to 47% compared to the no-management option.

An approximate allocation of total system-wide consumer days is presented in Figure 8.9. In the absence of a T&O control program, we estimate that about 64% of consumer days would have been < 20 ng/L and 36% of the consumer days would have had MIB > 20 ng/L. The T&O management program dealt with about 3/4 of the problem. In 2001, MIB exceeded 20 ng/L for only 7% of consumer days. Source switching had the largest impact at reducing MIB in water delivered to consumers, reducing the number of consumer days above 20 ng/L by 20%. PAC treatment reduced MIB < 20 ng/L for 9% of total consumer days. Modified operation of Lake Pleasant contributed no CDBT-20s in 2001, but would have contributed to a decrease in CDBT-20s in 1999 and probably in many other years.

Without the T&O management program, only 48% of consumer days would have been below the 10 ng/L threshold. The T&O management program increased the number of total consumer days with MB < 10 by another 25%. About one fourth of total consumer days remained above 10 ng/L. Source switching and modified operation of Lake Pleasant provided the greatest increases in CDBT-10s. PAC treatment was not very effective at increasing CDBT-10s, mostly because COP's WTPs are not yet using PAC as effectively as they could. Infrastructure improvements in PAC delivery systems would greatly increase the CDBT-10s.

In summary, implementation of the T&O reduction program in 2001 significantly improved the quality of water delivered to consumers.

THE FUTURE

Although early implementation of T&O control measures has been successful at substantially increasing the number of consumer days below threshold values, further improvements can be expected in 2002. Specifically:

• Delays in implementing canal treatments can be shortened by placing greater reliance on copper treatment and by improving communication among participants so that treatments are implemented more quickly. The measurement-to-implementation gap should always be less than one week and could be reduced to 3-4 days in most cases. During 2000 and 2001, delays between the time the need was identified to actual implementation of canal treatments was sometimes well over a week.

- PAC treatment can be made more effective by fixing the PAC delivery system at the Squaw Peak and Deer Valley WTPs and shifting entirely to Norit 20B.
- Each year PAC suppliers may offer new products or change prices, so performance based testing should be repeated and updated Index Values computed.
- To date, the rapid response-feedback system is based on actual measurements of T&O compounds. We are now developing a *predictive systems approach* that will use a variety of tools to predict MIB and Geosmin concentrations 2-4 weeks in advance. This predictive ability would give project participants advance warning of impending T&O episodes and allow action to be taken in advance of the actual episode.

SECTION 8 TABLES AND FIGURES

WTP LOCATION	PAC Utilization (Tons/year)* in each fiscal year				
AND PAC	1999	2000	2001	2002	Total
TYPE					
Val Vista WTP					
HDB	150	396	988	0	1533
20B	0	0	45	541	585
Squaw Peak WTP					
HDB	25	6	27	0	56
20B	0	0	0	419	419
Deer Valley WTP					
HDB		27	0	0	27
20B		0	0	34	34
Union Hills WTP					
HDB	11	0	0	0	11
20B	0	0	0	21	21
Total Usage					
HDB	186	429	1015	0	1630
20B	0	0	45	1015	1060

Table 8.1. Approximate PAC Utilization based upon PAC purchases

*Estimated based upon \$640/TonHDB and \$950/Ton20B

Table 8.2. Percentage of time that MIB concentrations were less than selected MIB levels in raw and treated water at two WTPs

MIB Level	Squaw Peak WTP		Val Vista WTP		
	Raw Water	Treated Water	Raw Water	Treated Water	
< 10 ng/L	0%	7%	13%	13%	
< 15 ng/L	0%	20%	40%	73%	
< 20 ng/L	0%	33%	67%	87%	

Table 8.3. Observed and predicted MIB removals for Squaw Peak WTP during Fall 2001 PAC Implementation

Date	Norit 20B PAC	Raw water MIB	Finish ed water	Percent MIE	8 Removal (1-0	C/Co)	Plant Production (MGD)	Detentio Time Basins (I	n in hour)
	Dose (mg/)	(ng/L)	MIB (ng/L)	Observed at Squaw Peak	Fall 2001 Predictive Model	Refined Predictive Model		Presed	Floc + Sed
9/27/01	14.7	66	29	56%	91%	74%	120	1.05	2.55
10/04/01	14.6	56	29	49%	90%	74%	120	1.05	2.55
10/17/01	15.7	28	23	16%	92%	77%	120	1.05	2.55
10/25/01	10.3	28	18	37%	79%	62%	120	0	2.55
11/1/01	15.4	27	10	63%	92%	76%	120	1.05	2.55
11/8/01	8.6	30	12	61%	72%	55%	100	1.25	3.05
11/14/01	11.6	28	8	71%	84%	66%	90	1.41	3.39

Table 8.4. Evaluation of consumer days below threshold (10 ng/L and 20 ng/L thresholds) for 2001, using various T&O control measures.

	Days
Total consumer days	446,641,123
1. Gains in CDBT-20s	
CDBT-20s (measured)	416,586,664
Likely CDBT-20s without management	314,138,337
Increase in CDBT-20s w/ management	102,448,327
Implemented management options	
Lake Pleasant operation*	0
PAC treatment	40,743,044
Source switching	91,332,490
Gain in CDBT-20s by summing T&O management practices	132,075,534
2. Gains in CDBT-10s	
CDBT-10s (measured)	324,490,660
Likely CDBT-10s without management	239,039,867
Increase in CDBT-10s w/ management	85,450,794
Implemented management options	
Lake Pleasant operation	30,007,702
PAC treatment	5,768,858
Source switching	77,320,503
Gain in CDBT-10s by summing T&O management practices	113,097,062

Table 8.5. Rankings of PAC Performance

PAC Rankings	Percentage M	IB Removed		
	External Samples	Internal Samples	5ppm PAC	15ppm PAC
Highest Removal (Best PAC)	PAC1		48%	76%
		Norit 20B	NA	72%
	PAC6		28%	69%
	PAC2		27%	48%
		PACarb Plus	NA	48%
		Norit HDB	NA	44%
│	PAC3		19%	39%
▼	PAC5		24%	39%
Lowest Removal	PAC4		4%	21%

Table 8.6. Rankings of PAC types and summary of Percentage MIB remaining (last two columns)

PAC Rankings	Percentage MIB Remaining			
	External Samples	Internal Samples	5ppm PAC	15ppm PAC
Highest Removal (Best PAC)	PAC1		52%	24%
		Norit 20B	NA	28%
	PAC6		72%	31%
	PAC2		73%	52%
		PACarb Plus	NA	52%
		Norit HDB	NA	56%
↓ ★	PAC3		81%	61%
▼	PAC5		76%	61%
Lowest Removal	PAC4		96%	79%

Table 8.7. Ranked evaluation of PAC sources based upon the Index Value and a PAC dose of 15 ppm.

PAC Rankings				Inde	x Value
	External Samples		Cost per Ton	5ppm PAC	15ppm PAC
Highest Removal (Best PAC)	PAC1-Norit20B	\$	950	498	230
	PAC2-Norit HDB	\$	640	468	335
	PAC6-Nuchar	\$	1,100	789	344
▲	PAC5-PACarb Plus**	\$	719	548	441
•	PAC3-PACarb Plus*	\$	784	638	477
Lowest Removal	PAC4-PACarb*	\$	620	593	492

* Provided by Thatcher

**Provided by Sweetwater

Table 8.8. Cost savings for using Norit20B rather than NoritHDB at three City WTPs to meet either 5 ng/l or 10 ng// concentrations of MIB in the WTP finished water.

	Cost savings of Using Norit 20B over HDB to meet different MIB concentrations in finished water				
	5 ng MIB /L 10 ng MIB /L				
Squaw Peak WTP	66% less for Norit 20B	34% less for Norit 20B			
Deer Valley WTP	78% less for Norit 20B	54% less for Norit 20B			
Val Vista WTP	58% less for Norit 20B	40% less for Norit 20B			

Figure 8.1. MIB in the CAP system near Lake Pleasant in fall, 1999. The arrow and text show the source of water to the CAP Canal below Lake Pleasant. The data label for the CAP Canal below Lake Pleasant (CAP below LP) is the MIB concentration of water delivered to the Phoenix area.



Figure 8.2. MIB at the CAP Siphon, Lake Pleasant (epilimnion and hypolimnion), and the CAP Canal below Lake Pleasant (at 7th St).





Figure 8.3. MIB in the SRP and CAP supplies at Granite Reef (A) and downstream, below the CAP inlet (site R13) (B).



Figure 8.4. Nomograph for full-scale use of Norit 20B at COP WTPs with a minimum presedimentation contact time of 1 hour (based upon Equation 8.1).



Figure 8.5. Water production at Phoenix's water treatment plants for the months of August to November, 1999 to 2001.



Figure 8.6. Average per capita daily water production for the City of Phoenix's water treatment plants.



Figure 8.7. Consumer days below threshold as percentage of total consumer days, August 1999 to December 2001.



Figure 8.8. CDBT-20s as percentage of total consumer days for all of Phoenix's water treatment plants, August-November of each year.





Figure 8.9. Pie chart showing consumer days with MIB < 20 ng/L (A) and < 10 ng/L (B) for 2001.





Figure 8.10. Concentration remaining in solution after 3 hour PAC contact time.





SECTION 9: SUMMARY AND RECOMMENDATIONS

The three-year project involved research and field-implementation activities focused at understanding algae-related drinking water problems for the metropolitan Phoenix area. A separate document, a T&O Control Guidance Manual, outlines effective field-scale implementation activities for T&O control. This section addresses the eight specific goals stated in Section 1 of this report:

- 1. Develop a thorough understanding of conditions leading to T&O problems.
- 2. Quantify the extent to which reservoir algae produce DOC and the reactivity of this DOC in forming DBPs.
- 3. Conduct controlled lab and field-scale experiments to evaluate specific T&O control practices.
- 4. Conduct a preliminary feasibility analysis for about 20 potential T&O control measures based on technical, economic, and political considerations.
- 5. Integrate results from the previous steps to begin implementation of a multiple-barrier approach for controlling the T&O problem.
- 6. Develop a long-term monitoring plan that will allow Phoenix and other municipalities to forecast the occurrence of T&O problems.
- 7. Develop a user-friendly taste and odor control manual that will help municipal water suppliers in arid environments develop effective T&O control programs.
- 8. Extrapolate applied research findings from Arizona to water treatment systems in other arid environments.

CONDITIONS LEADING TO T&O PROBLEMS

Spatial and temporal patterns in T&O occurrence were somewhat consistent over the three year project, although some "hot spots" for T&O production occurred only sporadically. MIB concentrations were higher than Geosmin concentrations in > 90% of the samples. Spatial and temporal patterns in Geosmin were similar to those for MIB with only minor exceptions. Therefore, MIB was considered the major cause of T&O problems.

The warm waters in the epilimnions of the reservoirs harbored green, blue-green, and diatom algae of which only a few of the blue-green algae were capable of producing MIB or Geosmin. As reservoir temperatures warmed above 20° C MIB production started, usually by May of any given year. A planktonic blue-green was presumed the culprit T&O producer, although, for example, only one periphytic algae (*Pseudanabaena sp.*) was confirmed to produce MIB from Saguaro Lake despite collection of over 280 algae isolates from the lake. All three reservoirs studied were thermally stratified, and MIB concentrations were also stratified with depth (lower concentrations with depth). Maximum MIB concentrations in the reservoir epilimnions ranged from 15 to > 100 ng/L and varied from year to year without any predictable relationship to nutrient levels. By August of each year MIB concentrations in the hypolimnion were > 5 ng/L. After thermal destratification (September- October) the reservoirs became completely

mixed and MIB concentrations were uniform throughout the water column. This resulted in a fairly rapid increase in MIB concentrations in the hypolimnion. Most reservoirs studied employed hypolimnetic water withdrawal, so thermal destratification caused a rapid rise in MIB leaving the reservoir. Initiating approximately one month after thermal destratification (~ November), MIB biodegradation occurred at rate of 1 to 5 ng/L/day. Biodegradation presumably occurred as algae biomass increased the bacterial population in the lake, allowing MIB to be degraded as a secondary metabolite. Consequently, MIB concentrations in the reservoirs were < 2 ng/L by the middle of the following January.

MIB and Geosmin concentrations increased after rainfall events. Three mechanisms for this release were developed. First, soil bacteria and fungi are capable of producing T&O compounds and rainfall either increased this production or solubilized T&O compounds and transported the compounds into rivers (e.g., lower Verde River). Irrigated soils produce more T&O compounds than non-irrigated soils. Second, rainfall events transported nutrients into nitrate limited water, resulting in a pulse of T&O compounds. Third, turbidity in the water decreased light penetration leading to algae cell lyses and release of stored intracellular MIB or Geosmin.

MIB and Geosmin are produced in concrete lined canals by periphytic algae. Extensive work was conducted with three such culprit blue-green periphytic algae (*Pseudanabaena sp., Oscillatoria splendida, Oscillatoria sp.*). T&O production in the canals occurred in "hot spots" that were of fairly short canal sections (< 1 to 4 miles) where T&O levels at least doubled. Every year T&O production between 24th St and 24th Ave along the Arizona Canal was observed. Wells located in this section lead to increased nitrate levels in the nitrogen limited surface water and was considered one factor for this production. Also the flowrate and water depth in the canal decreased allowing for dense periphytic algae to develop. A "hot spot" in the upper Arizona Canal was only observed one year, and no discernable water quality factor could be linked to the T&O production.

ALGAE-RELATED DOC AND DBP PRECURSORS

In laboratory experiments with algae cultures, green, blue-green, and diatom all produced DOC that upon chlorination formed DBPs. The yield of DBPs from this algae material was roughly 60% of that of lignin-derived fulvic acids, and verified that algae-DOC were DBP precursors. The DOC was determined to easily biodegraded by aquatic bacteria due to the enrichment of carbohydrates and amino acids. However, a refractory fraction of the algae-DOC remained after biodegradation and formed DBPs upon chlorination. THM and HAA production from algae DOC were documented, although other organic-nitrogen DBPs likely formed (haloacetonitriles, halomethanes, nitrosamines).

Based upon DOC mass balances in three reservoirs it was determined that algae-produced DOC accounted for 5% to 30% of the DOC in the reservoir. Upon chlorination at downstream WTPs this precursor material would form DBPs. Algae-DOC contribution to DBP formation could be minimized by increased hydraulic residence times in reservoirs, allowing the algae-DOC to biodegrade in-situ. The largest contribution of algae-DOC to downstream DBP precursors would occur during years of high snowmelt that (1) transport nutrients into reservoirs, and (2) fills reservoir to nearly maximum volume. Algae would grow during summer and early fall. Late summer / fall monsoon events would result in release of surface waters containing algae-DOC that had not had sufficient time to biodegrade.

T&O CONTROL EXPERIMENTS

Experiments in laboratory and field were conducted to identify environmental factors affecting T&O production, strategies to control T&O production, and strategies to remove T&O from water. Light intensity, temperature, and nutrient conditions all impacted the growth and production of T&O compounds by culprit algae. Of over 1000 algae cultures, approximately one dozen were confirmed to produce MIB or Geosmin in laboratory cultures. Approximately 15 others produced cyclocitrol, another earthy-musty-moldy odor, but one which had minimal occurrence in the field system. It was observed that temperatures above 20 °C increased algae growth and T&O production. Algae biomass contains large amounts of intracellular bound T&O compounds, that are slowly released during normal growth or rapidly released during cell lyses. Addition of nitrate to nitrogen limited surface water that contains algae, increased T&O production.

Liquid (e.g., copper, chlorine) and fixed-surface (e.g., polymers, paints) biocides reduced algae biomass and would lead to lower T&O production. Copper products added at total copper concentrations of 0.2 to 0.8 ppm for 6 to 8 hours of exposure inactivated most algae. Chlorine was also effective, but formed DBPs. Reactions between copper products (e.g., organically-complexed copper- Cutrine Plus) and chlorine resulted in a loss of free chlorine residual and formation of organic chloramines, and possibly DBPs of health concern. Polymeric coatings and paint products applied to concrete surfaces were effective in reducing the algae biomass capable of attaching to the walls. Since periphytic algae were responsible for T&O production, these fixed-surface biocides would likely be effective at reducing T&O production.

Powder (PAC) and granular (GAC) activated carbon and ozone are effective at removing > 90% of T&O compounds from water. The performance of these unit processes for WTPs were less effective in natural surface waters than in distilled water. As a result, in the bid specification process performance-based requirements in surface water were developed for PAC removal of MIB. The net outcome was selection of a more cost-effective PAC, rather than low-bid procurement. This was particularly important for the City of Phoenix, which had limited PAC feed capabilities (i.e., mg/L dosing) at the WTPs and selection of a PAC that removed more MIB was effective.

LONG-TERM T&O MONITORING AND T&O PREDICTION

The second two years of the three year study had below normal watershed snowmelt/runoff and precipitation and were considered to represent drought conditions. Continued monitoring into the future is necessary to evaluate T&O patterns in wetter than average years. Monitoring locations should continue to focus on the terminal (lowest elevation) reservoirs on the three main surface water sources for the metropolitan Phoenix region (Lake Pleasant, Bartlett Lake, Saguaro Lake). The reservoirs produce T&O that have the largest contribution to raw water entering drinking water treatment plants. Frequent and intensive monitoring (every 7 to 10 days) along canals and across WTPs between June and December is recommended to develop criteria for implementation of T&O control strategies.

T&O prediction was found to be difficult as < 5% of the biomass in the water system was apparently responsible for MIB and Geosmin production. However, general factors that reduce algae biomass should reduce T&O production. Mis-leading events, such as massive algae blooms in Saguaro Lake that turned the water green, can result in no MIB or Geosmin
production. A neural network model was developed to predict MIB in the epilimnion of the reservoirs based upon physical, chemical, and/or biological parameter inputs. However, such models often require 10 years of "training data" and an additional two years of validation data. So additional data collection is required. Conceptual models and simple empirical relationships clearly show that an exponential increase in MIB concentration within the epilimnion of the reservoirs occurs for water temperatures between 20°C and 32°C. Thermal and dissolved oxygen profiling of the reservoirs can be used to estimate when reservoirs will destratify and when MIB concentrations will peak in water released downstream. Therefore, MIB prediction from the reservoirs are feasible for 4 to 8 weeks into the future. This timeframe of prediction is useful and would allow WTPs to modify operations (e.g., shift production) or order PAC, or for alternative water sources to be discharged into the canals.

IMPLEMENTATION OF T&O CONTROL STRATEGIES

The central theme of the proposed T&O management strategy is the concept of multiple barriers. The multiple barrier concept in water treatment is widely used for pathogen control. "Barriers" in pathogen control include watershed management (for example, eliminating animal and human waste inputs into streams), sedimentation and filtration within water treatment plants to remove pathogens, initial chlorination to kill pathogens, and maintenance of chlorine residual to kill any pathogens that might enter the distribution system (by regrowth, plumbing malfunctions, etc.).

Technical feasibility, economic factors, and political infrastructure of approximately 20 T&O control options were evaluated for potential use in the metropolitan Phoenix region. This evaluation served as the baseline for decisions on which activities to conduct in the field during Task 7 (Phased-in Implementation). A multiple-barrier approach for controlling T&O was developed and comprised of (1) watershed controls, (2) source water controls, (3) canal distribution controls, and (4) in-plant controls. Achieving T&O control higher in the watershed would have the greatest benefit to the largest number of WTPs. Political obstacles associated with water rights and timing of water releases complicated implementation of regional controls, although the project has initiated efforts to evaluate such obstacles in the future. In-canal management and in-plant controls were deemed highly effective and were therefore the focus of Task 7 activities.

The concept is similar for T&O control. During the T&O study, more than 20 specific control measures were evaluated. Six control measures emerged as the key elements of an overall T&O management strategy:

- <u>Process Control Monitoring</u>. Frequent sampling, rapid analytical turnaround, and rapid data review are critical for implementing any control strategies. Experience indicated that MIB concentrations remained somewhat constant over 7 to 10 days, and that frequency of sampling is recommended. Implementation on T&O control measures should be conducted on a shorter duration timetable to be effective. Timely and accurate data on the status of T&O levels in a water supply system was determined critical to maximize the economic benefits on implementing control strategies.
- <u>Reservoir management.</u> The main reservoir management practice found to be effective was blending of waters from the Colorado River and the two outlet structures (upper and

lower) in Lake Pleasant. Through blending waters from these three sources, CAWCD has been able to keep MIB and Geosmin in the CAP Canal below Lake Pleasant below 10 ng/L.

- <u>Canal treatments.</u> The goal of canal treatments was to remove T&O-producing algae growing on the sides of the Arizona Canal, thereby reducing the production of MIB. Because algae growing on the canal walls can be a major source of MIB, sometimes contributing > 50 ng/L MIB to water flowing through the canal, canal treatments to remove algae are a very important part of the overall T&O management program.
- <u>SRP-CAP Blending.</u> During the late summer and fall, CAP water generally has lower concentrations of MIB than SRP water. This provides an opportunity for blending the two source waters to reduce MIB concentrations in water delivered to the treatment plants. For most years, using more SRP water early in the season, and more CAP water later in the season, would improve the quality of water delivered to Phoenix's municipal customers. The opportunity for blending depends upon the hydrologic status of the system. Revisions in the legislation controlling the SRP-CAP Water Exchange Agreement in 2002 enhance the opportunity for blending as a T&O control measure.
- <u>Source switching.</u> Phoenix has five water treatment plants and will have a sixth within about five years. The idea behind source switching is that water with higher MIB/Geosmin can sometimes be avoided by switching production from a plant that is receiving high MIB/Geosmin water to one or more plants that are receiving water with lower MIB/Geosmin. For example, taking the Deer Valley WTP off line during 2001, shifting production to the Union Hills and Squaw Peak WTPs, avoided the problem of high MIB in the lower end of the Arizona Canal and resulted in better quality of water delivered to consumers.
- <u>In-plant treatment.</u> PAC treatment in the WTPs has been an effective method of removing MIB from source waters. Although PAC treatment could theoretically keep MIB levels below 10 ng/L throughout the year with no upstream management, practical limitations constrain the effectiveness of PAC treatment. These limitations include limited storage capacity, problems with pumping systems, and hydraulic short-circuiting. Furthermore, even if these limitations could be overcome, a multibarrier strategy would be more cost-effective than reliance upon PAC treatment alone.

