

IUVA NEWS

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APPROACH FOR ACHIEVING SUSTAINABLE OPERATION OF THE 2-BGD CATSKILL/DELAWARE UV DISINFECTION FACILITY

EFFECT OF UV RADIATION ON THE VIABILITY OF CYANOBACTERIA (BLUE-GREEN ALGAE)

NOVEL UV LED ADVANCED OXIDATION SYSTEM FOR DISINFECTION AND REMOVAL OF ORGANIC AND HEAVY METAL CONTAMINANTS IN WATER



in the next issue . . .

Municipal Applications

ULTRAVIOLET LIGHT

THE TROJANUV SOLUTION

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Your new 2009 – 2011 Executive Operating Committee (please see page 11 for details)

Editor in Chief:

Mr. Paul Overbeck

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IUVA Executive Committee

- Linda Gowman, Ph.D.	- Oluf Hoyer, Ph.D.
- Bertrand Dussert, Ph.D.	- Karl Linden, Ph.D.
- Guus Ijpelaar, Ph.D.	- Jim Malley, Ph.D.
- Chris Schulz	- Regina Sommer, Ph.D.
- Andreas Kolch, Ph.D.	- Elliott Whitby, Ph.D.

Editorial

Paul Overbeck

Editor-in-Chief



Paul Overbeck

In our last issue, we published reflections on the last decade from some of our founding members that have remained active since 1999. Now, at the conclusion of 2009 and a successful 5th Ultraviolet World Congress, I would like to take a moment and reflect on the last two years' activities since I began with the IUVA as your Executive Director. Our many member volunteers have made great things happen under President Linda Gowman's direction.

Our thanks go to all who attended an IUVA sponsored workshop, conference or World Congress in 2008 and 2009. Our respect and thanks also go to the IUVA volunteers that made these events happen. (Please see the "News from the IUVA" where we recognize our volunteers.) And of course, thank you to our sponsor and exhibitor companies, who make UV events possible with their support.

Through these events, IUVA has provided valuable education on UV technology and application to nearly 1,000 individuals. From responses on event follow-up surveys, we know that attendees were positive about the technical content and event logistics. (And for those that made suggestions for the future, thank you, we can always do better!) Overall, positive feedback means that our impact factor was even higher - satisfied customers tell others about what they learned.

What about the future?

If Frost and Sullivan's "Global Ultraviolet Water and Wastewater Disinfection Systems Market Report" is correct, the global UV water and wastewater disinfection systems market will grow at a compound annual growth rate of 7.2% between 2008 and 2015, with the market growing from at \$388.3 million to reach \$629.8 million in 2015. The report goes on to state, "Water scarcity and increasing demand for high purity process water in some of the fast developing nations such as India, China, Singapore, Middle East & Africa to name a few are also expected to be major driving factors for this market".

Water market analysts have reported in market studies that place the global market in the \$425 to 450 Billion neighborhood with the municipal segment around \$300 billion. One specific report, by Lux Research, gives a higher figure placing the world's water business above \$500 billion in 2007; projecting it will rise to \$600 billion in 2010 and swell to near \$800 billion by 2015.

As an example, the US market was estimated at \$114 billion in 2007 or almost 25% of global activity. The US EPA estimated that \$450 billion is needed to rehabilitate water and wastewater infrastructure, with more than 2/3 of this amount needed for underground piping replacement. The US EPA conservatively forecasts \$277 billion will need to be spent on water infrastructure by 2019, while some market analysts put the price tag as high as \$600 billion.

There is potential for great opportunities. These opportunities of course depend on local, regional and global economies and a myriad of other variables. (For instance, the ongoing series of articles in The New York Times that is turning up the heat on politicians through public awareness of water infrastructure issues. <http://projects.nytimes.com/toxic-waters> Read on in Hot UV News for more details.) I will continue my running theme for this year – I still believe the future is bright for UV.

Most important for UV acceptance are the ongoing efforts of the IUVA, its members and stakeholders to continue to educate the world on the technology and its benefits. The IUVA Board of Directors, under new President, Bertrand Dussert has spent considerable time developing strategic initiatives to support our Mission. We hope many of you will commit to supporting these programs in 2010

Until then, we await Bertrand's return from holiday – he decided to go climbing Mount Kilimanjaro - we know he educated others about UV technology by using his new SteriPEN (the perfect speaker gift from the 5th UV World Congress) to disinfect his drinking water on his adventure.

We wish you Season's Greetings and a very happy, healthy & prosperous New Year to you all. May 2010 be your best year yet!