The surface water system that serves the City of Phoenix also serves every other municipality in the metropolitan Phoenix region. As can be seen in the above five effective control strategies, the first four would actually reduce T&O levels for all municipalities downstream of the implementation activity. A regional water sampling plan including locations, analytes, and sampling frequency has been developed in the Guidance Manual. Samples are collected by SRP, CAP, and a third party (e.g., ASU), analyzed at a central laboratory within 36 hours, and data reviewed within the following 48 hours. As this project ends, the Cities of Phoenix, Tempe, and Chandler are participating in an ongoing T&O monitoring project.

GUIDANCE MANUAL

A Guidance Document was prepared as a separate report from this Final Report. The Guidance Document was written for application by WTP operations personnel, and provides the

key decision making information required to establish a monitoring program, identify "hot spot" locations of MIB production, select T&O control measures, and implement the T&O control measures.

INTERACTIVE ALGAE TAXONOMIC GUIDE

The Interactive Taxonomic Guide was prepared to allow the user to navigate easily between the baseline-monitoring sites in the CAP/SRP/Phoenix water supply and treatment systems to observe photomicrographs of confirmed taste and odor organisms and dominant algae taxa at each site. Over 200 algae images were included to facilitate identification for water utilities personnel. In addition, 57 photographs of the baseline-monitoring sites and Global Positioning Satellite (GPS) locations were also included for each baseline-monitoring site in the guide. The Interactive Taxonomic Guide also includes pages with the following information: the chemical structures for 2-methylisoborneol and geosmin, a taxonomic key to distinguish between blue-green algae, green algae and diatoms, and a list of references for algae identification.

The Interactive Taxonomic Guide was designed and created using Netscape Composer version 6.2.3. Copies of the interactive taxonomic guide were copied to CD-ROM for distribution. The user will obtain optimum program performance by using Netscape version 6.2.3 as his/her active web browser. However, the program is also accessible using other web browsers, *i.e.*, Internet Explorer, MSN, or AOL. Free downloads of Netscape version 6.2.3 are available at http://www.netscape.com.

A series of figures have been included here to illustrate the interactive nature of the Interactive Taxonomic Guide (Figures 9.1 to 9.5):

- The title page provides the user with the opportunity to advance to view the "Interactive Site Map", "Taxa List", or "List of Producers" (Figure 9.1).
- The "Interactive Site Map" allows the user to select baseline-monitoring sites from a list
 of names or by directly clicking on the location on a map (Figure 9.2). After selecting a
 site, the user will observe the site name, GPS location and a link to site photographs on
 top of the page (Figure 9.3). The table below this information provides links to
 photomicrographs of dominant algae, MIB producers and Geosmin producers from that
 specific site.
- The "Taxa List" allows the user to proceed directly to an organism of interest or browse through photomicrographs of common algae taxa from the baseline-monitoring sites (Figure 9.4).
- The "List of Producers" allows the user to view a list of comfirmed MIB and geosmin producers. Links are provided to photomicrographs and descriptions of each confirmed producer (Figure 9.5).

EXTRAPOLATION OF RESULTS TO OTHER ARID REGIONS

The findings of this research are easily transferable to other arid-regions of the world. For example, T&O biodegradation and relationship to bacterial populations were presented at an

annual conference in 2001. In 2002 a study in Kansas, USA used similar data analysis methods for tracking T&O biodegradation. Current work in Arizona has revealed similar patterns in the number and type of culprit organisms as previously identified in southern California. New research on algal biotoxins appears to follow similar spatial and temporal trends as MIB and Geosmin, all of which are algae trace metabolites. Research initiated as part of this project involving genetic fingerprinting of culprit algae as a rapid field assessment tool parallels similar work in Australia on the topic. T&O occurrence and impacts to the perception of drinking water quality are ubiquitous throughout the world. The information gained during this project will directly be transferable worldwide and lead to improved control of T&O. Methods for dissemination of the results have included multidisciplinary regional, national, and international conferences, and peer-reviewed journal articles, which are available worldwide.

SECTION 9 TABLES AND FIGURES

Figure 9.1. Interactive Taxonomic Guide title page.



Figure 9.2. "Interactive Site Map" page from the Interactive Taxonomic Guide.



Figure 9.3. Example of a specific baseline monitoring site (CAP Canal at 7th Street (R4)) from the Interactive Taxonomic Guide title page.

CAP Canal at 7 th Street (R4)
(Latitude-N33 42.079; Longitude-W112 03.935)
Click here to view Site Photos
Dominant Algae MIB Producers Geosmin Producers <u>Achnanthes minutissima</u>
NONE <u>Oscillatoria splendida</u>
<u>Diatoma vulgare</u>
<u>Navicula spp.</u>
<u>Synedra spp.</u>
Return to Interactive Site Map
View Taxa List
Return to Home Page

Figure 9.4. "Taxa List" page from the Interactive Taxonomic Guide.



<u>Navicula spp.</u> Streptomyces sp.

Nitzschia sigmoidea

<u>Nitzschia spp.</u>

<u>Pinnularia brebissonii</u>

Rhoicosphenia curvata

<u>Rhopalodia gibba</u>

Surirella pseudovalis

Synedra affinis

Synedra spp.

View Interactive Site Map

View List of Producers

Return to Home Page

Figure 9.5. "List of Producers" page from the Interactive Taxonomic Guide.



APPENDIX A: BASELINE DATA TABLES

Month	R1	R2A	R2B	R3	R4	R4dup	R5	R6A	R6B	R7	R8	R9A	R9Adup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22	R25	R26
Aug-99	0.0						19.5					17.7						0.0			17.5								
Sep-99	0.0						12.2					27.6						8.3			27.1								
Oct-99	0.0	0.0	0.0	0.0	0.0		0.0	0.0	6.0	6.0	0.0	11.0		6.0	8.0	0.0	8.0	9.0	27.0	42.0	28.0	39.0	24.0	0.0	0.0				
Nov-99	0.0	15.0	7.7	0.0	0.0		0.0	0.0	0.0	0.0	7.2	12.8		6.9	9.3	0.0	8.6	5.9	13.7	8.6	17.9								
Dec-99	0.0	9.3	9.9	0.0	0.0		0.0	0.0	0.0	0.0	5.8	0.0			5.8	0.0	0.0	0.0	7.0	6.1	9.2	9.5							
Jan-00	0.0	0.0	2.9	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0		0.0	2.4	0.0	2.5						0.0	0.0	0.0				
Feb-00	0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0	2.1	0.0	2.2		5.6		0.0	0.0					
Mar-00	0.0	4.4	4.8	3.7	2.1	2.7	2.5	2.1	0.0	2.4	5.7	6.1		4.2	6.6	0.0	21.5	15.1	11.4	7.2	28.9	25.0	6.8	6.4	1.6				
Apr-00	4.0	4.6	4.5	3.4	3.1	2.2	5.2	2.2	2.4	4.6	8.3	10.1	6.9	5.4	4.2	0.0	6.5	4.2	4.9		16.2	12.0	6.5	6.5	4.4				
May-00	0.0	6.2	4.4	0.0	0.0	0.0	11.8	6.4	0.0	0.0	20.4	21.1	24.2	14.4	10.2	0.0	12.9	7.5	8.8	9.4	12.6	11.7	9.7	8.8	0.0	9.5	10.5		
Jun-00	0.0	3.7	0.0	0.0	0.0	0.0	24.1	17.4	0.0	4.8	18.6	25.3	20.9	15.7	12.3	0.0	14.3	10.8	12.5	11.6	11.2	11.9	8.5	9.0	7.5	14.1	11.7		
Jul-00	6.3	6.4	7.3	3.5	2.5	3.3	37.8	40.1	2.9	5.9	15.3	38.5	26.6	20.1	18.7	2.2	20.0	16.2	15.0	8.3	19.0	14.0	17.6	0.0	87.7	16.7	13.0		
Aug-00	8.9	14.3	16.5	2.6	2.6	0.0	16.8	54.2	32.2	7.1	34.6	43.6	37.2	16.0	14.2	2.6	15.7	10.1	14.8	8.9	51.5	42.6	10.5	9.4	11.5	17.9	10.7		
Sep-00	10.4	13.2	14.2	10.0	9.7	9.2	4.4	24.5	16.7	13.3	25.6	36.0	32.7	21.0	20.0	7.2	65.0	9.1	21.6	18.5	64.0	48.3	27.4	12.0	9.0	32.0	13.2		
Oct-00	10.4	6.6	6.8	8.7	4.9	4.7	3.1	5.7	13.1	14.1	23.4	18.4	19.6	18.4	24.4	6.9	38.4	20.4	26.0	21.6	46.5	44.1	16.9	3.3	5.7	23.0	20.2		
Nov-00	3.6	3.3	3.1	2.8	4.9	4.4	7.6	0.0	0.0	3.2	10.8	3.7	4.0	4.4	11.0	4.7	21.8	11.9	17.6	13.9	21.5	26.4	15.3	7.3	5.5	17.0	16.5		23.7
Dec-00	0.0	0.0	3.4	0.0	0.0	0.0	0.0	0.0	2.0	2.4	4.4	2.5	2.2	2.0	17.9	3.1	9.6	9.3	11.2	9.0	24.3	20.8			0.0	12.4	9.7		
Jan-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.1	0.0	0.0	3.5	8.6	0.0	15.9						12.4	10.5	0.0				
Feb-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.3	2.0	2.0		20.3		7.7	5.8	8.6		11.3		5.7	3.8	0.0	12.3	9.1	3.0	
Mar-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.1	3.7	4.1	2.4	51.6	0.0	24.6	15.0	15.0	9.7	14.9	15.5	4.6	2.6	0.0	12.4	19.9	2.0	16.6
Apr-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.0	4.2	4.4	0.0	12.0	0.0	5.2	5.1	5.7	5.7	6.0		0.0	0.0	0.0	5.2	4.3	0.0	4.8
May-01		0.0	0.0	0.0	0.0	0.0	4.1	5.8	0.0	0.0	16.5	11.7	10.7	4.3	5.7	0.0	5.9	5.5	5.7	5.2	6.0		4.8	5.2	2.0	7.9	5.5	18.6	7.0
Jun-01	5.2	0.0	0.0	2.0	0.0	0.0	16.5	5.0	0.0	0.0	5.1	9.9	10.0	7.7	5.4	0.0	7.0	5.0	7.6	5.1	53.4		3.6	3.2	2.2	47.5	4.1	8.0	8.6
Jul-01	2.9	0.0	0.0	0.0	0.0	0.0	26.0	4.8	0.0	0.0	8.1	7.3	7.6	6.5	4.9	0.0	6.3	4.8	17.4	16.8	30.1		4.3	5.1	9.0	27.8	6.9	10.3	9.7
Aug-01	7.0	3.2	0.0	0.0	2.2	2.2	4.4	12.9	0.0	0.0	9.8	24.8	23.8	10.0	8.3	0.0	13.5	10.1	20.6	15.9	30.0	8.0	10.1	13.5	3.3	19.0	17.2	9.7	17.2
Sep-01	14.4	14.0	0.0	0.0	3.5	3.6	11.7	8.1	0.0	2.8	20.1	105.1	101.2	13.8	13.8	15.8	3.4	27.5	29.6	59.9	45.9		20.5	15.7		64.7	49.5	15.3	47.9
Oct-01	7.3	17.5	13.4	4.3	4.2	5.0	6.3	7.2			38.4	51.7	48.4	42.1	16.7	8.4	21.2	22.8	27.6	23.2	62.5		15.1	11.5			31.0	4.2	40.1
Nov-01	8.9	19.2	18.6	6.6	10.9	8.9	8.1	6.8	6.7		4.9	3.1	2.8	3.7	3.2		17.8	20.5	28.1	8.1	74.0		17.1	7.4				3.3	
Dec-01	0.0	4.3		0.0	0.0	0.0	2.9	0.0		0.0	0.0	0.0		0.0	4.8	2.9	7.2	0.0	13.9	7.2	30.2		6.6	0.0	2.1			0.0	9.6
Jan-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0	28.5	27.0	2.9		290.0		8.8	5.3			6.7	52.8	0.0
Feb-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.0	3.0	22.9		26.4		5.8	4.8		18.8	13.4	0.0	14.9
Mar-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	2.3	0.0		0.0	0.0	15.0	4.1	12.5	14.3	11.2	11.3	5.7		2.9	9.8	7.5	0.0	13.0
Apr-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.1	8.2	9.0		0.0	0.0	3.8	5.5	3.2	4.5	2.9	0.0	2.3			2.8	4.8	3.0	5.1
May-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.1	8.2	9.0		0.0	0.0	3.8	5.5	3.2	4.5	2.9	0.0	2.3		0.0	2.8	4.8	3.0	5.1
Jun-02	0.0	2.8	0.0	0.0	0.0	0.0	2.3	0.0	0.0	0.0		10.0	9.8	7.6	6.1	0.0	3.4	4.3	3.5	4.0	3.5	3.4	2.1	2.3	0.0	3.1	3.1	5.4	4.9
Jul-02	0.0	0.0	0.0	0.0	0.0	0.0	11.8	2.9	0.0	0.0		11.3	10.0	9.3	6.7	0.0	6.8	5.7	4.4	4.5	5.3	5.9	5.3	6.1	6.6	6.3	4.9	5.8	5.2

Table A. 1. MIB (ng/L) from august 1999 to June 2002 - ASU analyses (0 < MDL of 2 ng/l).

Month	R1	R2A	R2B	R3	R4	R4dup	R5	R6A	R6B	R7	R8	R9A	R9Adup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22	R25	R26
Aug-99	0.0						0.0					0.0						0.0			9.1								
Sep-99	0.0						0.0					0.0						5.2			8.0								
Oct-99	0.0	0.0	0.0	43.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0		0.0	7.0	8.0	0.0	0.0	11.0	18.0	18.0	21.0	8.0	20.0	6.0				
Nov-99	5.1	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0		0.0	7.9	0.0	0.0	0.0	0.0	0.0	6.4								
Dec-99	8.4	0.0	0.0	8.1	6.7		0.0	0.0	0.0	0.0	0.0	0.0			9.9	0.0	0.0	0.0	6.1	0.0	8.7	9.0							
Jan-00	0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0		0.0	3.6	0.0	0.0						0.0	0.0	0.0				
Feb-00	0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0		0.0	2.1	0.0	0.0	0.0	0.0		2.8		0.0	0.0					
Mar-00	5.1	0.0	0.0	6.6	3.4	4.1	2.3	0.0	0.0	0.0	2.2	2.1		0.0	0.0	0.0	3.8	0.0	4.0	0.0	6.2	5.9	0.0	2.4	2.1				
Apr-00	4.1	0.0	0.0	7.1	7.1	6.1	2.0	0.0	2.3	4.9	6.2	0.0	2.4	0.0	0.0	3.1	0.0	2.3	5.4		8.5	9.3	9.7	7.0	3.7				
May-00	0.0	5.3	2.9	4.8	6.3	7.2	3.1	7.1	0.0	5.9	2.6	0.0	2.7	2.1	2.4	6.4	3.3	2.4	5.7	5.5	7.5	9.1	5.2	5.6	4.3	4.3	7.2		
Jun-00	2.2	0.0	0.0	0.0	2.2	0.0	4.9	4.5	3.0	5.1	0.0	3.9	3.7	2.3	3.5	2.7	2.6	2.8	4.6	3.7	4.5	5.3	3.0	2.5	39.2	4.1	3.6		
Jul-00	0.0	0.0	0.0	0.0	0.0	0.0	109.0	0.0	0.0	5.5	0.0	2.7	0.0	0.0	2.4	0.0	2.1	0.0	3.3	2.2	5.7	3.2	2.5	2.8	6.6	13.6	2.8		
Aug-00	7.0	4.3	2.4	3.4	3.1	2.7	0.0	2.4	3.0	7.1	5.2	4.5	3.3	2.7	3.5	4.2	4.1	4.1	5.4	3.6	7.1	6.7	6.7	6.9	5.1	8.2	4.4		
Sep-00	3.8	0.0	0.0	0.0	0.0	2.2	5.1	0.0	0.0	5.0	3.6	3.1	2.8	2.2	2.9	0.0	7.0	0.0	5.4	5.3	14.5	9.7	5.1	2.2	9.5	12.1	3.5		
Oct-00	2.5	0.0	0.0	0.0	2.5	2.2	2.3	0.0	2.7	4.4	3.4	2.4	2.7	3.3	2.8	2.7	2.8	2.9	6.6	5.1	12.9	15.5	4.2	0.0	0.0	8.8	3.9		
Nov-00	0.0	0.0	0.0	0.0	3.4	3.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.5	0.0	0.0	3.5	2.2	4.4	6.8	0.0	0.0	3.3	5.2	3.2		3.1
Dec-00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	4.1	2.5	11.6	9.2			0.0	6.5	0.0		
Jan-01	0.0	0.0	0.0	0.0	0.0	0.0	3.1	2.7	0.0	0.0	0.0	0.0	0.0	2.1	0.0	4.7	0.0						0.0	0.0	2.0				
Feb-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0		2.1		0.0	0.0	0.0	2.5	0.0	0.0	
Mar-01	0.0	0.0	0.0	3.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.3	4.2	0.0	4.1	2.7	2.7	0.0	3.0	2.2	6.9	8.0	2.6	0.0	0.0	2.5	6.0	2.9	4.3
Apr-01	0.0	0.0	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.7	3.0	2.7	2.7	3.2		0.0	0.0	0.0	2.9	0.0	0.0	2.2
May-01		0.0	0.0	0.0	0.0	0.0	0.0	43.7	8.9	3.1	4.0	9.4	8.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.6		2.5	2.0	2.2	4.1	2.0	3.0	2.3
Jun-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.1	0.0	0.0	3.5	5.1	6.0	2.9	3.0	0.0	2.6	2.1	3.0	2.9	19.1		0.0	0.0	8.5	16.5	2.5	3.4	3.8
Jul-01	2.6	0.0	0.0	0.0	0.0	0.0	2.1	0.0	0.0	0.0	2.1	4.0	3.8	0.0	2.8	0.0	2.7	2.6	6.7	6.8	10.7		3.3	2.7	9.8	10.4	4.1	2.4	5.4
Aug-01	3.1	0.0	0.0	0.0	2.6	2.6	0.0	0.0	0.0	0.0	0.0	2.7	2.8	0.0	2.8	0.0	2.4	2.7	6.3	2.4	6.6	0.0	3.7	5.9	4.8	4.6	4.4	3.3	5.9
Sep-01	3.2	0.0	0.0	3.4	2.8	3.2	0.0	0.0	0.0	2.8	3.2	4.0	3.8	2.6	2.6	3.0	4.1	4.0	3.6	7.3	5.9		3.1	2.6		6.5	4.9	4.0	6.2
Oct-01	0.0	0.0	0.0	3.2	3.7	3.9	0.0	0.0			2.7	2.5	0.0	0.0	3.3	4.8	3.4	2.9	4.7	0.0	4.7		3.9	0.0			3.1	2.4	4.8
Nov-01	10.4	0.0	0.0	13.2	12.5	11.7	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0		0.0	0.0	4.3	0.0	3.2		2.0	0.0				0.0	
Dec-01	0.0	0.0		0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0		0.0	18.9	21.7	0.0	0.0	3.6	1.5	2.6		3.6	0.0	2.8			0.0	3.4
Jan-02	5.0	2.1	3.0	4.8	6.7	7.1	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	9.0	10.4	8.5	8.2		2.1		4.2	2.6			2.1	12.1	0.0
Feb-02	2.7	0.0	0.0	2.5	3.3	3.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.5	0.0	2.2	6.5		3.6		3.7	5.0		4.8	4.7	0.0	5.2
Mar-02	3.7	0.0	0.0	3.4	3.2	3.6	0.0	0.0	0.0	0.0	2.6	2.5	2.6		3.0	3.0	2.0	3.0	3.2	3.0	2.5	2.7	2.5		2.4	3.0	2.8	3.0	2.7
Apr-02	6.0	0.0	0.0	4.5	4.2	4.3	0.0	0.0	0.0	0.0	0.0	3.1	2.8		0.0	4.9	0.0	3.3	2.2	2.0	2.2	0.0	2.6			2.5	0.0	3.0	2.1
May-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.7	0.0	0.0	2.3	0.0
Jun-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		3.3	2.5	0.0	0.0	0.0	0.0	0.0	2.2	2.0	2.1	2.6	2.1	2.0	8.7	2.7	2.3	6.2	2.8

Table A. 2. Geosmin (ng/L) from august 1999 to June 2002 - ASU analyses (0 < MDL of 2 ng/l).

Month	R1	R2A	R2B	R3	R4	R4dup	R5	R6A	R6B	R7	R8	R9A	R9Adup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19
Aug-99	0	12	0	0	0		38	9	0	0	12	34		4	6	0	10	5	0	12	19	22	14	9
Sep-99	4	45	0	0	0		14	10	10	8	13	22		19	13	0	12	9	29	33	46	33	31	23
Oct-99	5	30	20	6	3		6	12	11	12	16	20		19	15	4	18	19	42	43	39	44	37	21
Nov-99	0	27	15	2	0		2	0	0	2	13	16		14	12	0	10	7	23	22	19			
Dec-99	0	14	14	0			0	0	0	0	7	5			8	0	6	9	15	16	22	13		
Jan-00		10	6											5									10	11
Feb-00																			15		31			
Mar-00												15		0		0	24	21						
Apr-00																			7		18	9	4	
May-00																			7	5	5	5	6	
Jun-00																			8	7	8	10	7	
Jul-00																			10	7	12	15	10	
Aug-00																			15	10	51	35	9	
Sep-00																			17	15	52	37	30	
Oct-00																			29	25	37	34	20	
Nov-00																								
Dec-00																								
Jan-01					0											0	17						13	13
Feb-01																0	11						7	5
Mar-01																				8	8	11	4	4
Apr-01																			3	3	5		3	4
May-01																			4	3	4		4	
Jun-01																			8	7			4	
Jul-01																			15	11	22		0	
Aug-01																			44	35	54	20	23	
Sep-01																			50		50		17	
Oct-01																								
Nov-01																								
Dec-01														1										
Jan-02																					333		7	
Feb-02						1								Ī										
Mar-02																								
Apr-02														İ										

Table A. 3. MIB (ng/L) from august 1999 to June 2002 - COP analyses (0 < MDL of 2 ng/l).

Month	R1	R2A	R2B	R3	R4	R4dup	R5	R6A	R6B	R7	R8	R9A	R9Adup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19
Aug-99	2	0	0	0	0		0	0	0	7	0	0		0	0	0	2	3	0	7	6	9	4	3
Sep-99	2	0	0	3	9		0	0	0	8	0	0		0	4	8	3	3	10	10	14	11	4	3
Oct-99	0	0	0	50	6		0	0	0	2	3	2		2	5	13	4	5	9	7	9	10	8	2
Nov-99	2	0	0	2	0		0	0	0	0	3	2		2	8	2	0	0	5	5	5			
Dec-99	4	0	0	4			0	0	0	0	0	2			8	3	2	0	4	5	7	5		
Jan-00		0	0											3									3	3
Feb-00																			2		6			
Mar-00												8		0		5	3	6						
Apr-00																			4		5	4	3	
May-00																			3	2	2	3	2	
Jun-00																			2	2	3	3	2	
Jul-00																			3	2	4	5	2	
Aug-00																			5	4	7	6	6	
Sep-00																			5	4	15	9	5	
Oct-00																			9	6	15	18	3	
Nov-00																								
Dec-00																								
Jan-01					0											4	0						0	0
Feb-01																2	2						2	2
Mar-01																				3	3	3	2	0
Apr-01																			5	5	4		3	3
May-01																			2	2	3		2	
Jun-01																			2	0			0	
Jul-01																			4	3	8		0	
Aug-01																			17	6	24	0	9	
Sep-01																			5		4		2	
Oct-01																								
Nov-01																								
Dec-01																								
Jan-02																					0		6	
Feb-02																								
Mar-02																								
Apr-02																								
May-02																								
Jun-02																								

Table A. 4 Geosmin (ng/L) from august 1999 to June 2002 - COP analyses (0 < MDL of 2 ng/l).

Month	R1	R2A	R2B	R3	R4	R4-Dup	R5	R6A	R6B	R7	R8	R9A	R9A-Dup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R25	R26
Aug-99	0.301	0.231	0.316	0.390	0.345		0.552	0.202	0.270	0.282	0.235	0.268		0.346	0.207	0.354	0.199	0.254	0.247		0.269		0.291		0.168		
Sep-99	0.262	0.318	0.323	0.366	0.342		0.507	0.230	0.375	0.396	0.334	0.311		0.445	0.208	0.339	0.302	0.273	0.287		0.327		0.290		0.631		
Oct-99	0.318	0.333	0.337	0.325	0.275		0.441	0.320	0.285	0.410	0.266	0.276		0.358	0.279	0.281	0.314	0.328	0.370		0.392		0.275		0.200		
Nov-99	0.450	0.286	0.348	0.426	0.422		0.360	0.348	0.366	0.366	0.342	0.345		0.318	0.354	0.440	0.292	0.366	0.316		0.466				0.080		
Dec-99		0.280	0.280		0.390		0.230	0.310		0.350									0.420		0.310						
Jan-00	0.398	0.274	0.309	0.395	0.374		0.105	0.231	0.206	0.205	0.526	0.241		0.233	0.113	0.366	0.155						0.207		0.112		
Feb-00	0.406	0.340	0.290	0.406	0.406		0.370	0.180	0.210	0.244	0.236	0.248		0.260	0.166	0.416	0.156	0.342	0.324		0.184		0.412	0.284			
Mar-00	0.408	0.326	0.312	0.448	0.428	0.392	0.360	0.190	0.298	0.274	0.214	0.246		0.482	0.212	0.460	0.258	0.334	0.500		0.442		0.366		0.167		
Apr-00	0.440	0.298	0.308	0.368	0.418	0.406	0.330	0.192	0.206	0.230	0.264	0.260	0.250	0.326	0.234	0.406	0.262	0.302	0.486		0.750		0.370		0.156		
May-00	0.496	0.304	0.396	0.406	0.438	0.460	0.694	0.216	0.234	0.268	0.270	0.304	0.306	0.340	0.254	0.434	0.246	0.324	0.406		0.706		0.384		0.220		
Jun-00	0.472	0.258	0.260	0.338	0.318	0.376	0.312	0.236	0.428	0.196	0.270	0.334	0.290	0.330	0.236	0.360	0.240	0.258	0.274		0.436		0.274		0.206		
Jul-00	0.372	0.346	0.354	0.360	0.410	0.402	0.358	0.244	0.218	0.296	0.368	0.352	0.284	0.702	0.314	0.358	0.276	0.258	0.244		0.232		0.252		0.240		
Aug-00	0.320	0.350	0.334	0.282	0.334	0.286	0.308	0.306	0.338	0.236	0.310	0.442	0.334	0.220	0.280	0.294	0.270	0.266	0.290		0.294		0.268		0.678		
Sep-00	0.298	0.276	0.268	0.274	0.274	0.294	0.476	0.310	0.236	0.366	0.390	0.422	0.322	0.320	0.360	0.338	0.232	0.482	0.334		0.596		0.282		0.142		
Oct-00	0.234	0.258	0.310	0.316	0.228	0.260	0.262	0.378	0.628	0.512	0.376	0.338	0.314	0.332	0.264	0.252	0.326	0.360	0.370		0.720		0.304		0.282		
Nov-00	0.380	0.376	0.414	0.390	0.334	0.332	0.468	0.354	0.332	0.366	0.582	0.436	0.414	0.522	0.334	0.376	0.254	0.262	0.310		0.298		0.344		0.022		
Dec-00	0.256	0.286	0.296	0.270	0.274	0.274	0.232	0.294	0.388	0.296	0.458	0.376	0.386	0.374	0.128	0.270	0.158	0.186	0.472		0.496				0.096		
Jan-01	0.360	0.360	0.354	0.404	0.356	0.388	0.190	0.328	0.346	0.264	0.518	0.440	0.428	0.482	0.196	0.340	0.222						0.222		0.044		
Feb-01	0.432	0.334	0.392	0.420	0.404	0.398	0.168	0.208	0.230	0.232	0.450	0.392	0.396	0.436	0.168	0.392	0.210	0.194	0.280		0.218		0.266		0.118	0.196	
Mar-01	0.500	0.352	0.372	0.444	0.430	0.430	0.372	0.170	0.200	0.196	0.368	0.270	0.248	0.354	0.218	0.428	0.164	0.272	0.502		0.786		0.416		0.068	0.132	0.470
Apr-01	0.376	0.198	0.336	0.400	0.564	0.588	0.132	0.148	0.186	0.164	0.238	0.302	0.236	0.266	0.230	0.376	0.104	0.120	0.192		0.544		0.286		0.094	0.082	0.282
May-01		0.258	0.402	0.300	0.316	0.310	0.148	0.234	0.170	0.180	0.260	0.296	0.300	0.312	0.216	0.338	0.228	0.246	0.286		0.656		0.272			0.114	0.386
Jun-01	0.264	0.268	0.332	0.526	0.451	0.248	0.030	0.345	0.349	0.162	0.219	0.289	0.297	0.288	0.206	0.308	0.302	0.373	0.301		0.500		0.274		0.123	0.105	0.366
Jul-01	0.262	0.291	0.421	0.364	0.371	0.307	0.302	0.191	0.336	0.162	0.241	0.257	0.247	0.230	0.186	0.293	0.353	0.356	0.248		0.668		0.255			0.178	0.603
Aug-01	0.385	0.256	0.315	0.382	0.293	0.415	0.323	0.355	0.385	0.215	0.308	0.316	0.207	0.287	0.236	0.267	0.196		0.258		0.299		0.237			0.143	0.374
Sep-01	0.285	0.288	0.291	0.247	0.290	0.236	0.194	0.310	0.262	0.258	1.426	0.715	0.427	0.757	0.628	0.397	0.609	0.368	0.445		0.585		0.354		0.766	0.287	0.730
Oct-01	0.288	0.334	0.351	0.355	0.303	0.290	0.352	0.261		0.319	0.704	0.409	0.409	0.446	0.367	0.365	0.249	0.250	0.362	0.351	0.736		0.339	0.301	0.218	0.299	0.385
Nov-01	0.246	0.280	0.217	0.222	0.195	0.187	0.101	0.226	0.205	0.212	0.333	0.264	0.277	0.291	0.216		0.179	0.141	0.576		0.665		0.215		0.039	0.229	
Dec-01	0.339	0.285		0.327	0.315	0.310	0.056	0.222		0.201	0.399	0.279	0.262	0.256	0.129	0.322	0.160	0.122	0.117		1.267		0.134		0.000	0.120	0.255
Jan-02		0.283		0.336	0.318	0.310	0.028	0.213		0.190	0.295	0.276	0.253	0.264	0.198	0.334	0.120	0.154	0.619		0.316		0.185			0.039	
Feb-02	0.380	0.351	0.294	0.392	0.439	0.431	0.047	0.245	0.221	0.166	0.268	0.257	0.263	0.274	0.189	0.374	0.207	0.238	0.294		0.248		0.240		0.155	0.120	0.275
Mar-02	0.435	0.288	0.355	0.436	0.459	0.461	0.083	0.150	0.337	0.179	0.827	0.342	0.364		0.214	0.485	0.247	0.378	0.489		0.666		0.388			0.157	0.568
Apr-02	0.420	0.234	0.371	0.409	0.436	0.423	0.175	0.135	0.264	0.213	0.262	0.299	0.315	0.238	0.420	0.473	0.263	0.262	0.393		0.617		0.384		0.157	0.198	0.450
May-02	0.344	0.223	0.342	0.334	0.341	0.322	0.081	0.100	0.127	0.149		0.298	0.345	0.229	0.198	0.335	0.187	0.238	0.273		0.279		0.265			0.124	0.321
Jun-02	0.310	0.211	0.311	0.315	0.317	0.281	0.109	0.147	0.101	0.116		0.311	0.376	0.250	0.204	0.301	0.239	0.224	0.281		0.376		0.244			0.486	0.309

Table A. 5. Total nitrogen (mg/L) from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R4-Dup	R5	R6A	R6B	R7	R8	R9A	R9A-Dup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R25	R26
Aug-99	0.266	0.243	0.336	0.379	0.348		0.448	0.173	0.326	0.286	0.237	0.213		0.266	0.203	0.352	0.212	0.225	0.225		0.241		0.234		0.110		
Sep-99	0.233	0.262	0.315	0.335	0.322		0.372	0.207	0.343	0.363	0.281	0.283		0.311	0.211	0.334	0.201	0.215	0.250		0.226		0.238		0.380		
Oct-99	0.279	0.284	0.255	0.275	0.251		0.318	0.230	0.226	0.331	0.226	0.233		0.284	0.256	0.273	0.253	0.235	0.268		0.343		0.228		0.188		
Nov-99	0.364	0.273	0.292	0.372	0.365		0.292	0.318	0.276	0.338	0.362	0.336		0.270	0.287	0.408	0.292	0.280	0.285		0.335				0.080		
Dec-99		0.260	0.280		0.380		0.120	0.240		0.260									0.400		0.430						
Jan-00	0.380	0.225	0.288	0.362	0.362		0.053	0.197	0.136	0.149	0.230	0.220		0.222	0.106	0.354	0.109						0.156		0.042		
Feb-00	0.352	0.326	0.298	0.392	0.372		0.200	0.152	0.140	0.202	0.206	0.196		0.202	0.142	0.378	0.130	0.270	0.224		0.196		0.292	0.268			
Mar-00	0.378	0.300	0.286	0.410	0.398	0.380	0.146	0.132	0.248	0.146	0.196	0.198		0.220	0.184	0.370	0.152	0.258	0.414		0.404		0.368		0.146		
Apr-00	0.412	0.238	0.266	0.320	0.380	0.376	0.188	0.158	0.142	0.188	0.226	0.220	0.236	0.254	0.232	0.382	0.224	0.288	0.330		0.560		0.334		0.104		
May-00	0.446	0.404	0.422	0.466	0.404	0.410	0.528	0.188	0.182	0.234	0.252	0.280	0.304	0.264	0.240	0.420	0.224	0.338	0.378		0.632		0.306		0.260		
Jun-00	0.434	0.278	0.228	0.332	0.312	0.358	0.150	0.160	0.168	0.162	0.216	0.244	0.270	0.266	0.188	0.322	0.200	0.246	0.256		0.382		0.228		0.128		
Jul-00	0.262	0.216	0.258	0.322	0.316	0.314	0.158	0.196	0.146	0.164	0.288	0.196	0.220	0.322	0.204	0.388	0.232	0.230	0.322		0.296		0.238		0.188		
Aug-00	0.296	0.258	0.258	0.252	0.282	0.242	0.178	0.250	0.295	0.248	0.270	0.310	0.248	0.238	0.220	0.258	0.246	0.290	0.262		0.282		0.314		0.402		
Sep-00	0.268	0.216	0.244	0.240	0.232	0.252	0.226	0.194	0.180	0.310	0.278	0.238	0.234	0.220	0.246	0.256	0.188	0.230	0.240		0.478		0.228		0.076		
Oct-00	0.238	0.234	0.254	0.238	0.216	0.248	0.152	0.194	0.524	0.458	0.350	0.252	0.248	0.288	0.238	0.208	0.270	0.238	0.322		0.680		0.230		0.280		
Nov-00	0.362	0.338	0.342	0.348	0.330	0.318	0.452	0.350	0.314	0.344	0.504	0.426	0.394	0.440	0.310	0.292	0.248	0.256	0.266		0.280		0.312		0.014		
Dec-00	0.242	0.252	0.266	0.260	0.254	0.256	0.232	0.256	0.282	0.250	0.450	0.352	0.372	0.356	0.090	0.220	0.126	0.146	0.396		0.486				0.062		
Jan-01	0.330	0.318	0.338	0.378	0.340	0.358	0.100	0.282	0.272	0.246	0.504	0.418	0.426	0.386	0.178	0.328	0.194						0.224		0.020		
Feb-01	0.386	0.306	0.338	0.384	0.386	0.376	0.104	0.162	0.204	0.224	0.456	0.356	0.356	0.424	0.168	0.348	0.190	0.142	0.242		0.212		0.232		0.108	0.160	
Mar-01	0.490	0.340	0.360	0.424	0.408	0.420	0.278	0.172	0.180	0.166	0.338	0.242	0.246	0.342	0.204	0.406	0.138	0.270	0.486		0.776		0.402		0.070	0.126	0.498
Apr-01	0.380	0.190	0.316	0.372	0.536	0.536	0.082	0.138	0.140	0.154	0.230	0.270	0.222	0.250	0.190	0.350	0.112	0.114	0.180		0.520		0.258		0.066	0.080	0.280
May-01		0.232	0.400	0.296	0.282	0.292	0.134	0.182	0.158	0.174	0.242	0.250	0.278	0.300	0.204	0.346	0.210	0.202	0.262		0.656		0.224			0.116	0.370
Jun-01	0.235	0.193	0.322	0.397	0.281	0.244	0.037	0.297	0.388	0.138	0.227	0.210	0.230	0.283	0.253	0.301	0.312	0.273	0.203		0.469		0.201		0.164	0.122	0.345
Jul-01	0.235	0.200	0.371	0.324	0.280	0.297	0.112	0.215	0.261	0.140	0.183	0.183	0.199	0.183	0.179	0.282	0.141	0.168	0.201		0.560		0.156		1.246	0.081	0.330
Aug-01	0.298	0.257	0.281	0.336	0.290	0.281	0.281	0.347	0.346	0.197	0.213	0.276	0.237	0.284	0.216	0.265	0.186		0.261		0.311		0.230			0.118	0.373
Sep-01	0.243	0.264	0.253	0.225	0.250	0.233	0.213	0.333	0.275	0.262	0.448	0.349	0.305	0.715	0.278	0.276	0.270	0.349	0.539		0.544		0.248		0.301	0.235	0.396
Oct-01	0.289	0.295	0.315	0.332	0.271	0.265	0.210	0.213		0.269	0.297	0.351	0.338	0.356		0.265	0.205	0.147	0.346	0.410	0.733		0.310	0.293	0.158	0.246	0.376
Nov-01	0.301	0.179	0.131	0.194	0.179	0.188	0.077	0.141	0.186	0.165	0.234	0.237	0.224	0.226	0.149		0.138	0.142	0.532	0.135	0.681		0.187	0.141	0.044	0.083	
Dec-01	0.340	0.262		0.301	0.327	0.328	0.042	0.184		0.188	0.371	0.206	0.197	0.224	0.127	0.330	0.097	0.123	0.081	0.048	1.199		0.176	0.602	0.000	0.108	0.237
Jan-02		0.265		0.304	0.329	0.290	0.028	0.187		0.146	0.268	0.208	0.233	0.202	0.155	0.251	0.111	0.134	0.525		0.327		0.144	0.132		0.027	
Feb-02	0.411	0.327	0.280	0.362	0.375	0.408	0.045	0.239	0.203	0.143	0.226	0.216	0.214	0.256	0.173	0.327	0.140	0.214	0.259		0.192		0.238	0.183	0.101	0.079	0.238
Mar-02	0.387	0.248	0.304	0.377	0.387	0.393	0.076	0.120	0.223	0.167	0.230	0.196	0.205		0.192	0.381	0.147	0.299	0.343	0.357	0.522	0.650	0.331			0.138	0.444
Apr-02	0.394	0.214	0.296	0.371	0.394	0.391	0.116	0.108	0.141	0.180	0.158	0.227	0.225	0.221	0.208	0.368	0.207	0.215	0.261	0.234	0.569	0.563	0.296	0.295	0.090	0.150	0.369
May-02	0.308	0.210	0.286	0.282	0.297	0.269	0.046	0.071	0.156	0.138		0.225	0.218	0.186	0.155	0.301	0.186	0.200	0.173	0.079	0.141	0.112	0.176	0.108		0.115	0.263
Jun-02	0.270	0.187	0.282	0.325	0.257	0.253	0.062	0.112	0.068	0.096		0.179	0.221	0.164	0.169	0.266	0.135	0.182	0.169	0.103	0.235	0.163	0.143	0.108	0.083	0.225	0.233

Table A. 6. Total dissolved nitrogen (mg/L) from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R4-Dup	R5	R6A	R6B	R7	R8	R9A	R9A-Dup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R25	R26
Aug-99	4.1	5.5	2.1	9.5	5.6		39.2	9.5	31.6	34.3	28.5	12.8		42.4	24.3	1.5	28.0	19.5	9.5		22.7		16.6		15.6		
Sep-99	0.0	15.4	39.7	9.6	0.0		43.0	6.4	30.3	40.2	17.9	6.0		13.9	25.6	0.0	28.0	15.8	32.3		29.5		14.4		154.0		
Oct-99	0.0	3.2	9.4	6.5	0.0		53.7	27.5	15.4	40.1	23.1	9.7		17.6	20.1	0.0	44.0	28.9	48.6		28.8		16.8		29.3		
Nov-99	15.1	8.1	12.8	6.4	7.1		34.5	34.6	62.6	32.1	25.9	18.4		19.8	13.5	40.3	31.8	44.2	33.1		50.6				5.8		
Dec-99	5.3	6.6	8.8	5.2	5.5		31.3	32.6	160.6	36.0	24.2	72.6		0.0	6.6	20.0	31.1	27.8	21.0		14.0						
Jan-00	12.2	13.0	10.0	12.6	3.3		14.2	10.1	22.9	12.4	15.3	6.5		5.8	0.0	0.0	12.3						8.4		3.2		
Feb-00	7.4	5.2	1.2	3.0	7.2		91.4	15.8	20.0	26.6	23.4	8.0		17.8	6.4	3.2	15.8	13.0	29.2		7.2		22.0	0.2			
Mar-00	1.4	6.0	2.8	1.8	4.0	3.2	101.0	27.0	43.8	34.8	19.6	8.2		85.6	10.2	7.2	40.0	27.0	30.8		11.8		4.2		27.2		
Apr-00	2.8	2.0	0.6	2.8	1.0	0.6	54.2	7.4	8.6	18.2	13.0	5.6	5.0	12.8	8.0	0.0	11.0	10.0	45.4		38.0		6.2		11.6		
May-00	11.0	9.6	11.2	11.0	10.4	10.6	113.8	16.4	29.0	26.6	23.2	22.0	21.4	46.0	22.6	11.4	17.4	15.6	19.2		38.2		21.8		35.0		
Jun-00	9.6	9.0	8.2	8.8	8.8	10.0	85.2	17.6	266.8	28.2	22.2	18.8	18.6	29.4	19.2	11.0	21.6	14.6	14.8		18.2		17.0		50.2		
Jul-00	10.2	7.6	15.2	10.6	10.2	8.8	52.2	12.6	25.8	27.2	29.2	21.2	18.0	139.8	28.2	9.8	30.8	25.4	15.0		12.8		15.6		46.4		
Aug-00	4.6	4.8	7.4	4.6	6.2	7.2	35.6	10.2	35.4	26.8	22.0	18.8	10.0	15.8	17.0	8.4	17.4	11.4	12.0		11.6		11.4		80.2		
Sep-00	4.4	7.2	11.2	11.0	11.2	11.4	43.0	12.0	18.6	42.0	28.0	11.8	7.2	7.6	20.0	11.4	19.8	11.8	12.0		7.6		9.8		20.4		
Oct-00	5.6	9.4	10.4	13.6	7.0	7.2	67.6	18.6	93.2	84.4	38.4	23.6	22.2	27.6	18.2	9.4	44.4	30.8	20.2		14.8		17.4		15.4		
Nov-00	7.8	9.2	16.0	8.2	7.2	8.0	25.4	28.0	34.8	36.6	43.6	32.0	32.2	32.8	18.0	5.0	28.0	21.0	31.4		26.2		17.0		10.6		
Dec-00	7.4	7.6	13.2	9.2	9.4	9.4	34.4	28.8	47.6	39.6	39.8	30.2	31.4	30.0	12.8	9.6	33.2	31.8	28.2		20.0				0.0		
Jan-01	2.0	2.0	3.0	0.0	0.0	0.0	27.4	14.2	24.8	12.2	24.8	17.4	13.4	15.6	0.0	0.0	12.8						6.8		7.6		
Feb-01	10.6	2.0	8.0	3.4	8.2	2.2	16.0	11.6	13.8	14.0	26.8	17.0	17.0	19.0	7.8	3.8	29.4	24.8	30.0		14.6		14.2		5.4	15.8	
Mar-01	6.2	0.0	5.0	1.8	2.0	1.6	59.6	5.6	10.8	6.6	17.4	5.0	7.0	15.0	9.8	1.6	9.8	3.6	8.2		7.0		4.8		8.6	5.4	
Apr-01	2.6	2.8	3.4	3.6	2.8	3.0	12.6	6.4	25.8	15.4	14.6	7.6	7.8	13.8	12.0	3.0	12.4	13.8	22.4		8.4		10.8		11.0	10.2	13.6
May-01		14.8	0.0	4.2	0.0	0.0	26.6	6.8	2.4	12.0	12.4	5.8	5.8	21.4	8.4	0.0	6.0	3.4	1.8		1.8		2.6			9.6	4.6
Jun-01	3.4	0.8	0.9	3.7	7.8	4.6	24.0	16.9	2.1	26.4	19.1	14.2	15.6	15.4	16.4	2.8	18.6	17.0	30.9		19.4		14.5		163.5	6.8	34.4
Jul-01	0.0	4.7	8.7	4.9	5.6	2.0	30.9	4.4	6.5	20.5	16.2	11.2	3.8	9.9	12.6	0.4	9.2	10.4	16.7		5.7		5.0			0.4	15.0
Aug-01	13.1	11.6	14.1	15.0	14.3	13.7	84.6	15.4	19.4	35.9	25.4	19.0	20.2	31.9	30.5	13.2	33.0		26.5		19.8		22.7			14.8	23.8
Sep-01	3.4	9.6	11.4	13.4	14.2	10.2	73.4	15.6	15.0	40.8	36.2	20.0	17.8	29.0	31.0	14.6	37.8	36.4	35.2		23.4		11.4		149.8	14.6	27.2
Oct-01	6.1	9.7	12.4	31.0	16.7	16.0	65.9	15.9		87.0	19.7	21.2	23.4	23.7	14.2	28.9	25.0	24.7	8.0	15.2	28.9		7.4	37.8	32.6	20.1	
Nov-01	6.4	24.2	7.3	5.2	7.5	4.4	27.4	13.0	18.8	15.9	29.0	13.7	18.2	16.3	11.3		18.5	21.0	16.9		15.9		22.4		7.3	24.0	
Dec-01	8.0	13.3		46.1	7.3	6.4	15.6	14.0		24.3	37.3	13.7	12.4	12.6	6.8	9.8	14.2	14.6	11.5		9.5		12.5		5.9	11.8	13.9
Jan-02		6.1		7.3	8.3	7.0	16.1	19.1		23.7	25.6	9.7	12.4	12.1	11.3	4.9	9.4	12.1			9.1		13.9			10.1	
Feb-02	5.1	14.0	9.7	8.5	12.9	6.0	13.4	18.4	17.9	15.6	20.3	14.8	11.1	12.8	9.4	24.0	15.1	9.7	11.1		13.2		11.8		9.9	9.9	11.6
Mar-02	5.5	6.4	6.6	8.9	7.6	7.4	15.2	8.6	20.2	14.9		19.3	21.1		11.0	51.9	19.9	9.5	34.6		30.6		17.7			8.4	32.3
Apr-02	7.6	8.6	5.7	6.2	4.4	4.1	37.5	4.9	7.6	13.3	15.7	8.4	9.8	3.5	21.2	8.9	20.3	14.2	21.0		31.4		20.9			13.2	18.4
May-02	7.6	7.3	7.3	7.4	7.0	7.5	32.9	10.1	15.6	14.1		19.7	22.3	18.9	29.3	8.9	18.9	15.7	21.0		23.4		12.2			12.8	18.3
Jun-02	5.4	5.3	5.4	5.9	6.4	6.3	32.3	6.9	12.6	20.2		17.6	17.5	10.9	18.9	3.5	20.9	19.4	19.4		18.9		18.2			78.5	20.5

Table A. 7. Total phosphorous (mg/L) from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R4-Dup	R5	R6A	R6B	R7	R8	R9A	R9A-Dup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R25	R26
Aug-99	7.0	1.8	0.0	3.1	0.0		15.9	2.6	22.9	22.2	15.8	0.0		25.6	17.3	0.0	33.6	18.9	11.5		7.8		33.3		6.3		
Sep-99	10.0	10.6	0.0	9.0	3.5		26.9	1.9	42.1	30.2	16.8	0.0		2.4	12.9	0.0	9.9	19.4	15.2		4.8		5.6		28.2		
Oct-99	0.0	0.0	0.0	0.0	0.0		20.6	4.7	2.5	23.0	13.5	6.2		10.3	13.7	0.0	22.2	9.0	10.2		5.7		5.2		4.7		
Nov-99	3.4	5.1	8.2	3.0	2.7		10.5	19.7	16.0	12.8	19.6	9.9		9.6	10.8	32.4	14.9	14.5	15.8		18.0				4.4		
Dec-99	3.6	5.7	5.8	4.1	3.3		7.1	19.2	17.0	15.0	22.6	13.4		10.7		12.4	13.3	11.8	10.2		9.0						
Jan-00	0.0	0.0	0.0	0.0	0.0		0.0	5.5	4.1	3.9	14.8	3.8		3.1	0.0	0.0	1.4						0.0		3.0		
Feb-00	2.4	2.8	0.0	0.0	0.0		16.6	4.0	5.6	10.6	16.1	4.2		6.4	4.0	0.0	9.4	0.0	5.2		5.2		0.8	0.2			
Mar-00	1.0	3.8	1.4	0.6	0.4	0.0	9.8	5.2	16.2	8.4	16.0	4.0		14.6	5.6	0.0	7.4	3.2	4.2		4.6		0.2		3.6		
Apr-00	0.0	0.0	0.0	0.0	0.0	0.0	7.4	0.0	0.0	5.8	2.4	0.0	0.0	6.8	3.6	0.0	1.4	0.0	1.2		2.0		0.2		0.0		
May-00	9.6	8.8	7.8	8.0	8.0	8.2	30.4	14.4	12.2	19.4	18.4	14.4	15.6	25.0	16.6	9.4	15.2	10.2	13.8		14.8		11.6		10.0		
Jun-00	7.8	7.2	6.4	7.2	7.2	7.4	18.6	10.6	13.4	18.8	15.6	10.2	14.0	16.0	13.4	8.8		4.2	12.2		12.8		10.0		10.2		
Jul-00	7.2	6.4	6.6	8.0	9.0	7.4	18.0	10.2	25.0	24.0	16.6	10.0	9.8	55.6	24.2	7.8	19.4	19.2	9.4		11.2		14.8		4.0		
Aug-00	2.2		4.8	4.6	2.4	1.8	11.6	5.6	27.6	22.2	11.8	7.6	5.8	14.0	13.2	4.4	12.0	9.4	7.8		6.0		6.6		7.4		
Sep-00	18.0	15.4	15.2	19.4	17.4	16.8	29.2	16.2	19.4	49.4	28.0	14.8	18.6	14.0	30.0	17.4	21.2	16.4	20.8		15.6		6.4		18.8		
Oct-00	5.6	5.2	6.2	5.6	8.4	4.4	18.6	10.8	62.8	57.4	27.8	14.4	19.8	21.8	15.0	17.6	34.4	21.0	23.6		21.6		21.4		9.6		
Nov-00	4.8	5.6	6.0	5.4	5.2	7.4	12.6	19.6	19.0	19.4	35.8	26.2	23.0	25.2	12.4	3.6	10.2	9.4	8.8		19.8		10.6		8.8		
Dec-00	4.4	4.2	6.8	7.0	6.2	7.2	25.6	21.4	25.6	24.4	35.2	25.6	26.2	26.4	9.4	5.8	12.8	14.6	14.4		13.8				0.0		
Jan-01	1.6	0.0	0.0	0.0	0.0	0.0	2.0	6.0	12.0	5.2	21.6	15.6	9.6	9.0	0.0	0.0	1.0						0.0		2.0		
Feb-01	5.2	2.0	1.8	1.4	0.0	1.0	5.2	4.6	9.2	7.2	22.8	11.4	11.0	16.8	5.4	2.0	7.2	8.0	13.2		8.4		4.8		4.6	6.6	
Mar-01	3.2	0.0	1.0	0.0	0.0	0.0	21.4	4.6	7.0	5.6	14.6	4.2	3.8	9.4	3.8	1.6	8.0	2.6	6.0		3.4		1.2		7.2	3.8	
Apr-01	1.4	2.0	2.4	1.6	2.8	1.6	10.8	6.2	16.2	14.4	13.8	6.4	5.4	13.2	10.4	2.2	8.6	8.0	8.8		5.8		4.4		4.0	7.4	7.4
May-01		8.4	0.0	2.4	0.0	0.0	13.6	3.2	0.0	12.0	10.4	5.4	4.6	20.0	7.4	0.0	5.4	2.2	1.0		1.0		0.0			4.8	1.6
Jun-01	0.0	0.0	0.0	0.0	0.0	0.0	5.7	0.0	0.0	6.4	5.5	0.0	0.0	6.5	10.4	0.0	5.4	3.6	0.0		0.0		0.0		5.6	5.9	7.3
Jul-01	5.4	3.8	6.5	6.5	4.7	2.2	23.8	18.1	5.7	15.6	2.2	0.0	4.6	10.1	12.0	0.0	7.7	7.7	3.6		49.7		2.4			2.6	19.5
Aug-01	11.1	12.9	12.1	13.5	12.6	36.1	40.9	12.8	19.5	36.1	22.7	19.2	15.7	30.4	28.4	11.0	28.1		17.9		13.8		19.1			14.5	20.5
Sep-01	3.0	7.8	9.0	8.0	9.4	7.4	20.4	3.8	14.2	27.6	17.0	18.6	8.0	22.0	18.0	7.4	16.8	18.4	13.6		17.2		19.8		16.0	12.4	19.4
Oct-01	5.0	6.5	5.0	20.6	14.5	11.4	23.5	6.2		8.7	12.3	12.0	14.7	21.6	9.7	13.1	16.5	14.2	7.6	8.1	12.7		7.3	9.9	20.6	23.2	
Nov-01	5.0	4.2	3.2	1.5	5.3	3.5	11.1	5.9	11.1	8.5	15.8	6.3	8.6	9.6	6.5		11.7	11.8	11.4	8.7	9.1		13.1	20.9	5.4	12.4	
Dec-01	4.8	9.1		2.4	6.7	5.7	9.8	11.3		13.3	25.1	8.3	7.1	8.3	6.1	6.0	10.8	14.5	7.1	3.2	5.2		10.2	3.7	4.2	9.7	8.7
Jan-02		5.1		2.3	5.0	5.8	8.9	9.3		11.8	22.3	7.7	7.0	8.5	5.6	2.6	9.1	7.4			5.1		5.3	4.0		7.6	
Feb-02	4.5	3.3	6.1	7.4	2.2	3.6	7.2	12.1	11.4	8.7	16.4	6.3	6.7	11.3	8.3	7.9	8.0	5.6	6.3		6.5		8.3	4.1	6.6	8.4	8.0
Mar-02	3.3	5.2	5.4	3.8	4.7	4.8	9.9	5.9	11.4	8.9	9.0	7.4	7.6		7.1	9.4	6.7	5.1	6.8	6.9	8.3	5.8	9.2			9.9	23.2
Apr-02	5.7	5.8	4.8	2.9	1.8	1.4	10.9	2.6	4.0	5.5	3.1	1.4	1.9	1.4	9.9	5.6	11.5	7.2	7.2		7.5		8.1			8.2	8.1
May-02	5.3	4.8	6.2	4.5	5.5	7.2	12.4	9.1	10.2	9.7		9.1	10.9	13.3	24.0	5.8	14.6	9.6	14.0		9.2		4.2			9.9	9.5
Jun-02	3.9	1.7	5.6	6.0	2.6	8.0	7.1	2.8	5.1	5.1		4.5	5.1	3.6	10.2	2.8	6.6	7.2	6.2		6.6		6.7			10.7	6.6

Table A. 8. Total dissolved phosphorous (mg/L) from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R4dup	R5	R6A	R6B	R7	R8	R9A	R9Adup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R25	R26
Aug-99	0.3	0.3	0.6	0.8	1.1		7.6	3.8	2.1	3.6	1.7	9.0		5.1	4.2	1.7	5.4	5.1	0.6		3.1		2.8				
Sep-99	1.9	2.6	0.0	0.3	0.0		7.5	3.7	2.8	2.4	2.0	7.7		5.1	7.1	0.0	5.1	4.0	3.1		2.8		2.6				
Oct-99	1.2	2.3	2.2	1.7	1.1		6.0	5.7	5.9	5.1	7.4	4.8		4.2	4.0	2.8	4.8	4.8	5.9		2.2		2.8				
Nov-99	2.6	4.3	2.1	1.4	0.8		8.6	2.0	1.7	1.8	1.7	10.0		4.5	1.5	1.2	4.6	4.9	4.8		1.1						
Dec-99	0.3	0.0	0.4	0.0	2.0		15.2	2.1	4.9	0.2	1.1	7.2			1.1	1.4	4.0	5.5	6.0		2.8						
Jan-00	2.8	4.8	3.4	1.9	1.7		7.7	2.8	3.4	4.3	1.4	2.8		2.8	4.8	1.6	4.2						6.8				
Feb-00	0.9	0.1	0.1	0.9	2.6		5.5	2.3	3.4	2.0	1.8	3.5		2.9	2.1	11.2	2.7	5.8	3.8		1.5		10.4				
Mar-00	0.8	0.5	0.0	0.3	1.1	0.6	9.0	2.0	1.4	2.2	0.5	2.5		5.5	2.2	3.7	6.2	4.2	9.2		1.4		2.0		0.8		
Apr-00	0.9	2.9	2.6	0.9	0.9	1.2	8.6	4.3	2.3	1.4	2.6	1.2	0.9	1.1	4.3	0.6	1.7	1.7	5.4		5.2		2.0		0.3		
May-00	0.6	0.9	0.3	0.0	0.3	0.3	12.9	3.1	3.1	1.1	1.4	4.3	4.0	2.5	2.0	1.2	2.0	1.7	3.8		4.9		1.4				
Jun-00	2.0	0.3	0.0	0.1	0.6		9.5	4.3	7.0	1.2	0.6	4.6	4.3	2.9	2.0	1.5	2.0	2.3	6.6		3.4		5.2		1.7		
Jul-00	2.1	2.0	0.9	0.9	0.6	0.6	9.7	2.6	1.4	2.8	4.9	9.9	10.2	15.6	4.3	0.9	3.8	3.8	4.3		0.8		4.8		1.4		
Aug-00	0.9	3.2	2.0	1.2	2.3	2.0	6.7	2.3	2.2	3.2	2.5	14.5	5.2	1.1	3.1	5.4	3.1	4.2	6.3		1.7		2.5		6.7		
Sep-00	0.3	3.4	3.1	2.8	1.7	1.1	21.0	4.3	3.7	3.8	7.7	7.7	7.4	8.0	2.8	2.5	2.8	1.7	3.1		1.4		2.0		2.4		
Oct-00	2.6	4.0	2.9	4.9	4.3	4.0	2.4	6.0	2.5	4.8	2.3	9.0	7.6	2.8	4.3	4.8	4.2	4.2	2.8		1.1		3.5		2.3		
Nov-00	3.4	3.7	3.5	3.4	0.9	1.2	3.8	3.7	4.8	5.4	2.0	4.0	4.9	4.3	3.5	4.0	3.5	3.5	1.5		1.5		1.7				
Dec-00	4.5	4.5	4.0	4.2	2.9	3.4	6.9	2.9	3.1	3.4	0.3	1.7	1.7	2.0	2.8	6.0	2.6	3.7	4.3		12.6				0.0		
Jan-01	2.6	3.7	4.5	4.8	2.8	3.7	4.9	4.3	4.3	3.2	0.6	7.4	6.6	5.7	0.6	5.7	2.4						2.3				
Feb-01	4.8	6.4	7.1	6.5	4.5	3.6	2.2	2.8	2.5	5.1	2.0	4.0	4.0	1.1	0.8	4.5	2.8	2.3	4.3		1.7		6.3		0.0	7.1	
Mar-01	1.8	2.5	2.0	1.2	1.8	1.7	2.0	3.1	0.9	1.1	1.4	3.4	4.1	0.9	0.9	5.5	2.3	2.6	3.7		0.6		2.3		0.9	1.7	6.1
Apr-01	0.6	3.1	0.0	0.9	0.6	0.6	3.5	0.9	10.0	1.1	2.3	3.7	3.2	0.6	2.3	0.9	4.1	3.8	12.5		2.9		2.6		0.9	5.2	
May-01		2.6	0.3	2.9	1.1	1.1	4.9	13.8	2.8	2.0	1.8	3.7	4.6	0.9	14.6	1.2	3.5	3.5	5.1		0.9		2.9			1.1	7.1
Jun-01	1.7	1.4	1.4	0.5	0.9	0.9	5.9	9.2	0.6	2.0	2.3	9.7	10.3	4.5	6.6	1.4	3.4	3.4	5.4		2.3		5.4			1.1	4.5
Jul-01	1.2	4.7	0.0	0.8	1.7	1.7	5.2	10.8	0.3	1.5	5.2	12.5	10.5	0.6	1.5	1.2	1.8	1.8	2.0		1.4		2.0			0.3	1.4
Aug-01	0.3	1.4	0.3	0.9	2.0	1.7	4.3	0.9	0.0	1.2	1.7	1.9	3.9	0.3	4.5	1.1	4.6	3.4	2.0		1.5		3.1			0.6	2.6
Sep-01	0.6	1.2	0.0	1.7	1.2	0.9	4.6	0.3	0.0	0.6	0.9	1.1	0.9	0.9	8.9	0.4	2.9	2.6	2.4		2.0		1.2		0.0	0.0	1.7
Oct-01	0.9	1.7	0.8	1.5	1.7	1.6	1.8			1.1	66.9	4.9	4.6	2.6	1.1	8.2	2.8	2.5	1.1		1.1		2.3			3.4	0.2
Nov-01																											
Dec-01																											
Jan-02																											
Feb-02	1.5	2.3	2.3	1.7	1.2	1.4	0.0	2.0	1.4	2.3	6.0	9.1	10.2	2.3	2.3	1.4	5.6	1.1	1.4		2.6		2.8		0.0	0.3	1.4

Table A. 9. Chlorophyll-a (ug/L) from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R4dup	R5	R6A	R6B	R7	R8	R9A	R9Adup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R25	R26
Aug-99	800	890	850	870	830		500	490	490	500	1200	1220		1210	1200	850	1120	1120	1130		1060		1030				
Sep-99	750	800	785	790	780		480	480	460	450	1060	1080		1085	1055	770	1025	1015	1020		1010		1020				
Oct-99	760	850	810	770	760		425	495	490	480	1120	1150		1180	1180	780	1010	1000	995		995		995				
Nov-99	705	745	775	690	705		439	432	439	435	1185	1120		1125	1190	730	495	495	500		495						
Dec-99	715	755	745	703	655		504	417	420	427	1230	1225			1233	795	503	520	415		420						
Jan-00	762	790	775	728	742		520	486	499	494	1141	1104		1102	1145	719	496						593				
Feb-00	704	715	732	700	690		488	483	466	473	1077	1081		1079	1094	698	495	612	619		490		627				
Mar-00	740	760	770	715	703	702	443	497	501	495	1120	1103		1104	1127	712	511	652	660		655		709		402		
Apr-00	810	857	835	790	818	811	495	503	500	506	1203	1212	1205	1211	1199	785	1047	931	984		972		930		499		
May-00	737	790	795	728	748	749	592	475	500	502	1298	1253	1252	1253	1262	798	1190	1000	923		951		1000				
Jun-00	799	900	897	841	897	899	605	485	502	515	1255	1190	1170	1154	1162	760	1145	1009	1252		1290		1182		749		
Jul-00	830	898	912	846	875	860	670	503	500	502	1453	1399	1400	1400	1435	890	1405	1348	1143		1189		1247		587		
Aug-00	758	805	810	792	712	711	587	480	480	490	1510	1500	1500	1500	1455	804	1370	1221	990		995		875		470		
Sep-00	837	945	920	918	916	914	640	535	530	517	1485	1435	1436	1420	1451	892	1195	890	939		980		998		552		
Oct-00	745	837	840	866	810	800	590	530	495	491	1422	1365	1367	1372	1394	802	1210	980	995		1000		912		412		
Nov-00	740	762	760	750	770	765	548	600	503	510	1397	1369	1370	1390	1380	723	985	908	900		999		885				
Dec-00	721	712	710	699	700	700	479	498	453	491	1345	1315	1310	1301	1300	700	499	503	545		570				500		
Jan-01	702	705	702	695	721	717	448	448	650	427	1285	1306	1305	1330	1290	702	501						585				
Feb-01	645	623	622	627	725	720	319	399	396	385	1383	1376	1370	1360	1402	757	501	500	495		481		567		485	403	
Mar-01	830	805	800	790	780	780	220	455	510	503	1315	1399	1400	1403	1415	807	590	685	695		730		745		420	508	702
Apr-01	775	722	720	691	700	700	298	345	445	435	1207	1233	1233	1227	1298	700	475	495	500		510		600		380	480	
May-01		615	600	575	725	720	422	237	265	345	1470	1407	1400	1402	1375	738	1299	1170	1045		1050		1070			480	1065
Jun-01	670	633	648	687	660	658	501	258	292	412	1435	1380	1347	1385	1398	719	1322	1324	1208		1160		1089			423	1200
Jul-01	662	670	660	682	595	590	528	265	298	330	1376	1278	1290	1330	1342	695	1280	1125	998		1000		1036			355	1009
Aug-01	640	625	605	615	607	605	412	292	285	325	1305	1320	1318	1335	1345	695	1350	1195	1155		1180		1125			325	1175
Sep-01	605	600	598	587	600	599	433	275	245	269	1201	1198	1201	1196	1210	615	1187	1169	1183		1198		1070		400	288	1185
Oct-01	601	611	608	600	622	620	425			266	1201	1298	1296	1293	1236	602	362	394	500		624		500			297	531
Nov-01																											
Dec-01																											
Jan-02																											
Feb-02	717	703	701	692	706	702	429	397	399	421	1334	1327	1324	1342	1400	698	1149	970	999		1022		1020			423	1022

Table A. 10. Specific conductance (uS/cm) from August 1999 to June 2002 (Empty box = Sample not collected).

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$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	R2-50
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Feb-00 12.1 12.1 12.1 12.1 12.1 12.0 11.8 11.6 11.6 11.5 Mar-00 14.8 13.8 13.7 13.5 13.3 12.5 12.3 12.2 12.2 12.1 Apr-00 19.0 18.3 17.1 15.4 15.0 14.7 14.5 12.5 12.5 12.4 May-00 21.3 21.1 19.0 15.2 13.8 13.1 12.8 12.6 12.6 12.8 Jun-00 26.5 25.8 24.1 19.6 15.5 14.8 14.5 12.9 12.8 12.7 Jul-00 29.6 28.4 28.0 21.3 16.9 15.0 14.6 14.1 14.0 14.0 Aug-00 29.8 29.3 29.1 26.7 22.7 22.2 22.4 22.2 22.1 Sep-00 28.5 27.7 27.4 27.1 27.1 <t< td=""><td></td></t<>	
Mar-00 14.8 13.8 13.7 13.5 13.3 12.5 12.3 12.2 12.2 12.1 Apr-00 19.0 18.3 17.1 15.4 15.0 14.7 14.5 12.5 12.5 12.4 May-00 21.3 21.1 19.0 15.2 13.8 13.1 12.8 12.6 12.6 12.8 Jun-00 26.5 25.8 24.1 19.6 15.5 14.8 14.5 12.9 12.8 12.7 Jul-00 29.6 28.4 28.0 21.3 16.9 15.0 14.6 14.1 14.0 14.0 Aug-00 29.8 29.3 29.1 26.7 22.7 22.2 22.4 22.2 22.1 Sep-00 28.5 27.7 27.4 27.1 27.1 15.5 15.5 15.5 5.5 Dec-00 13.5 13.3 13.3 13.3 13.3 13.3 <td< td=""><td></td></td<>	
Apr-00 19.0 18.3 17.1 15.4 15.0 14.7 14.5 12.5 12.5 12.4 May-00 21.3 21.1 19.0 15.2 13.8 13.1 12.8 12.6 12.6 12.8 Jun-00 26.5 25.8 24.1 19.6 15.5 14.8 14.5 12.9 12.8 12.7 Jul-00 29.6 28.4 28.0 21.3 16.9 15.0 14.6 14.1 14.0 14.0 Aug-00 29.8 29.3 29.1 26.7 22.7 22.2 22.4 22.2 22.1 Sep-00 28.5 27.7 27.4 27.1 27	
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Jun-00 26.5 25.8 24.1 19.6 15.5 14.8 14.5 12.9 12.8 12.7 Jul-00 29.6 28.4 28.0 21.3 16.9 15.0 14.6 14.1 14.0 14.0 Aug-00 29.8 29.3 29.1 26.7 22.7 22.2 22.2 22.4 22.2 22.1 Sep-00 28.5 27.7 27.4 27.1 27.1 7 7 7 7.4 27.1 27.1 7 7 7 7 7.4 27.1 27.1 7 7 7 7 7.4 27.1 27.1 7 7 7 7 27.4 27.1 27.1 7 7 7 7 7 27.4 27.1 27.1 7 7 27.4 27.1 27.1 27.1 27.1 27.1 27.1 27.1 27.1 27.1 27.1 27.1 27.1 27.1 27.1 27.1 27.	
Jul-0029.628.428.021.316.915.014.614.114.014.0Aug-0029.829.329.126.722.722.222.222.422.222.1Sep-0028.527.727.427.127.1 </td <td></td>	
Aug-00 29.8 29.3 29.1 26.7 22.7 22.2 22.4 22.2 22.1 Sep-00 28.5 27.7 27.4 27.1 27.1 22.2 22.4 22.2 22.1 Sep-00 28.5 27.7 27.4 27.1 27.1 22.2 22.4 22.2 22.1 22.7 22.2 22.2 22.1 22.1 1 1 1 1 22.1 1 1 1 1 1 1 1 1 1 1 <td></td>	
Sep-00 28.5 27.7 27.4 27.1 <th27.1< th=""> 27.1 27.1 <t< td=""><td></td></t<></th27.1<>	
Oct-00 24.1 23.6 23.6 23.6 15.6 15.6 15.5 15.5 15.5 Nov-00 16.4 16.0 15.9 15.6 15.6 15.6 15.5 15.5 15.5 15.5 Dec-00 13.5 13.3 <td< td=""><td></td></td<>	
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Jan-01 11.2 11.1 11.0 10.9 Mar-01 13.0 12.5 12.4 12.2 12.2 11.5 11.2 11.1 11.0 10.9 Apr-01 19.9 17.0 16.8 13.1 12.8 12.2 11.8 11.7 11.4 11.3 May-01 24.4 22.4 17.0 14.1 12.8 12.2 11.9 12.0 12.0 12.0 12.0 12.0 12.0 12.0 12.0 12.0 <th1< td=""><td></td></th1<>	
Feb-01 10.8 10.9 10.9 11.0 11.0 11.0 10.9 Apr-01 19.9 17.0 16.8 13.1 12.8 12.1 11.6 11.5 11.4 11.3 May-01 24.4 22.4 17.0 14.1 12.9 12.2 11.8 11.7 11.7 11.6 Jun-01 28.0 27.5 24.6 15.3 13.6 12.9 12.5 12.3 12.1 12.0 12.0 12.0 12.0 12.0 12.0 <	
Mar-01 13.0 12.5 12.4 12.2 12.2 11.5 11.2 11.1 11.0 10.9 Apr-01 19.9 17.0 16.8 13.1 12.8 12.1 11.6 11.5 11.4 11.3 May-01 24.4 22.4 17.0 14.1 12.9 12.2 11.8 11.7 11.7 11.6 Jun-01 25.9 25.3 19.1 14.1 12.8 12.2 11.9 12.0	
Apr-01 19.9 17.0 16.8 13.1 12.8 12.1 11.6 11.5 11.4 11.3 May-01 24.4 22.4 17.0 14.1 12.9 12.2 11.8 11.7 11.7 11.6 Jun-01 25.9 25.3 19.1 14.1 12.8 12.2 11.9 12.0 12.0 12.0 Jul-01 28.0 27.5 24.6 15.3 13.6 12.9 12.5 12.3 12.1 12.0 Aug-01 12.0<	10.9
May-01 24.4 22.4 17.0 14.1 12.9 12.2 11.8 11.7 11.7 11.6 Jun-01 25.9 25.3 19.1 14.1 12.8 12.2 11.9 12.0 12.0 12.0 Jul-01 28.0 27.5 24.6 15.3 13.6 12.9 12.5 12.3 12.1 12.0 Aug-01 Colspan="4">Colspan="4">Colspan="4">Colspan="4">Colspan="4">Colspan="4">Colspan="4">Colspan="4">Colspan="4">Colspan="4"Colspan="4">Colspan="4"Colspan="4">Colspan="4"Colspa="4"Colspan="4"Colspa="4"C	11.3
Jun-01 25.9 25.3 19.1 14.1 12.8 12.2 11.9 12.0 12.0 12.0 Jul-01 28.0 27.5 24.6 15.3 13.6 12.9 12.5 12.3 12.1 12.0 Aug-01 -	11.6
Jul-01 28.0 27.5 24.6 15.3 13.6 12.9 12.5 12.3 12.1 12.0 Aug-01	12.0
Aug-01	12.0
Sep-01 27.5 27.1 27.0 26.8 19.5 16.8 15.1 14.0 Oct-01 22.6 22.9 22.7 22.6 22.5 22.4 19.3 15.4 15.0 15.1	
Oct-01 22.6 22.9 22.7 22.6 22.5 22.4 19.3 15.4 15.0 15.1	
Nov-01 20.4 20.9 20.9 20.1	
Dec-01 14.6 14.6 14.4 14.2 13.8 13.8 13.8 13.8	
Jan-02 11.8 11.7 11.6 11.6 11.6 11.6 11.5 11.3 11.3	
Feb-02 11.7 10.7 10.6 8.0 8.1 7.9 7.8	
Mar-02 13.0 12.3 12.2 12.1 12.1 11.8 11.4 18.8 19.9 20.2	
Apr-02 18.7 16.8 14.2 12.9 12.1 11.7 11.4 11.4 11.6 11.6	
May-02 21.8 20.5 19.8 12.9 12.1 11.7 11.5 11.4 11.4 11.4	
Jun-02 26.2 25.0 20.8 13.9 12.4 11.8 11.6 11.6 11.5	

Table A. 11. Temperature (°C) for Lake Pleasant from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R2-0	R2-5	R2-10	R2-15	R2-20	R2-25	R2-30	R2-35	R2-40	R2-45	R2-50
Aug-99	6.80										
Sep-99	9.80	10.50	9.36	9.15	5.60	5.45	5.15	3.45	2.80	2.63	
Oct-99	8.59	9.73	8.29	7.40	7.10	5.18	3.56	2.77	2.30	2.10	
Nov-99	9.03	10.70	9.38	8.94	8.67	8.45	8.16	7.05	3.93	1.26	
Dec-99	9.15	8.58	7.80	7.51	7.15	6.94	6.51	6.41	6.46	5.18	
Jan-00	9.03	9.33	9.06	8.89	9.03	9.25	8.83	8.78	8.83	8.45	
Feb-00	11.50	10.03	8.53	8.49	8.05	7.86	7.44	6.71	6.36		
Mar-00	10.58	10.22	10.09	9.17	8.76	8.52	8.12	7.87	7.67	7.38	
Apr-00	11.11	10.74	9.78	9.03	7.62	7.08	6.95	6.65	6.56	6.43	
May-00	9.89	9.50	9.94	9.27	8.48	7.67	7.12	7.02	3.47	3.35	
Jun-00	7.16	7.20	7.99	8.40	7.77	6.46	5.21	4.66	4.65	1.65	
Jul-00	7.02	6.92	6.22	7.04	6.40	5.35	4.88	2.39	2.47	2.45	
Aug-00	7.56	6.85	6.11	3.35	3.84	2.46	2.62	2.47	2.42	2.45	
Sep-00	7.45	6.20	5.91	3.04	3.04						
Oct-00	6.72	5.96	5.80	5.60	5.78						
Nov-00	7.98	7.19	7.01	7.43	7.46	7.41	7.32	7.06	7.07		
Dec-00	9.05	7.84	7.63	7.49	7.08	4.89	4.94	4.61	4.34	4.17	
Jan-01	9.73	9.35	9.33	9.29	9.06	8.96	8.90	8.49	7.73	8.64	
Feb-01	10.40	9.45	9.34	8.92	9.27	8.63	8.55	8.34	8.35		
Mar-01	10.51	10.14	9.59	9.58	9.70	9.31	8.90	8.80	8.43	8.41	8.31
Apr-01	9.93	10.22	9.65	8.68	8.47	8.33	7.81	7.76	7.48	7.32	7.39
May-01	10.07	10.15	9.80	8.72	8.60	8.60	8.38	8.06	7.80	7.45	7.30
Jun-01	8.30	8.52	7.35	5.77	5.97	5.93	5.82	2.71	2.70	2.72	2.85
Jul-01	6.26	6.09	5.44	3.03	3.65	3.76	3.51	3.30	3.28	3.29	3.29
Aug-01											
Sep-01	6.23	6.24	6.05	5.84	0.31	0.31	0.29	0.29			
Oct-01		6.26	6.61	6.27	6.53	6.39	1.30	1.35	1.22	1.30	
Nov-01	8.33	8.24	7.85	7.81							
Dec-01	7.52	7.43	7.43	7.40	7.38	7.69	7.65				
Jan-02	5.20	4.80	4.60	4.50	4.40	4.30	4.20	4.20	4.20		
Feb-02	10.49	10.52	10.54								
Mar-02	9.70	9.80	9.70	9.60	9.40	9.30	9.10	4.80	4.80	4.70	
Apr-02	10.60	10.30	10.55	10.10	9.53	9.20	8.95	8.60	8.45	8.00	
May-02	7.66	7.45	7.35	7.50	7.20	6.80	6.74	6.77	6.71	6.72	
Jun-02	7.80	7.00	7.10	6.70	5.80	5.38	5.20	5.00	4.85		

Table A. 12. Dissolved oxygen (mg/L) for Lake Pleasant from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R2-0	R2-5	R2-10	R2-15	R2-20	R2-25	R2-30
Aug-99							
Sep-99							
Oct-99							
Nov-99	8.20	8.38	8.38	8.39	8.35	8.32	8.24
Dec-99	8.18	8.27	8.26	8.25	8.25	8.23	8.22
Jan-00	8.22	8.31	8.33	8.33	8.31	8.30	8.26
Feb-00	8.00	8.11	8.10	8.07	8.03	8.00	8.00
Mar-00	8.23	8.23	8.11	8.01	7.89	7.77	7.66
Apr-00	8.32	8.14	7.74	7.60	7.04	4.44	3.69
May-00	8.38	8.39	8.29	8.02	7.02	6.37	5.88
Jun-00	8.08	7.97	7.86	7.61	7.01	6.65	3.88
Jul-00	8.78	7.87	7.63	7.05	6.20	6.23	5.71
Aug-00	8.20	8.70	7.83	6.88	6.35	5.77	2.38
Sep-00	8.37	8.24	8.06	7.68	7.45		
Oct-00	7.90	7.86	7.79	7.71			
Nov-00	8.14	8.05	7.98	7.93	7.94	7.73	7.63
Dec-00	8.20	8.02	7.87	7.74	7.62	7.36	6.74
Jan-01							
Feb-01	8.48	8.49	8.45	8.39	8.28	8.18	8.07
Mar-01	8.81	8.66	8.55	8.34	8.04	7.73	7.38
Apr-01	8.42	8.35	8.24	7.81	7.56	7.29	7.02
May-01	8.41	8.37	8.02	7.27	6.90	6.58	6.30
Jun-01	8.36	8.43	8.26	7.90	7.77	7.69	7.60
Jul-01	8.24	8.27	8.18	7.76	7.18	7.00	6.84
Aug-01							
Sep-01	7.60	6.54	4.14	1.86	6.86	4.70	2.70
Oct-01	8.00	8.04	7.84	7.27	6.27	5.44	
Nov-01	8.19	8.19	8.14	7.97			
Dec-01	7.30	7.74	7.84	7.90	7.91	7.87	7.83
Jan-02	8.60	8.60	8.58	8.50	8.43	8.32	8.23
Feb-02	8.22	8.19	8.70	8.12	8.10	8.05	8.04
Mar-02	8.07	8.33	8.60	8.53	8.41	8.25	
Apr-02	8.41	8.63	8.60	8.38	8.23	8.02	7.85
May-02	8.09	8.23	8.32	7.92	7.64	7.39	7.23
Jun-02	8.62	8.61	8.59	8.15	7.98	7.77	7.59

Table A. 13. pH for Lake Pleasant from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R6-0	R6-5	R6-10	R6-15	R6-20	R6-25	R6-30	R6-35	R6-40	R6-45
Aug-99	28.7	28.1	27.6	21.5	18.5	16.8	15.9	15.8	15.9	16.0
Sep-99	27.5	27.1	26.8	26.5	22.0	19.5	17.9	17.0	17.4	17.5
Oct-99	23.0	23.1	23.1	23.0	23.0	22.9	22.8	21.3	21.4	21.4
Nov-99	18.0	18.0	18.0	18.0	17.9	17.9	17.9	17.9	17.9	17.9
Dec-99	12.7	12.8	12.8	12.8	12.8	12.7	12.6	12.5	12.5	12.5
Jan-00	9.9	9.9	9.9	9.9	9.6	9.2	9.0	8.8	8.8	8.8
Feb-00	12.4	12.3	11.2	10.9	10.6	10.3	10.0	10.1	10.1	10.1
Mar-00	14.8	14.8	13.5	12.7	12.5	11.9	11.8	11.1	11.1	11.1
Apr-00	19.9	19.6	16.9	14.9	13.5	13.3	13.3	13.3	13.3	13.3
May-00	22.3	22.0	18.2	16.1	15.4	15.3	15.4	15.3	15.2	15.2
Jun-00	26.3	25.5	21.1	18.0	15.7	14.6	14.6	14.6	14.6	14.6
Jul-00	28.2	28.1	23.5	18.5	16.2	15.0	14.5	14.4	14.4	14.4
Aug-00	29.0	29.2	27.3	21.1	19.0	18.2	15.3	15.5	15.6	15.7
Sep-00	26.7	26.7	26.5	26.0	22.8	19.0	17.9	17.7		
Oct-00	22.3	22.3	22.3	22.3	22.3	22.2	19.7	17.9	18.1	
Nov-00	17.1	17.1	17.1	17.1	17.1	17.1	17.1	17.1	17.1	
Dec-00	13.2	13.3	13.3	13.3	12.9	12.6	12.5	12.5		
Jan-01	10.3	10.2	10.2		10.2	10.2	10.2	10.2		
Feb-01	10.0	10.0	10.0	10.0	10.0	9.9	9.9			
Mar-01	13.3	13.2	12.6	11.9	11.0	10.6	10.4	10.4		
Apr-01	18.7	18.6	16.8	14.8	13.1	12.2	11.8	11.2	11.2	11.2
May-01	23.6	23.4	18.7	16.5	15.2	13.7	13.7			
Jun-01	26.6	25.3	20.0	16.8	15.2	14.2	13.6	13.0	12.3	
Jul-01	27.7	27.6	21.5	17.7	15.8	14.9	14.2	13.3	12.9	12.7
Aug-01										
Sep-01	27.2	27.1	27.0	21.6	17.5	16.4	15.6	14.8	14.3	13.8
Oct-01	22.6									
Nov-01	20.0	19.9	19.9	19.9	19.8	19.8	19.7	19.6	19.6	
Dec-01	14.3	14.3	14.3	14.3	14.2	14.1	13.7			
Jan-02	10.7	10.6	10.6	10.5	10.3	10.0	10.0			
Feb-02	9.6	9.5	9.5	4.9	4.7	4.6	4.4			
Mar-02	12.5	12.4	12.4	11.0	10.5	10.2	10.1	10.1	12.8	
Apr-02	19.4	18.6	14.0	12.0	11.0	10.8	10.6	10.6		
May-02	22.4	21.4	19.0	12.9	11.9	11.3	11.0	11.1	11.0	11.0
Jun-02	26.2	25.5	20.8	15.2	13.1	12.1	11.4	11.3	16.2	

Table A. 14. Temperature ($^{\circ}$ C) for Bartlett Lake from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R6-0	R6-5	R6-10	R6-15	R6-20	R6-25	R6-30	R6-35	R6-40	R6-45
Aug-99	7.80	8.82	6.20	0.30			0.27			0.12
Sep-99	6.51	5.58	5.24	3.30	0.04	0.10	0.12	0.08	0.14	0.14
Oct-99	6.99	5.95	5.57	5.54	5.49	4.54	3.43	0.68	0.59	0.61
Nov-99	7.57	7.53	7.53	7.35	7.18	7.06	7.02	0.57	0.39	0.28
Dec-99	8.57	8.30	7.95	7.12	6.78	6.36	1.15	1.04	0.96	0.89
Jan-00	10.41	9.14	8.51	8.17	8.01	7.72	7.55	7.36	4.40	4.01
Feb-00	11.27	10.36	8.61	8.04	7.51	6.71	4.93	4.88	4.64	4.52
Mar-00	11.48	10.03	9.38	7.89	7.00	5.04	4.17	0.42	0.37	0.35
Apr-00	9.92	9.60	9.06	6.37	5.37	0.75	0.49	0.41	0.41	0.39
May-00	9.66	8.25	4.31	4.01	3.22	2.31	2.23	2.50	2.57	2.36
Jun-00	15.25	12.85	4.34	2.96	4.32	1.77	1.75	1.65	1.59	1.55
Jul-00	7.50	6.61	0.85	0.80	0.70	0.54	0.40	0.27	0.20	0.20
Aug-00	7.72	5.85	1.23	0.90	0.89	0.76	0.63	0.42	0.34	0.30
Sep-00	7.99	7.01	4.99	1.68	0.56	0.56	0.50	0.40		
Oct-00	5.70	5.52	5.52	5.62	4.93	1.31	1.34	1.23		
Nov-00	7.73	6.53	5.89	5.66	5.80	5.47	5.13	5.20	4.45	
Dec-00	8.14	6.62	6.76	7.03	6.74	6.05	4.96	5.27		
Jan-01	9.30	8.50	8.56	8.25	8.28	8.15	8.17	6.95		
Feb-01	10.25	9.24	8.63	9.02	8.74	6.81	6.42			
Mar-01	11.72	11.97	11.92	11.28	10.26	9.85	9.91	9.84		
Apr-01	9.30	9.40	8.30	7.30	8.70	9.00	8.70	8.01	6.05	6.30
May-01	9.79	9.05	6.10	6.74	8.27	8.75				
Jun-01	9.00	7.03	3.20	3.21	5.06	5.53	5.45	6.60	5.45	
Jul-01	6.05	5.70	2.37	2.79	2.93	3.30	3.35	3.60	3.17	2.05
Aug-01										
Sep-01	6.76	6.65	6.45	1.46	1.60	1.37	1.31	1.24	1.20	1.17
Oct-01										
Nov-01	8.23	8.18	8.90	8.73	8.40	8.34	8.36	8.22		
Dec-01	8.95	8.76	8.64	8.48	8.37	8.38	8.22			
Jan-02	11.40	11.60	12.00	12.10	12.40	11.90	12.00			
Feb-02	9.90	9.80	9.80							
Mar-02	10.15	9.75	9.95	9.31	8.95	8.43	8.60	11.26	2.35	
Apr-02	8.36	8.48	8.30	7.15	7.60	7.25	7.05	6.30		
May-02	14.85	14.80	13.10	14.80	14.40	14.30	13.97	10.80	8.80	8.45
Jun-02	7.60	3.20	2.50	2.17	2.25	2.40	2.80	2.20		

Table A. 15. Dissolved oxygen (mg/L) for Bartlett Lake from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R6-0	R6-5	R6-10	R6-15	R6-20	R6-25	R6-30	R6-35
Aug-99								
Sep-99								
Oct-99		8.52	8.52	8.52		8.45	8.45	8.45
Nov-99	8.5	8.49	8.46	8.45	8.42	8.39	8.36	
Dec-99	8.31	8.42	8.42	8.42	8.39	8.36	7.57	
Jan-00	8.3	8.42	8.42	8.38	8.33	8.28	8.28	
Feb-00	8.5	8.56	8.52	8.41	8.35	8.22	7.68	
Mar-00	8.71	8.62	8.42	8.23	8.03	7.74	7.5	
Apr-00	8.45	8.2	7.86	7.5	7.19	6.5		
May-00	8.4	8.39	8.18	8.07	8.01	7.97	7.94	
Jun-00	8.41	8.32	7.71	7.27	7.02	6.96	6.8	
Jul-00	8.49	8.22	7.22	6.69	6.26	5.96	5.56	
Aug-00	8.56	8.29	7.36	6.73	6.27	5.81		
Sep-00	8.45	8.17	7.7	7.02	7.26	7.2	7.11	
Oct-00	8.4	8.02	7.98	7.88	7.89	7.83	7.66	
Nov-00	8.61	8.26	8.03	8.05	8.06	7.91	7.78	
Dec-00	8.33	8.03	7.79	7.54	7.21	6.89	4.6	
Jan-01								
Feb-01	8.68	8.69	8.61	8.53	8.42	8.16	8.24	
Mar-01	8.82	8.65	8.39	8.05	7.64	7.16	6.4	
Apr-01	8.42	8.13	7.8	7.55	7.45	7.1	6.75	
May-01	8.77	8.62	8.17	7.73	7.51	7.33	7.24	
Jun-01	8.82	8.89	8.1	7.9	7.84	7.78	7.7	
Jul-01	8.96	8.79	8.33	8.01	7.87	7.7	7.61	
Aug-01								
Sep-01	8.4	8.35	8.22	7	5.81	4	1.9	
Oct-01	8							
Nov-01	8.31	8.03	7.92	7.5	6.75	5.4	6.21	
Dec-01	7.6	7.48	7.7	7.2	6.7	6	5.2	
Jan-02	8.47	7.78	6.87	5.01	3.71	2.32	1	
Feb-02	8.38	8.42	8.47	8.39	8.34	8.29	8.23	
Mar-02	8.5	8.62	8.58	8.43	8.29	8.09	7.89	
Apr-02	7.97	8.26	8.27	8.05	7.5	6.47	5.05	
May-02	8.44	8.46	8.4	8.15	8	7.8	7.63	
Jun-02	8.69	8.69	8.55	8.2	7.94	7.81	7.62	

Table A. 16. pH for Bartlett Lake from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R9-0	R9-5	R9-10	R9-15	R9-20	R9-25	R9-30	R9-35	R9-40	R9-45
Aug-99	30.0	27.4	24.5	23.9	23.7	23.6	23.6	23.6	23.6	23.6
Sep-99	27.5	26.9	25.2	24.6	24.2		23.7		23.5	
Oct-99	25.4	24.0	23.9	23.6	23.2	23.1	22.9	22.9	22.9	22.9
Nov-99	20.4	20.1	20.0	20.0	19.9	19.9	19.9	19.9	19.9	19.9
Dec-99	15.5	15.5	15.5	15.5	15.5	15.5	15.5			
Jan-00	12.8	12.5	12.4	12.4	12.4	12.4	12.3	12.2	12.2	12.2
Feb-00	14.5	13.6	13.1	12.9	12.8	12.8	12.8	12.5	12.5	12.5
Mar-00	16.7	16.1	13.9	13.4	13.1	13.0	12.9	12.9	13.0	12.9
Apr-00	20.6	20.1	15.4	13.7	13.4	13.3	13.2	13.2	13.2	13.2
May-00	23.8	22.8	18.9	18.2	17.7	17.0	16.1	15.6	15.8	15.8
Jun-00	26.9	25.3	20.9	20.6	20.0	20.0	19.3	18.9	18.9	18.9
Jul-00	29.1	25.5	23.8	23.0	22.6	22.2	21.7	21.6	21.7	21.7
Aug-00	30.0	27.1	24.9	24.4	24.2	24.0	23.5	23.4	23.4	23.4
Sep-00	28.1	27.3	25.9	25.1	24.7	24.5	23.9	23.8		
Oct-00	23.9	24.0	24.1	24.3	24.4	24.6	24.8			
Nov-00	18.6	18.7	18.7	18.7	18.7	18.7	18.6	18.6		
Dec-00	15.4	15.4	15.4	15.4	15.4	15.4	15.4	15.4		
Jan-01	13.4	12.8	12.7	12.7	12.6	12.6	12.6			
Feb-01	13.0	12.5	12.3	12.2	12.1	12.1	12.1			
Mar-01	14.8	14.1	13.5	12.6	12.5	12.6	12.5			
Apr-01	20.8	18.6	15.3	13.7	13.1	12.9	12.8			
May-01	25.0	22.4	19.7	18.8	18.3	17.2	15.6			
Jun-01	25.8	23.3	21.7	20.7	20.5	20.2	19.7	19.7	19.8	
Jul-01	27.5	27.1	22.7	22.0	21.7	21.5	21.3			
Aug-01	29.6	26.4	23.7	23.2	23.0	22.8	22.5	22.3		
Sep-01	27.9	27.5	25.5	24.7	24.2	24.2	24.1			
Oct-01	23.0	22.4	22.4	22.3	22.3	22.1	22.0	22.0		
Nov-01	20.7	20.6	20.6	20.6	20.6	20.6	20.6	20.6	20.6	20.6
Dec-01	15.5	15.9	16.0	16.0	16.0	16.0	16.0			
Jan-02	12.8	12.8	12.8	12.8	12.8	12.8	12.8			
Feb-02	12.2	12.0	12.0	9.3	9.3	9.5	9.6			
Mar-02										
Apr-02	20.8	19.5	15.2	13.5	13.3	12.9	12.8	13.0		
May-02	22.6	17.9	17.2							
Jun-02	21.5	19.2	18.7	18.4	18.2	17.9	17.7	17.8	17.9	

Table A. 17. Temperature (°C) for Saguaro Lake from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R9-0	R9-5	R9-10	R9-15	R9-20	R9-25	R9-30	R9-35	R9-40	R9-45
Aug-99	7.58	4.40	0.60	0.70	1.20	1.50	1.70	1.60	1.70	1.40
Sep-99	7.89	7.22	0.34	0.32	1.86		2.37		0.44	
Oct-99	6.79	6.59	4.92	2.70	4.20	4.45	3.89	3.37	3.22	3.18
Nov-99	8.48	7.38	7.31	6.88	6.55	6.38	5.68	0.70	0.53	0.48
Dec-99	6.53	5.87	5.14	5.43	5.33	5.20	5.17	4.00	4.00	4.20
Jan-00	10.32	9.93	9.48	9.27	8.85	8.43	8.27	7.56	7.40	7.18
Feb-00	10.16	8.90	7.35	7.10	7.04	5.88	5.58	4.00	3.73	3.71
Mar-00	10.35	9.58	7.30	5.88	5.20	4.73	4.52	3.80	3.57	3.52
Apr-00	9.40	8.02	6.82	4.75	4.29	3.65	2.99	3.21	2.61	2.57
May-00	8.99	8.47	5.90	5.04	4.92	4.10	3.05	0.68	0.52	0.43
Jun-00	7.82	7.86	4.25	3.95	3.54	4.55	3.31	0.40	0.36	0.33
Jul-00	8.35	4.24	0.91	0.87	0.81	0.70	0.32	0.30	0.29	0.35
Aug-00	9.18	3.59	0.69	0.58	1.05	1.42	0.39	0.48	0.36	0.37
Sep-00	6.82	5.97	0.43	0.37	0.32	0.28	0.28	0.27		
Oct-00	5.85	5.31	4.69	4.45	3.96	3.51	3.49	2.28		
Nov-00	5.77	5.05	4.70	4.98	4.94	4.96	4.65	1.38		
Dec-00	6.84	6.18	5.68	5.67	5.70	5.72	5.63	4.92		
Jan-01	7.96	7.23	6.90	6.74	7.02	6.77	6.72			
Feb-01	10.01	9.18	8.45	7.62	7.05	7.03	7.07			
Mar-01	10.62	10.23	8.60	6.69	6.71	6.67	6.13			
Apr-01	8.95	9.80	5.95	6.20	6.40	6.10	5.74			
May-01	8.62	9.31	6.01	5.72	5.75	5.22	3.56			
Jun-01	8.50	7.20	2.86	4.13	4.70	4.84	3.00	2.30	2.14	
Jul-01	5.04		1.29	1.43	2.06	1.87	1.22			
Aug-01	7.20	3.70	2.20	2.00	2.00	2.40	1.90	1.70		
Sep-01										
Oct-01	4.30	4.36	4.10	3.96	2.81	2.45	1.65	0.52		
Nov-01	7.42	7.29	7.29	7.33	7.33	7.37	7.36	6.70	6.60	6.55
Dec-01	9.20	9.47	9.62	9.76	9.75	9.77	9.69			
Jan-02	0.27	0.27	0.27	0.27	0.27	0.27	0.27			
Feb-02	9.87	9.40	9.18							
Mar-02										
Apr-02	11.16	9.89	3.74	2.23	2.93	2.40	1.40	1.30		
May-02										
Jun-02										

Table A. 18. Dissolved oxygen (mg/L) for Saguaro Lake from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R9-0	R9-5	R9-10	R9-15	R9-20	R9-25	R9-30	R9-35	R9-40	R9-45
Aug-99										
Sep-99										
Oct-99		7.83	7.83	7.83			7.72	7.72	7.72	
Nov-99	7.66	7.83	7.85	7.84	7.81	7.77	7.74			
Dec-99	7.90	7.96	7.93	7.91	7.90	7.90	7.80			
Jan-00	7.69	7.91	7.99	8.30	8.80	7.96	7.95			
Feb-00	8.15	8.30	8.21	8.05	7.97	7.91	7.81			
Mar-00	8.33	8.34	8.14	7.84	7.62	7.46	7.34			6.67
Apr-00	7.60	8.00	7.86	7.50	7.29	7.10	5.15			
May-00	8.44	8.34	7.90	7.74	7.63	7.56	7.49			
Jun-00	8.67	8.43	7.96	7.57	7.30	7.02	6.65			
Jul-00	8.55	7.92	7.64	7.39	7.22	7.05	6.88			
Aug-00	8.44	7.25	6.91	6.62	6.39	3.74				
Sep-00	8.26	8.22	7.30	7.07	6.89	6.72	6.52			
Oct-00	7.70	7.59	7.41	7.25	7.08	6.91	6.80			
Nov-00	7.89	7.78	7.64	7.52	7.41	7.30	7.05			
Dec-00	7.70	7.60	7.49	7.40	7.30	7.17	7.00			
Jan-01										
Feb-01	8.39	8.32	8.04	7.73	7.45	7.20	6.96			
Mar-01	8.98	8.89	8.51	8.02	7.74	7.44	7.14			
Apr-01	8.52	8.93	7.65	6.95	6.74	6.53	6.41			
May-01	8.34	8.27	7.74	7.37	7.16	6.92	6.52			
Jun-01	8.62	8.22	7.79	7.63	7.55	7.56	7.47			
Jul-01	8.34	7.70	7.34	7.04	6.81	6.63	5.98			
Aug-01	8.80	8.33	7.97	7.55	7.23	6.75	5.20			
Sep-01	8.03	7.28	6.60	5.92	5.43	5.60	5.90			
Oct-01	7.86	7.82	7.75	7.67	7.51	7.26	7.28	7.05		
Nov-01	7.51	7.59	7.64	7.65	7.63	7.58	7.53			
Dec-01	8.12	8.18	8.18	8.16	8.11	8.04	7.97			
Jan-02										
Feb-02	8.20	8.13	8.08	7.92	7.84	7.73	7.62			
Mar-02										
Apr-02	8.93	9.13	8.32	7.96	7.58	7.20	6.89			
May-02	8.94	8.22	7.82	7.52	7.36	7.22				
Jun-02										

Table A. 19. pH for Saguaro Lake from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R3	R4	R5	R7	R8	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R21	R22	R25	R26
Aug-99	31.1	15.9	18.1										30.0								
Sep-99		18.0	17.0		27.1	24.7		26.6			27.0	28.0		28.0							
Oct-99	24.1	23.5	23.6	21.5				22.5	21.0	21.2	25.0		24.3		21.8						
Nov-99			18.6			20.3	18.3	19.0	17.3	17.2	18.7		19.0								
Dec-99	12.5	12.8	10.1	8.5	13.0	14.6	9.1	1.7	10.2	10.3	4.2		9.6								
Jan-00	11.0	11.0	12.0	8.0	11.0	12.5	9.3	9.5	9.3						10.2	12.4					
Feb-00	12.2	15.1	14.3	14.0	12.5	14.6	14.5	13.7	13.1	13.7	14.4		15.2		13.9						
Mar-00	17.5	17.5	17.3	16.4	12.6	13.3	18.0	16.8	17.9	17.5	19.1		20.3		17.1						
Apr-00	21.8	30.1	21.2	20.7	14.9	18.7	16.0	21.1	17.9	19.4	18.3		21.8		18.6						
May-00	23.0	23.8	22.0	21.5	15.6	17.8	18.0	22.2	18.5	20.7	20.0	21.5	21.8	21.6	18.9	20.0					
Jun-00	27.3	14.0	17.8	25.6	18.1	19.2	21.6	17.0	20.0	19.3	24.0		24.9		19.4						
Jul-00	29.3	14.6	15.4	28.6	18.0	25.9	23.6	15.8	22.5	22.8	22.9		23.6		21.3						
Aug-00	31.2	17.9	19.7	30.0	19.2	28.7	24.8	20.0	25.2	23.0	25.6		26.6		22.3						
Sep-00	28.2	25.8	25.3	26.4	18.0	27.9	23.8	25.3	26.8	25.4	24.9		27.7		25.2						
Oct-00	21.5	23.9	21.7	18.7	18.4	23.1	21.9	21.8	20.7	21.3	22.0		21.9		22.0			22.3	21.8		
Nov-00	15.0	15.3	15.0	11.3	16.6	18.2	16.2	13.6	14.4	14.4	10.7	14.2	14.1		15.6						
Dec-00	13.1	13.0	12.2	11.0	13.0	14.7	10.8	12.3	11.2	11.4	11.5	11.4	11.1	11.9				11.3			
Jan-01	11.0	11.0	10.1	9.9	10.2	12.4	12.8	13.1	16.3	10.0											
Feb-01	8.4	11.0	11.4	10.6	10.4	11.9	12.7	11.3	10.6		11.0		12.2		11.9	10.9		12.0	12.2	12.4	
Mar-01	14.9	14.9	15.6	11.9	12.1	15.3	16.1	14.2	16.1	15.3	16.8		17.9	17.8	15.3	15.5			17.9	19.3	24.7
Apr-01	20.0	22.2	19.7	17.0	13.5	18.3	22.4	19.9	16.6	16.7	19.7	24.4	20.9		19.0	22.0		20.0	19.8		21.3
May-01		23.6	23.5	24.2	14.7	23.1	18.5	23.0	17.6	17.0	21.6		23.9		18.9			22.7		29.6	
Jun-01	26.2	13.4	21.1	24.8	15.8	20.8	21.8	20.8	20.4	20.6	22.4	25.5	22.7		20.1	23.0		22.2	22.0	30.4	23.3
Jul-01	29.3	13.2	17.3	26.8	16.7		23.3	18.7	22.8	21.3	25.3		27.2		22.1			26.0	24.8	34.0	26.4
Aug-01	30.8	14.4	18.6	28.0	16.9	22.5	24.4	18.5	23.7	22.4	26.4	25.8	27.8	21.0	23.6	25.1	26.8	27.1		34.2	28.3
Sep-01	28.0	15.2	17.8	24.8	16.3	22.4	24.6	19.2	23.7	24.1	27.7	28.3	26.7		22.6	26.0		26.4	26.1	30.3	26.8
Oct-01	18.2	21.0	18.8	18.9	16.2	24.0	20.4	18.8	17.3	17.5	22.0		20.0		18.2			20.9	19.7	20.4	
Nov-01																					
Dec-01	12.6	12.6	12.8	8.4	13.9		9.4	8.6	11.5	11.9	11.3		13.3		10.9			11.1	11.7	13.8	
Jan-02	11.1	11.2	10.9	9.1	9.4	12.2	12.3	11.1	10.0	10.4					12.8					13.8	
Feb-02	11.2	11.4	11.1	9.5	9.8		10.9	10.6	11.9	11.6	12.8		13.1		12.5	15.0		13.9	12.5	15.8	13.8
Mar-02	14.5	13.8	14.1	13.8	10.6		13.9	13.7		14.2	15.5		16.5	17.5	21.0			16.4	14.5	22.5	16.7
Apr-02	20.5	19.7	20.1	19.6	13.0	16.8	14.0	20.1	16.4	17.3	19.4	23.3	22.1		18.5	22.0		20.6	19.1	25.8	
May-02		22.0	23.1	23.5	14.0	23.4	16.9	22.5	17.4	18.7	22.0	24.0	22.2	24.2	20.3	23.0		21.6	21.6	26.1	24.2
Jun-02		17.5	22.0	26.7	27.8		19.6	22.5	18.7	19.0	23.6		24.3		19.8			24.0	22.6	28.0	24.3
																				_	and the local division of the local division

Table A. 20. Temperature (oC) for streams and canals from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R4	R8	R10	R11	R12	R13	R14	R16	R18	R19	R21	R22	R25	R26
Aug-99															
Sep-99															
Oct-99	7.90	7.68				7.70	6.80	10.40	24.30	7.20					
Nov-99		10.02	9.20		11.52	9.84	9.94	10.38	10.60						
Dec-99		10.21	7.47	9.27	10.80	9.30	8.95	10.43	11.59						
Jan-00			10.72	11.86	10.62	10.23				10.94	11.50				
Feb-00	10.03	11.21	9.37	8.05	10.50	9.00	9.23	8.93	10.15	8.75					
Mar-00		10.98	7.80	8.06	10.13	7.86	9.32	9.52	9.38	9.44					
Apr-00			9.27	8.22	7.60	8.13	8.43	11.31	9.61	9.65					
May-00			7.23	8.82	9.38	8.98	9.12	11.62	10.48	10.03					
Jun-00			6.42	7.31	10.37	8.20	9.42	9.25	8.20	9.02					
Jul-00		7.12	7.01	6.08	10.37	6.63	6.59	10.42	8.41	9.05					
Aug-00			8.24	7.20	11.65	7.22	9.72	8.12	7.90	7.74					
Sep-00		7.73	5.67	7.49	8.43	7.53	9.26	8.00	7.41	7.15					
Oct-00		8.10	5.51	6.92	8.80	7.30	8.33	7.22	7.67	8.01		7.62	8.75		
Nov-00		10.12	6.16	8.51	8.58	8.54	8.96	13.60	10.02	9.14			12.80		
Dec-00		9.81	7.68	8.01	9.71	8.97	8.76	10.12	10.30						
Jan-01		9.98	8.07	9.64	7.93	9.38	8.57								
Feb-01		10.12	10.56	10.05	13.45	12.37		10.63	10.27	9.47				10.83	
Mar-01		9.46	8.78	8.08	10.58	8.60	9.48	8.89	8.19	8.83	7.85		8.07	8.35	5.69
Apr-01		9.50		6.31	10.20	9.37	9.77	8.61	8.10	7.87		6.50	9.03		
May-01			9.65	9.77	8.89	8.81	8.69	8.55	8.90	9.02				9.01	
Jun-01		6.57	6.88		9.50	8.12	8.02	7.10	7.15	6.60		7.28	6.93	8.40	7.50
Jul-01		8.00		4.45	5.22	4.34	5.15	8.86	7.92	8.75		8.25	8.72		8.65
Aug-01		5.76	5.39	9.05	9.73	6.96	8.35	7.56	7.50	7.61		7.45		10.50	
Sep-01		4.45			10.89			6.40	6.50	6.31					
Oct-01		6.30	8.20	6.06	8.62	7.20	7.43	8.75	9.50	8.20		7.70	8.49	8.51	
Nov-01															
Dec-01				9.67	10.23	9.84	9.88			1.39					
Jan-02		11.70	0.39	0.27	0.28	0.28	0.27			10.40				0.20	
Feb-02		11.14		9.78	10.89	9.60	10.52	10.31	10.23	9.73		9.92	10.86	11.10	10.25
Mar-02		9.61		8.84	10.48		11.71	9.02	7.85	7.31		8.11	9.37	9.80	8.36
Apr-02		9.87	9.65	7.79	9.30	7.21	8.74	10.22	8.57	9.83		9.58	8.99	10.59	
May-02		8.60		6.92	9.20	7.77	9.00	8.50	8.48	8.64		8.90	8.71	9.95	
Jun-02		8.30		8.17		8.41	9.64	10.75	10.04	9.95		9.98	10.80		7.30

Table A. 21. Dissolved oxygen (mg/L) for streams and canals from August 1999 to June 2002 (Empty box = Sample not collected).

									B (0	B 10			D / 0			540	Dat			
Month	R1	R3	R4	R5	R/	R8	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R21	R22	R25	R26
Aug-99																				
Sep-99																				
Oct-99	8.34	8.38	8.35	8.01				8.95	8.06	8.09	8.62		8.41		8.29					
Nov-99			8.38			8.10	7.40	8.30	8.40	8.50	8.74		8.74							
Dec-99			8.30			7.70	7.98	8.60	8.60	8.55	8.67	7.76	8.67	7.80						
Jan-00			7.80			8.02	8.09	8.29	8.35						8.30					
Feb-00			8.15			7.79	7.98	8.24		8.39	8.07		8.18		8.05					
Mar-00	8.62	8.56	8.66	8.67	8.66	8.43	8.07	8.49	8.39	8.46	8.57		8.69		8.45					
Apr-00	8.34	8.26	8.38	8.24	8.33	7.91	7.72	8.37	7.97	8.19	8.34		8.22		8.26					
May-00	8.46	8.43		8.26	8.41	7.76	8.12	8.73	8.21	8.52	8.52	7.64	8.40	7.64	8.32	7.83				
Jun-00	8.27	7.76	8.05	8.11	7.76	7.40	7.91	8.16	7.66	7.96	8.42		8.42		8.07					
Jul-00	8.40	7.58	7.94	8.16	7.78	7.53	7.91	8.28	7.98	8.02	8.41		8.51		8.10					
Aug-00	8.33	7.54	7.94	8.45	8.00	7.71	7.69	8.06	7.73	7.94	8.40		8.32		8.09					
Sep-00	7.84	7.80	8.21	8.30	7.90	7.57	7.99	8.16	8.60	8.37	8.30		8.43		8.40					
Oct-00	8.61	8.48	8.49	8.57	8.15	7.35	8.11	8.62	8.41	8.48	8.51		8.29		8.40		8.58	8.30		
Nov-00	8.60	8.60	8.59	8.29	8.58	7.77	8.15	8.55	8.61	8.65	8.63	7.36	8.70	7.61	8.42			8.49		
Dec-00	8.61	8.62	8.59	8.29	8.58	7.58	8.26	8.63	8.53	8.61	8.89	6.74	8.74	8.18			8.30			
Jan-01		8.50	8.45	8.87	8.48					8.64										
Feb-01	11.10	8.44	8.46	8.42	8.51	8.21	8.25	8.34	8.44		8.54		8.68		8.46	7.99	8.57	8.61	8.45	
Mar-01	8.40	8.42	8.41	8.21	8.41	8.29	8.08	8.42	8.56	8.51	9.38		8.38	7.80	8.21	8.18		8.54	8.51	8.42
Apr-01	8.50	8.48	8.52	9.39	8.31	7.90	8.03	8.61	8.56	8.59	8.00	7.16	8.47		8.49	7.76	8.54	8.51		8.57
May-01		8.25	8.50	8.23	8.36	7.41	8.07	8.34	7.94	8.11	8.35		8.46		8.16		8.23		8.54	
Jun-01	8.42	7.89	8.34	8.41	8.39	7.23	8.17	8.30	7.90	8.08	8.40	7.73	8.24		8.22	7.73	8.26	8.43		8.43
Jul-01	8.01	7.58		7.85	7.76		7.34	7.36	6.84	7.12									8.45	
Aug-01	8.22	7.38	7.72	8.18	8.06	7.85	7.99	8.00	7.76	7.86	8.23	7.00	8.11	7.59	7.86	7.66	8.03		8.55	8.38
Sep-01	8.22	7.31	7.45	8.28	8.01	7.50	7.95	8.07	7.78	7.77	8.06	7.73	7.30		7.75	7.63	7.60	8.20	8.60	8.01
Oct-01			7.64	6.80		8.12	7.83	8.06	8.50	8.06	7.73		8.17		7.92	7.86	7.97	8.07	8.53	
Nov-01																				
Dec-01	8.45	8.45	8.05	8.43	8.30		7.93	8.57	8.40	8.43	8.82		8.44		8.50		8.54	8.70	8.59	
Jan-02	8.45	8.45	8.10	8.50	8.44		7.94	8.36	8.33	8.25					8.05				7.31	
Feb-02	7.40	6.70	8.21	7.80	7.10		7.83	8.30	8.32	8.34	8.31		8.46		7.96	8.32	8.35	8.15	8.44	8.28
Mar-02	8.41	8.39	8.29	8.20	7.25		8.04	8.37		8.35	8.33		8.06	7.63	7.94		8.28	8.24	8.42	8.26
Apr-02	8.37	7.85	8.58	8.42	7.20	8.33	7.26	8.37	7.26	7.26	8.62	7.80	8.55		8.12	7.78	8.53	8.52	9.40	
May-02		8.23	8.58	8.36	7.31	8.76	7.95	8.57	8.15	18.70	8.50	7.66	8.51	7.60	8.34		8.44	8.35	9.41	8.55
Jun-02		7.40	8.42	7.98			8.15	8.50	7.77	7.98	8.42		8.42		8.05		8.25	8.30	8.10	8.33

Table A. 22. pH for streams and canals from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R4-Dup	R5	R6A	R6B	R7	R8	R9A	R9A-Dup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R25	R26
Aug-99	2.87	3.09	2.88	2.72	2.76		2.75	1.93	1.74	1.78	2.75	2.94		2.91	2.94	2.73	3.02	2.60	2.49	2.36	2.73	2.45	2.58	2.38	1.01		
Sep-99	2.78	3.19	2.83	2.59	2.62		2.47	2.06	1.93	1.69	2.75	3.45		3.10	2.83	2.76	2.60	2.57	2.91	2.37	2.92	2.49	2.65	2.45	3.53		
Oct-99	3.80	3.42	3.10	3.19	2.78		3.23	2.28	2.19	2.30	2.77	2.95		2.96	2.79	2.81	2.60	2.70	2.67	2.22	2.55	2.41	2.49	2.03	0.89		
Nov-99	2.90	3.33	3.18	2.94	2.98		3.09	2.81	2.86	3.01	3.30	3.32		3.45	2.43	3.07	2.24	2.29	2.72	2.18	2.56	2.43	2.87		1.37		1
Dec-99	2.63	6.65	2.90	2.61	2.75		1.34	2.48	2.45	2.58	3.40	3.21		3.10	2.17	2.68	2.06	2.11	2.07	1.79	2.09	1.88					
Jan-00	2.73	2.88	2.88	2.69	2.62		1.00	2.31	1.74	1.85	2.77	2.97		2.91	2.05	2.70	1.68						2.04	1.67	1.02		
Feb-00	2.83	3.04	3.12	2.76	2.65		1.14	2.16	2.12	2.13	2.59	3.08		3.00	2.15	2.70	1.84	2.43	2.64		1.89		2.37	2.23			
Mar-00	2.50	2.68	2.78	2.48	2.50	2.51	1.75	1.48	1.74	1.70	2.66	3.30		3.27	2.06	2.55	1.29	1.92	2.06	1.67	1.99	1.87	2.06	1.96	2.26		
Apr-00	2.54	2.96	3.35	2.82	2.61	2.61	2.63	1.62	1.69	1.59	2.88	3.32	3.00	2.99	2.40	2.40	2.04	2.27	2.32		2.17	1.92	2.23	2.14	0.86		
May-00	2.50	2.87	2.56	2.57	2.53	2.53	1.04	1.49	1.33	1.34	2.61	2.62	2.73	2.75	2.75	2.61	2.60	2.49	2.50	2.30	2.73	2.52	3.01	2.42	1.92		
Jun-00	3.34	3.55	3.62	3.19	3.22	3.19	1.81	2.31	2.03	1.83	3.42	4.02	3.49	3.49	3.15	3.20	3.06	3.24	3.10	2.99	3.47	3.01	2.99	3.06	1.49		
Jul-00	3.43	3.46	3.37	2.92	2.93	3.03	1.47	1.97	1.67	1.56	3.29	3.25	3.10	3.66	2.91	3.02	2.96	3.07	3.09	2.75	3.04	2.75	2.68	2.58	1.39		
Aug-00	3.10	3.56	3.28	2.91	2.90	2.97	1.32	4.50	1.95	1.53	3.12	3.21	3.36	2.93	2.93	3.11	2.78	2.78	3.37	2.79	2.97	2.75	2.74	2.74	2.06		
Sep-00	3.24	3.25	3.30	3.12	3.22	3.44	2.53	2.30	2.08	1.66	3.66	3.62	3.50	3.54	2.96	3.10	2.29	2.91	2.97	2.78	3.05	2.80	2.90	2.39	0.96		
Oct-00	2.91	3.06	3.04	3.07	2.84	2.90	1.16	3.66	1.74	1.66	2.92	3.00	3.05	3.10	3.00	2.97	2.82	2.87	3.08	2.70	2.82	2.65	2.77	1.86	2.77		
Nov-00	2.67	2.81	2.83	2.66	2.64	2.62	1.28	2.04	1.98	1.93	2.75	3.02	2.95	3.00	2.91	2.88	2.25	2.34	2.35	2.09	2.42	2.35	1.45	1.13	1.03		
Dec-00	2.81	2.97	4.06	3.61	2.97	2.95	3.32	2.20	3.15	2.52	3.08	5.97	3.18	3.03	2.78	2.95	2.07	8.23	2.84	1.83	2.41	2.22			0.79		
Jan-01	2.88	3.11	3.08	2.89	2.74	2.77	1.74	2.67	2.65	2.51	2.99	3.11	3.15	3.25	2.42	3.02	1.79						1.71	1.58	0.79		
Feb-01	2.72	3.07	3.15	2.70	2.64	2.79	2.30	2.25	2.26	2.27	2.86	3.00	2.97	3.00	2.19	2.86	2.19	2.01	2.01		2.03		2.13	1.91	2.82	1.93	
Mar-01	2.78	2.92	2.97	2.66	2.68	2.62	5.16	2.54	2.05	2.11	3.05	3.17	3.23	3.08	2.11	2.64	1.54	1.98	1.96	1.90	2.13	1.81	2.07	1.59	1.51	1.56	1.99
Apr-01	2.83	3.45	2.86	3.08	3.09	3.58	3.04	3.05	2.11	2.03	3.10	3.48	3.21	3.07	2.22	2.68	1.87	2.25	2.18	2.08	2.15		2.30	2.11	1.54	2.15	
May-01		4.32	4.00	3.75	3.10	2.98	1.57	3.82	3.26	2.42	3.25	3.84	3.76	3.33	3.38		3.26	3.12	3.18	3.12	3.51		3.75	2.93		1.59	
Jun-01	2.58	3.53	2.73	2.70	2.93	2.85	0.81	4.35	2.92	2.03	2.91	3.21	3.16	2.93	2.86	2.71	2.61	2.62	3.03	2.20	3.15		2.60	2.43	0.72	1.35	
Jul-01	3.07	3.90	3.31	3.15	3.09	3.05	1.77	3.82	3.24	2.62	3.31	3.46	4.87	3.44	3.13	3.11	3.12	3.04	2.99	2.54	3.14		2.90	3.24	21.00	2.11	
Aug-01	2.52	3.54	2.63	2.64	2.64	2.60	2.17	3.71	3.54	2.31	3.07	3.50	3.14	3.49	2.81	2.74	2.73	2.63	2.69	2.15	2.79	1.95	2.59	2.35		1.80	
Sep-01	3.75	4.79	3.59	3.34	3.27	3.32	1.53	3.79	3.49	3.28	3.66	3.73	3.92	3.67	3.72	3.30	3.42	3.61	3.84	2.93	5.26		3.39	2.96		2.32	
Oct-01	3.18	4.19	3.97	3.34	3.37	3.53	1.95	3.70		3.46	4.53	3.77	3.66	3.88	3.47	3.43	3.11	3.48	3.11	2.43	3.25		3.30	2.69		4.09	
Nov-01	3.31	3.90	3.84	3.21	3.40	3.49	1.12	2.99	2.96	3.28	3.67	3.64	3.64	3.87	0.50		2.61	2.62	2.88	2.06	2.67		2.78	2.28		2.77	
Dec-01	2.95	3.55		3.21	3.13	2.99	1.11	20.59			4.49		4.23	4.09	2.36	5.29	2.26	2.29	2.16	1.52	2.27		2.25	12.31		1.36	
Jan-02	2.85	3.82	10.29	2.96	15.64	9.95	1.28	24.78		2.33		3.91	3.93	3.65	18.09	3.08	26.17	11.81	5.46		3.00		8.43	2.79	1.50	1.35	
Feb-02	2.72	4.73	3.00	4.71	2.72	2.66	42.99	2.81	2.28	8.54	3.53	21.82	3.76	3.53	1.40	2.77		2.88	2.83		2.78		2.66	2.43		3.32	
Mar-02	3.24	3.29	3.58	2.84	2.88	3.10	1.13	2.12	2.17	2.17	10.99	4.31	4.31		3.34	3.01	2.26	2.67	2.81	2.33	2.72	2.41	2.39		1.29	1.49	
Apr-02	3.21	3.79	3.55	4.11	3.48	3.16	2.20	2.16	1.93	2.23	3.72	4.62	4.66	6.33	5.31	3.19	4.12	3.36	3.45	2.90	3.34	2.98	3.32	2.99		1.77	
May-02	3.07	4.12	3.38	3.30	3.12	3.36	1.20	1.95	1.97	2.02		4.84	4.98	4.03	3.79	3.26	3.76	3.49	3.51	2.97	4.66	3.52	3.45	3.53	1.14	1.78	
Jun-02	3.67	3.57	4.84	3.68	3.52	3.53	1.50	2.64	2.14	2.40		5.91	5.37	4.63	4.59	3.44	4.04	4.04	4.91	3.24	3.85	3.38	3.59	3.63		5.89	

Table A. 23. Total organic carbon (mg/L) from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R4-Dup	R5	R6A	R6B	R7	R8	R9A	R9A-Dup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R25	R26
Aug-99	2.94	3.11	2.84	2.71	2.71		2.78	1.85	1.61	1.63	2.67	2.85		2.82	2.71	2.61	2.63	2.53	2.41	2.31	2.67	2.28	2.53	2.31	0.95		
Sep-99	2.72	3.07	2.70	2.64	2.71		2.43	1.99	1.92	1.69	2.69	3.00		3.00	2.60	2.62	2.54	2.55	2.67	2.21	2.57	2.31	2.51	2.28	3.74		
Oct-99	2.80	3.33	3.10	3.20	2.82		3.28	2.23	2.17	2.20	2.71	3.03		3.07	2.84	3.09	2.40	2.40	2.58	2.28	2.82	2.25	2.81	2.07	0.88		
Nov-99	2.78	3.24	3.17	2.96	2.94		3.07	2.78	2.72	3.08	3.23	3.25		3.13	2.45	3.02	2.17	2.18	2.57	2.11	2.35	2.36	2.48		1.15		
Dec-99	2.61	2.99	2.95	2.59	2.74		1.56	2.78	2.42	2.46	2.71	2.90		3.19	1.86	2.81	2.87	2.38	2.13	1.78	2.74	1.92					
Jan-00	2.63	2.92	2.77	2.69	2.61		1.03	2.20	1.64	1.82	2.71	2.98		2.94	2.01	2.63	1.73						1.84	1.72	1.15		
Feb-00	2.80	3.12	3.11	2.74	2.72		1.28	2.16	2.08	2.14	2.69	3.20		2.95	2.35	2.78	1.77	2.52	2.52		1.97		2.33	2.22			
Mar-00	2.48	2.64	2.67	2.44	2.51	2.43	1.83	1.51	1.73	1.71	2.64	2.88		2.73	1.97	2.55	1.18	1.91	2.04	1.86	2.02	1.67	2.09	1.97	1.56		
Apr-00	2.69	2.74	2.92	2.55	2.45	2.38	2.46	1.51	1.47	1.47	2.67	2.86	2.70	2.64	2.42	2.33	2.08	2.44	2.24		2.11	1.86	2.16	2.21	0.56		
May-00	2.65	2.83	2.62	2.70	2.57	2.82	1.12	1.45	1.22	1.29	2.66	2.81	2.89	2.84	2.67	2.57	2.44	2.54	2.75	2.48	2.56	2.26	2.38	2.27	1.70		
Jun-00	3.29	3.59	3.61	3.22	3.15	3.31	1.73	2.31	2.01	1.85	3.07	4.10	3.39	3.37	3.11	3.20	3.30	3.08	3.01	2.97	3.16	2.85	3.08	3.04	1.48		
Jul-00	3.21	3.29	3.13	2.94	4.08	3.37	1.41	2.02	1.48	1.59	3.00	3.09	3.06	3.43	2.81	2.96	2.75	2.80	2.81	2.54	2.84	2.62	2.74	2.54	1.13		
Aug-00	3.01	3.48	3.25	2.89	2.88	2.88	1.28	4.39	1.84	1.58	3.12	3.05	3.07	2.80	2.77	3.01	2.64	2.72	2.77	2.59	3.52	2.85	3.42	2.56	1.98		
Sep-00	3.11	3.22	3.29	3.15	3.13	3.09	2.39	2.02	1.90	1.56	3.21	3.40	4.00	3.35	3.03	3.38	2.32	2.97	3.25	2.79	3.18	2.79	2.84	2.39	0.95		
Oct-00	2.92	2.91	3.02	2.97	2.81	2.82	0.77	1.84	1.72	1.58	2.87	3.05	2.92	3.02	2.93	3.05	2.58	2.77	2.82	2.69	2.70	2.52	2.76	1.86	2.61		
Nov-00	2.50	2.92	2.81	2.66	2.69	2.97	1.27	1.95	1.92	1.97	2.91	2.88	2.90	3.03	2.85	2.67	2.14	2.23	2.49	2.05	2.49	2.31	1.43	1.04	1.88		
Dec-00	4.17	5.77	3.08	2.81	3.79	2.81	4.17	2.26	2.56	2.47	4.25	3.21	3.15	3.24	2.13	3.48	2.07	2.12	3.90	1.78	2.31	2.12			0.88		
Jan-01	2.75	3.05	3.01	2.91	2.85	2.84	1.69	2.65	2.65	2.62	2.94	3.17	3.13	3.56	2.19	2.91	2.03						1.88	1.76	0.77		
Feb-01	2.63	2.82	2.99	2.66	2.61	2.68	1.99	2.29	2.22	2.19	2.89	2.99	3.01	3.01	2.09	2.68	2.02	1.93	1.98		2.02		2.14	1.94	2.57	1.83	
Mar-01	2.58	2.82	2.89	2.49	2.62	2.61	4.71	2.28	2.07	2.02	3.00	3.10	3.02	2.99	2.01	2.57	1.38	1.89	1.89	1.80	2.04	1.81	2.08	1.61	1.72	1.59	1.99
Apr-01	2.85	3.63	3.70	3.30	2.93	3.88	3.40	3.60	2.08	2.06	3.22	3.59	3.15	5.44	2.34	2.74	1.84	1.95	2.17	1.71	2.10		2.27	2.00	1.56	1.88	
May-01		4.06	3.33	3.31	3.15	3.21	1.91	4.00	3.39	3.19	3.44	3.68	3.71	3.18	3.51	2.99	3.03	3.14	3.12	2.64	3.43		3.85	3.09		2.01	
Jun-01	2.78	3.99	2.85	2.70	2.78	2.77	0.88	3.64	3.03	1.88	2.88	3.54	3.22	2.97	2.74	2.64	2.71	2.54	3.06	2.15	3.07		2.58	2.26	0.77	1.20	
Jul-01	3.10	3.83	3.18	3.00	3.06	3.04	1.55	3.72	2.94	2.60	3.36	3.41	3.25	3.11	3.18	3.18	3.01	3.00	3.19	2.46	3.09		2.92	2.61	19.61	1.72	
Aug-01	3.46	3.44	2.59	2.41	2.61	2.49	1.97	3.37	3.13	2.26	3.00	3.21	2.88	3.27	2.76	2.67	2.65	2.76	2.63	2.13	2.65	2.01	2.39	2.33		2.14	
Sep-01	3.62	4.52	3.64	3.53	3.35	3.63	1.52	4.06	3.43	3.16	3.52	4.08	3.80	3.55	3.41	3.31	3.79	3.66	3.50	3.34	5.13		3.24	2.84		1.94	
Oct-01	3.28	4.07	3.94	3.36	3.31	3.70	1.65	3.58		3.85	4.08	3.79	3.71	3.86	3.49	3.34	3.33	3.65	3.12	2.31	3.06		3.34	2.95		3.24	
Nov-01	3.42	4.27	3.94	3.20	3.36	3.57	1.09	3.10	2.91	2.91	4.35	3.90	3.61	3.69	2.62		2.82	2.71	2.87	2.07	2.64		2.62	2.22	0.87	2.85	
Dec-01	2.77	3.15		2.85	2.84	2.94	1.26	2.64			3.45		3.77	3.46	5.08	4.99	2.17	2.29	2.26	1.78	2.03		1.93	1.56		2.38	
Jan-02	2.79	3.22	3.56	2.82	2.78	2.69	0.96	2.58		1.85	3.91	3.63	3.60	3.58	3.49	2.82	3.11	3.05	4.99		2.75		2.72	2.57	1.01	2.15	
Feb-02	2.71	3.02	2.96	2.68	2.89	2.58	0.89	2.05	2.01	1.97	3.16	8.47	3.46	3.32	1.40	2.87	3.06	2.85	2.79		2.82		2.61	2.30		4.16	
Mar-02	3.25	3.33	3.57	2.91	2.92	2.86	1.35	2.38	2.61	1.99	4.09	4.13	4.14		3.36	2.85	2.24	2.82	2.72	2.31	2.77	2.31	1.61		1.28	1.51	
Apr-02	3.36	4.33	3.61	4.35	3.23	3.31	1.98	2.05	2.39	2.19	3.83	4.19	4.45	3.94	3.90	3.02	3.90	3.79	3.47	2.81	3.29	2.96	3.39	2.93		1.70	
May-02	3.43	4.23	3.62	3.48	3.48	3.36	1.47	2.23	2.03	2.13		4.63	4.97	3.89	4.32	3.31	3.62	3.78	3.67	3.06	3.89	3.18	3.74	3.04	1.02	1.63	
Jun-02	2.94	3.11	3.98	3.10	3.24	3.02	1.11	2.22	1.81	1.85		4.50	4.74	3.85	3.66	3.16	3.58	3.52	3.71	2.97	3.58	2.97	3.33	3.09	1.45	3.86	

Table A. 24. Dissolved organic carbon (mg/L) from August 1999 to June 2002 (Empty box = Sample not collected).
Month	R1	R2A	R2B	R3	R4	R4-Dup	R5	R6A	R6B	R7	R8	R9A	R9A-Dup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20	R25
Aug-99	0.0152	0.0145	0.0158	0.0164	0.0161		0.0286	0.0220	0.0255	0.0229	0.0193	0.0195		0.0196	0.0203	0.0168	0.0210	0.0195	0.0198	0.0193	0.0186	0.0186	0.0204	0.0164	0.0338	
Sep-99	0.0162	0.0150	0.0167	0.0167	0.0163		0.0309	0.0206	0.0235	0.0254	0.0208	0.0187		0.0187	0.0204	0.0164	0.0205	0.0204	0.0221	0.0177	0.0198	0.0173	0.0199	0.0189	0.0321	
Oct-99	0.0147	0.0132	0.0142	0.0131	0.0142		0.0289	0.0220	0.0226	0.0236	0.0189	0.0172		0.0176	0.0194	0.0139	0.0200	0.0196	0.0201	0.0149	0.0174	0.0165	0.0167	0.0136	0.0228	
Nov-99	0.0150	0.0142	0.0141	0.0142	0.0141		0.0243	0.0223	0.0233	0.0204	0.0164	0.0160		0.0168	0.0151	0.0139	0.0214	0.0216	0.0209	0.0122	0.0210	0.0163	0.0204		0.0135	
Dec-99	0.0164	0.0146	0.0144	0.0161	0.0154		0.0210	0.0227	0.0258	0.0250	0.0184	0.0179		0.0172	0.0171	0.0146	0.0176	0.0217	0.0254	0.0138	0.0172	0.0180				
Jan-00	0.0161	0.0151	0.0154	0.0160	0.0160		0.0198	0.0241	0.0240	0.0234	0.0172	0.0166		0.0169	0.0149	0.0156	0.0225						0.0211	0.0100	0.0144	
Feb-00	0.0157	0.0143	0.0141	0.0161	0.0162		0.0204	0.0223	0.0216	0.0212	0.0160	0.0161		0.0172	0.0155	0.0157	0.0231	0.0172	0.0185		0.0219		0.0193	0.0154		
Mar-00	0.0170	0.0158	0.0155	0.0169	0.0166	0.0167	0.0238	0.0249	0.0251	0.0253	0.0177	0.0173		0.0182	0.0180	0.0159	0.0232	0.0183	0.0187	0.0099	0.0187	0.0148	0.0169	0.0148	0.0278	
Apr-00	0.0154	0.0152	0.0142	0.0157	0.0172	0.0171	0.0192	0.0218	0.0226	0.0245	0.0193	0.0174	0.0186	0.0185	0.0195	0.0173	0.0194	0.0167	0.0188		0.0194	0.0166	0.0182	0.0181	0.0373	
May-00	0.0164	0.0147	0.0158	0.0160	0.0170	0.0158	0.0311	0.0236	0.0286	0.0290	0.0179	0.0183	0.0180	0.0176	0.0182	0.0166	0.0186	0.0176	0.0171	0.0103	0.0195	0.0155	0.0183	0.0170	0.0140	
Jun-00	0.0130	0.0112	0.0113	0.0130	0.0134	0.0126	0.0169	0.0140	0.0181	0.0188	0.0152	0.0131	0.0148	0.0151	0.0160	0.0136	0.0152	0.0149	0.0164	0.0090	0.0152	0.0140	0.0149	0.0134	0.0217	
Jul-00	0.0138	0.0129	0.0139	0.0142	0.0107	0.0131	0.0232	0.0171	0.0243	0.0224	0.0178	0.0176	0.0175	0.0173	0.0186	0.0147	0.0189	0.0184	0.0170	0.0109	0.0174	0.0161	0.0174	0.0159	0.0284	
Aug-00	0.0133	0.0115	0.0126	0.0142	0.0146	0.0145	0.0169	0.0069	0.0179	0.0200	0.0167	0.0160	0.0154	0.0162	0.0156	0.0133	0.0177	0.0173	0.0169	0.0104	0.0144	0.0148	0.0129	0.0148	0.0327	
Sep-00	0.0136	0.0125	0.0128	0.0137	0.0138	0.0136	0.0256	0.0204	0.0209	0.0220	0.0180	0.0159	0.0141	0.0161	0.0169	0.0133	0.0179	0.0143	0.0134	0.0097	0.0139	0.0125	0.0156	0.0122	0.0214	
Oct-00	0.0142	0.0138	0.0134	0.0135	0.0145	0.0143	0.0270	0.0210	0.0220	0.0221	0.0187	0.0175	0.0185	0.0181	0.0181	0.0129	0.0192	0.0166	0.0167	0.0104	0.0170	0.0148	0.0157	0.0115	0.0334	
Nov-00	0.0175	0.0174	0.0168	0.0163	0.0162	0.0145	0.0251	0.0261	0.0272	0.0276	0.0227	0.0230	0.0233	0.0220	0.0224	0.0184	0.0252	0.0251	0.0216	0.0164	0.0237	0.0204	0.0265	0.0089	0.0145	
Dec-00	0.0110	0.0098	0.0122	0.0132	0.0110	0.0126	0.0216	0.0186	0.0221	0.0208	0.0126	0.0164	0.0160	0.0156	0.0143	0.0115	0.0197	0.0188	0.0123	0.0140	0.0175	0.0155			0.0190	
Jan-01	0.0151	0.0144	0.0141	0.0139	0.0140	0.0139	0.0230	0.0223	0.0219	0.0230	0.0172	0.0168	0.0171	0.0151	0.0154	0.0135	0.0180						0.0165	0.0129	0.0243	
Feb-01	0.0156	0.0151	0.0148	0.0152	0.0157	0.0150	0.0252	0.0241	0.0247	0.0250	0.0182	0.0179	0.0178	0.0180	0.0162	0.0155	0.0234	0.0246	0.0254		0.0260		0.0187	0.0113	0.0265	0.0242
Mar-01	0.0163	0.0156	0.0151	0.0164	0.0160	0.0159	0.0365	0.0271	0.0257	0.0260	0.0214	0.0184	0.0190	0.0186	0.0185	0.0161	0.0258	0.0204	0.0237	0.0096	0.0209	0.0102	0.0181	0.0089	0.0225	0.0239
Apr-01	0.0148	0.0140	0.0131	0.0131	0.0151	0.0122	0.0265	0.0231	0.0279	0.0264	0.0189	0.0169	0.0191	0.0111	0.0202	0.0157	0.0269	0.0263	0.0250	0.0140	0.0256		0.0206	0.0188	0.0224	0.0262
May-01		0.0120	0.0130	0.0130	0.0140	0.0130	0.0210	0.0220	0.0260	0.0180	0.0160	0.0160	0.0160	0.0180	0.0160	0.0140	0.0180	0.0170	0.0180	0.0080	0.0160		0.0140	0.0130		0.0170
Jun-01	0.0150	0.0120	0.0160	0.0160	0.0160	0.0160	0.0340	0.0210	0.0270	0.0300	0.0180	0.0160	0.0170	0.0220	0.0190	0.0160	0.0200	0.0190	0.0220	0.0080	0.0190		0.0180	0.0170	0.0290	0.0280
Jul-01	0.0140	0.0130	0.0150	0.0150	0.0150	0.0150	0.0280	0.0210	0.0270	0.0260	0.0180	0.0200	0.0200	0.0200	0.0190	0.0150	0.0190	0.0180	0.0170	0.0120	0.0180		0.0200	0.0160		0.0230
Aug-01	0.0120	0.0130	0.0180	0.0190	0.0180	0.0180	0.0390	0.0210	0.0270	0.0310	0.0200	0.0190	0.0210	0.0190	0.0250	0.0170	0.0220	0.0200	0.0210	0.0130	0.0210	0.0170	0.0210	0.0200		0.0180
Sep-01	0.0110	0.0100	0.0140	0.0140	0.0140	0.0130	0.0250	0.0170	0.0250	0.0240	0.0170	0.0150	0.0160	0.0170	0.0180	0.0140	0.0150	0.0160	0.0180	0.0100	0.0130		0.0160	0.0150		0.0210
Oct-01	0.0130	0.0120	0.0120	0.0150	0.0140	0.0130	0.0320	0.0180		0.0230	0.0170	0.0170	0.0170	0.0160	0.0170	0.0140	0.0250	0.0210	0.0230	0.0160	0.0210		0.0200	0.0160		0.0260
Nov-01	0.0124	0.0108	0.0115	0.0134	0.0132	0.0125	0.0237	0.0191	0.0200	0.0201	0.0145	0.0157	0.0173	0.0169	0.0167		0.0194	0.0203	0.0199	0.0129	0.0199		0.0202	0.0161	0.0193	0.0196
Dec-01	0.0148	0.0141		0.0149	0.0144	0.0137	0.0208	0.0202			0.0181		0.0164	0.0176	0.0078	0.0115	0.0187	0.0179	0.0181	0.0115	0.0188		0.0207	0.0130		0.0179
Jan-02	0.0150	0.0135	0.0123	0.0155	0.0150	0.0173	0.0280	0.0199		0.0229	0.0148	0.0173	0.0178	0.0173	0.0175	0.0147	0.0167	0.0176	0.0180		0.0163		0.0182	0.0161	0.0230	0.0116
Feb-02	0.0164	0.0148	0.0147	0.0159	0.0149	0.0163	0.0223	0.0231	0.0226	0.0224	0.0184		0.0182	0.0188	0.0188	0.0153	0.0161	0.0163	0.0179		0.0169		0.0178	0.0155		0.0143
Mar-02	0.0130	0.0130	0.0120	0.0150	0.0150	0.0150	0.0210	0.0180	0.0160	0.0240	0.0160	0.0150	0.0150		0.0170	0.0150	0.0180	0.0160	0.0160	0.0120	0.0160	0.0120	0.0150		0.0160	0.0180
Apr-02	0.0130	0.0110	0.0120	0.0100	0.0140	0.0130	0.0220	0.0150	0.0150	0.0190	0.0150	0.0150	0.0140	0.0160	0.0160	0.0140	0.0140	0.0140	0.0150	0.0120	0.0150	0.0120	0.1490	0.0120		0.0160
May-02	0.0127	0.0112	0.0124	0.0124	0.0128	0.0127	0.0219	0.0139	0.0193	0.0180		0.0140	0.0134	0.0156	0.0146	0.0128	0.0158	0.0159	0.0150	0.0122	0.0138	0.0137	0.0136	0.0128	0.0273	0.0180
Jun-02	0.0148	0.0140	0.0111	0.0136	0.0133	0.0145	0.0294	0.0130	0.0204	0.0208		0.0141	0.0133	0.0155	0.0157	0.0141	0.0161	0.0156	0.0181	0.0140	0.0168	0.0138	0.0164	0.0148	0.0167	0.0257

Table A. 25. SUVA ($cm^{-1}(mg/L)^{-1}$) from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R5	R6A	R6B	R7	R8	R9A	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20
Aug-99	147	76	18	18	61	302	522	127	204	44	849	420	208	337	464	258	86		366		171		
Sep-99	41	65	22	15	25	141	352	136	272	42	274	0	135	28	388	252	192		194		186		
Oct-99	75	136	201	150	121	100	128	142	266	72	135	137	122	187	531	359	156		127		366		
Nov-99	115	87	452	1022	612	476	244	425	581	112	1043	474	49	525	503	490	395		539				
Dec-99	350	152	158	332	51	525	95	266	171	73	322		94	157	358	302	712		524				
Jan-00	712	230	157	827	1252	310	316	424	273	143	76	136	495	229	265						272		
Feb-00	87	56	22	130	331	286	46	51	102	7	11	30	19	711	237	394	273		309		877		
Mar-00	382	51	81	236	236	221	26	19	287	8	0	251	115	271	461	194	273		193		216		157
Apr-00	55	56	26	22	40	87	44	29	62	4	4	23	381	38	164	243	394		531		73		26
May-00	92	22	35	75	87	59	7	22	171	18	34	91	238	150	288	227	460		330		237		
Jun-00	257	44	40	51	164	619	243	93	215	18	108	229	317	80	307	330	763		446		440		92
Jul-00	167	337	48	22	178	391	323	42	329	313	1518	5201	237	237	503	482	358		266		301		49
Aug-00	141	488	252	113	143	251	81	65	308	45	148	55	191	218	229	159	992		920		274		179
Sep-00	164	532	337	273	229	365	115	98	193	66	171	178	136	108	193	136	271		431		193		130
Oct-00	1267	288	202	295	274	468	432	806	734	346	706	1246	151	166	497	497	108		223		158		684
Nov-00	612	122	295	418	151	562	1303	799	648	670	403	583	323	252	432	814	648		346		310		0
Dec-00	418	1123	382	302	425	619	1678	245	302	475	878	1267	65	547	446	367	259		2938				
Jan-01	317	972	475	526	281	446	482	396	331	526	482	533	115	202	626						252		14
Feb-01	490	482	324	562	828	216	446	187	389	144	29	101	158	576	389	245	490		418		864		144
Mar-01	173	43	29	180	101	36	65	72	115	14	22	7	137	1080	108	418	180		72		367		144
Apr-01	288	58	22	144	202	317	36	655	130	58	58	36	202	425	295	317	598		130		425		166
May-01		86	43	605	137	268	283	137	165	129	770	57	454	331	274	274	324		36		404		201
Jun-01	129	14	7	29	144	187	734	14	173	57	1137	72	360	173	547	648	533		677		663		
Jul-01	201	21	35	35	100	375	474	86	144	331	1731	118	100	122	360	259	274		244		476		
Aug-01																							
Sep-01	116	50	86	72	57	245	35	22	230	43	166	14	259	50	533	749	417		792		360		
Oct-01	115	144	129	36	201	187			172	5919	100	57	159	446	533	403	259		302		360		
Nov-01	137	7	43	122	7	65	36	7	58	115	173	187	144		252	58	58		403		151		14
Dec-01	115	50		151	43	65	50		94	43	281	274	22	36	655	482	130		562		302		14
Jan-02	338	58	72	115	130	65	288		288	72	137	158	446	43	461	324	137		1080		1087		
Feb-02	346	310	130	295	310	101	43	58	130	806	115	58	209	425	742	158	94		518		223		

Table A. 26. Planktonic algae (total organisms/ml) from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R5	R6A	R6B	R7	R8	R9A	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20
Aug-99	135	76	0	18	54	195	493	91	189	19	777	297	165	302	402	229	0		366		164		
Sep-99	22	61	15	7	7	63	317	115	222	28	137		128	28	352	245	178		158		172		
Oct-99	68	94	136	78	100	86	93	107	180	7	57	86	108	158	481	345	142		120		338		
Nov-99	79	57	309	1022	569	368	186	360	503	36	1000	438	41	504	489	483	395		474				
Dec-99	346	148	137	328	51	511	91	266	171	62	301		90	153	337	295	648		517				
Jan-00	705	223	143	820	1245	303	295	417	266	122	72	108	474	229	265						258		
Feb-00	87	48	22	130	331	257	34	37	102	0	4	22	19	711	230	387	273		309		870		
Mar-00	382	47	62	215	208	164	15	11	266	8	0	251	108	271	403	166	273		186		188		143
Apr-00	44	44	26	11	25	55	0	11	58	4	4	23	374	30	157	236	387		517		69		26
May-00	81	18	27	75	87	41	7	8	171	18	26	91	231	136	281	227	460		330		237		
Jun-00	78	18	0	44	129	166	201	57	201	14	101	201	259	62	300	330	735		432		440		78
Jul-00	22	273	44	18	152	355	129	28	301	247	1094	5030	230	237	503	482	337		259		301		49
Aug-00	51	424	223	63	129	179	40	39	128	33	65	19	187	199	229	138	985		906		245		136
Sep-00	100	475	302	216	222	344	58	72	193	55	71	93	136	65	193	129	192		388		100		94
Oct-00	1152	274	180	166	216	425	346	720	677	216	590	1238	137	108	338	418	94		173		115		648
Nov-00	324	115	274	223	50	562	1296	792	468	468	158	482	223	216	79	706	641		338		266		0
Dec-00	389	1116	317	288	425	619	1656	245	302	446	871	1267	65	533	446	353	238		2938				
Jan-01	144	432	389	281	101	439	324	259	317	526	475	526	108	101	626						216		14
Feb-01	310	101	86	497	511	202	439	187	374	65	0	29	130	274	374	238	490		418		482		130
Mar-01	151	21	22	151	101	29	36	72	108	7	7	0	115	1080	108	396	180		65		367		144
Apr-01	259	7	22	144	202	317	36	648	130	50	0	36	202	410	295	317	598		130		425		166
May-01		79	43	605	137	216	158	108	158	115	727	50	432	302	274	274	317		36		382		158
Jun-01	86	7	0	29	43	173	720	0	144	43	1123	72	360	130	518	634	490		619		634		
Jul-01	158	14	21	21	93	317	446	72	130	288	1397	101	72	108	331	259	245		230		418		
Aug-01																							
Sep-01	58	36	72	58	43	245	14	22	187	22	101	14	245	50	504	720	374		749		331		
Oct-01	58	86	115	29	187	187			158	101	72	43	130	432	504	389	245		288		302		
Nov-01	122	0	14	122	0	58	14	0	50	94	173	187	122		238	50	58		403		151		14
Dec-01	94	43		151	36	65	43		86	14	259	259	14	14	655	482	115		562		302		14
Jan-02	338	36	65	115	130	58	274		281	72	101	122	439	43	461	324	137		1080		1080		
Feb-02	331	310	130	295	302	101	29	58	130	792	36	22	180	425	742	108	72		511		223		

Table A. 27. Planktonic diatoms (total organisms/ml) from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R4dup	R5	R5dup	R6A	R6B	R7	R8	R9A	R9Adup	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20
Aug-99	0	0	18	0	0		21		4	4	4	0	29		29	0	14	7	0	0		0		0		
Sep-99	0	0	0	0	7		14		14	0	14	0	65			0	0	0	0	0		7		0		
Oct-99	0	14	7	0	14		0		14	14	43	36	35		0	7	0	0	0	0		0		0		
Nov-99	0	4	14	0	29		36		0	14	28	0	7		14	4	0	7	7	0		0				
Dec-99	0	0	21	4	0		0		4	0	0	0	7			0	0	7	0	7		0				
Jan-00	0	7	7	0	7		7		14	7	0	14	4		21	14	0	0						0		
Feb-00	0	8	0	0	0		0		12	7	0	0	7		4	0	0	7	7	0		0		0		
Mar-00	0	0	11	0	0		7		0	8	7	0	0		0	0	0	0	7	0		0		14		0
Apr-00	0	8	0	0	4		0		40	7	0	0	0		0	7	0	0	7	0		0		0		0
May-00	11	4	8	0	0		0		0	0	0	0	0		0	0	0	0	0	0		0		0		
Jun-00	93	0	0	0	7		0		21	7	0	0	0		7	0	0	0	0	7		0		0		0
Jul-00	36	7	4	0	11		0		14	0	7	4	122		0	0	0	0	0	0		0		0		0
Aug-00	29	14	7	0	0		7		19	8	0	4	36		0	0	4	0	0	0		0		0		7
Sep-00	14	21	14	14	0		7		36	11	0	0	50		57	0	0	0	7	0		7		7		0
Oct-00	115	14	0	29	50		0		0	0	0	0	22		0	0	22	0	0	7		0		0		0
Nov-00	22	0	22	22	14		0		0	7	22	7	0		22	7	0	0	0	0		0		7		0
Dec-00	7	7	0	14	0		0		14	0	0	7	7		0	0	0	0	0	0		0				
Jan-01	7	7	7	0	0		7		43	36	14	0	7		7	7	94	0						0		0
Feb-01	0	7	7	29	0		0		7	0	14	22	29		72	7	7	14	0	0		0		0		0
Mar-01	14	7	0	0	0		0		14	0	0	0	14		7	7	0	0	0	0		0		0		0
Apr-01	7	29	0	0	0		0		0	0	0	0	50		0	0	0	0	0	0		0		0		0
May-01		0	0	0	0		0		79	7	7	7	14		0	22	0	0	0	0		0		0		0
Jun-01	0	7	7	0	0		0		14	7	0	0	14		0	0	0	0	0	0		0		0		
Jul-01	29	0	0	0	0		0		14	0	14	0	158		0	0	0	0	0	0		0		0		
Aug-01																										
Sep-01	29	7	0	0	0		0		7	0	0	7	22		0	0	0	0	0	0		0		0		
Oct-01	43	58	0	0	14		0				0	5818	14		0	22	14	0	0	0		0		0		
Nov-01	14	0	7	0	0		7		14	0	7	0	0		0	22		14	0	0		0		0		0
Dec-01	7	7		0	0		0		7		7	22	22		14	7	0	0	0	0		0		0		0
Jan-02	0	22	7	0	0		7		14		7	0	14		22	0	0	0	0	0		0		7		
Feb-02	7	0	0	0	7		0		14	0	0	0	79		36	22	0	0	43	22		7		0		

Table A. 28. Planktonic green algae (total organisms/ml) from August 1999 to June 2002 (Empty box = Sample not collected).

Month	R1	R2A	R2B	R3	R4	R5	R6A	R6B	R7	R8	R9A	R9B	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19	R20
Aug-99	8	0	0	0	7	79	25	92	7	25	36	87	43	21	58	29	86		0		7		
Sep-99	19	4	7	8	11	64	14	21	36	14	72		7	0	36	7	14		29		14		
Oct-99	7	28	58	72	7	14	21	21	43	29	43	51	7	29	50	14	14		7		28		
Nov-99	36	26	129	0	14	72	58	51	50	76	36	22	4	21	7	0	0		65				
Dec-99	4	4	0	0	0	14	0	0	0	11	14		4	4	14	7	58		7				
Jan-00	0	0	7	7	0	0	7	0	7	7	0	7	7	0	0						14		
Feb-00	0	0	0	0	0	0	0	7	0	0	0	4	0	0	0	0	0		0		7		
Mar-00	0	4	8	21	28	43	11	0	14	0	0	0	7	0	58	21	0		7		14		14
Apr-00	11	4	0	11	11	32	4	11	4	0	0	0	0	8	7	0	7		14		4		0
May-00	0	0	0	0	0	18	0	14	0	0	4	0	0	14	7	0	0		0		0		
Jun-00	86	18	36	7	14	439	14	29	14	4	7	21	58	18	7	0	21		14		0		14
Jul-00	26	50	0	4	15	29	144	14	21	8	252	157	7	0	0	0	14		7		0		0
Aug-00	50	50	22	50	14	65	22	18	180	8	47	36	4	15	0	21	7		14		29		36
Sep-00	36	36	21	43	7	14	21	15	0	11	50	28	0	43	0	0	79		36		79		36
Oct-00	0	0	14	101	7	43	86	86	58	130	50	7	14	36	22	79	7		50		43		36
Nov-00	58	7	0	36	0	0	7	0	158	194	245	79	94	29	353	108	7		7		36		0
Dec-00	22	0	65	0	0	0	0	0	0	7	0	0	0	14	0	14	22		0				
Jan-01	0	14	79	14	0	0	65	86	0	0	0	0	0	7	0	0	0		0		36		0
Feb-01	7	0	0	0	0	0	0	0	0	0	0	0	22	7	7	7	0		0		0		14
Mar-01	7	7	7	22	0	7	14	0	7	7	0	0	14	0	0	22	0		7		0		0
Apr-01	22	22	0	0	0	0	0	7	0	7	7	0	0	14	0	0	0		0		0		0
May-01		0	0	7	0	22	36	22	0	7	29	7	0	29	0	0	7		0		22		43
Jun-01	43	0	0	14	101	14	14	7	29	14	0	0	0	43	29	14	43		58		29		
Jul-01	14	7	14	14	7	58	14	0	0	43	158	7	14	14	29	0	29		14		58		
Aug-01																							
Sep-01	29	0	14	14	14	0	14	0	29	14	43	0	14	0	29	29	43		43		29		
Oct-01	14	0	0	7	0	0			14	0	14	14	7	0	29	14	14		14		58		
Nov-01	0	0	0	0	0	0	0	0	7	0	0	0	22		14	7	0		0		14		0
Dec-01	14	0		0	7	0	0		0	7	0	0	0	22	0	0	14		0		0		
Jan-02	0	0	0	0	0	0	0		0	0	14	14	7	0	0	0	0		0		0		
Feb-02	7	0	0	0	0	0	0	0	0	14	0	0	7	0	0	7	0		0		0		

Table A. 29. Planktonic blue-green algae (total organisms/ml) from August 1999 to June 2002 (Empty box = Sample not collected).