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A Message

from the IUVA President
Bertrand Dussert



President Bertrand
W. Dussert, Ph.D.

Hello, IUVA Members -

It is my sincere honor to be your new President. I am humbled that the people for whom I have the utmost respect have elected me to be their new leader. I would like to thank Dr. Linda Gowman for her many achievements over the last two years during her term in office. I feel very privileged to have been working with Linda - I have learnt a lot. Under her leadership, the Association has had tremendous success in delivering the UV

message to a new, broader and more international audience.

For those that joined us in Amsterdam this past September for the 5th UV World Congress, thank you. It became clear over the course of many conversations that we all share a common vision – we want to see the IUVA thrive and continue to grow.

Our goal is clear as the IUVA enters its second decade. There is much work to be done! Determining how to go about this work was my first challenge as your new President. Earlier this year, I took a few minutes to think, “Where are we, and where do we want to be 2 years from now?” It became clear to me that in our eleventh year as an Organization, a Strategic Plan was the top priority to continue our growth, in line with our Mission Statement. I am pleased to report that, with the help of many Board members, a plan was recently finalized. I would like to especially thank Secretary Dr. Guus Ijpelaar and President-Elect Paul Swaim for their support and leadership in completing this plan.

So, what’s in store for the IUVA? I would like to share with you our new key initiatives. We will...

Increase Value to You, Our Members

Be on the lookout for exciting new member benefits in the months to come! As we grow, our diverse membership brings with it unique and varied talents in many areas of expertise. Through surveys, additions to iuva.org and open dialogue we will work with you, the members, to learn how we can serve you better, each & every day.

Continue to Grow Internationally

As our membership continues to expand, we are able to provide more regionally-focused resources and more local events. We are proud to provide UV enthusiasts from around the world a forum in which to forge new friendships; we are a truly global community.

Champion Key Technical Issues Facing the Industry

There is an urgent need for the acceptance of universal protocols/guidelines/regulations. The IUVA is committed to being involved in creating accurate, comprehensive information that responsibly represents your interests.

Strengthen Partnerships with Other Associations

We strive to continually find new audiences for our UV message. By

partnering with other associations, we assure that Ultraviolet becomes thoroughly integrated into the language of these many new forums we look to support. We also take advantage of a wealth of additional resources and venues by joining forces toward a common goal.

Develop More End-User Content

We look to support the daily use of UV across a variety of applications. We are encouraged by the number of end users that have joined as IUVA members, and want this trend to continue!

Showcase UV as a Green Technology

Collectively, we are at the forefront of the “Green Revolution” ...it’s time to tell the world! Who doesn’t love the winning trifecta of safe, effective & clean? History is being forged right here and now, with the world taking initiatives such as the Copenhagen Climate Change Summit. UV is integral to a cleaner, brighter future for us all.

Expand Our Horizons Beyond Municipal Water and Wastewater Treatment

Our Mission Statement identifies a clear commitment to bettering Public Health and the Environment. Accordingly, our focus will be broadened to include Air Treatment, Residential/Commercial Treatment (e.g. swimming pools), and Industrial Treatment.

Acknowledge the Tireless Efforts of Our Volunteers

The IUVA is comprised of some of the most passionate, intelligent, dedicated people that I have ever known. Thank you for all that you have done over the past ten years and thank you for all that I know you will continue to do in the future. Together, I know that there is no limit to what we can achieve. I am very much looking forward to working with each and every one of you.

I wish you all a wonderful holiday season and a Happy New Year!

ABOUT OUR PRESIDENT-ELECT

Paul D. Swaim, P.E. is Vice President and Senior Principal Technologist for the Water Business Group of CH2M HILL. Paul is based in Denver, Colorado, USA, and he has been with CH2M HILL since 1999. Paul works on water projects across the globe, bringing technical expertise to deliver solutions to complex problems. As CH2M HILL’s Global Technology Leader for Water Treatment, Paul’s responsibilities include leadership across the spectrum of drinking water treatment processes and services including best practices, tools, and resources.

Paul has been an active member of the IUVA since its inception. In 2007, he was named to the IUVA Board of Directors.

Paul received his M.S. in Civil and Environmental Engineering and his B.S. in Civil Engineering from the University of California, Berkeley. He is a registered professional engineer in California, Arizona, and Colorado. Shortly after graduate school, Paul was a co-author of the Water Environment Research Foundation’s 1991 project, “Comparison of UV Irradiation to Chlorination: Guidance for Achieving Optimal UV Performance.” He has continued to work on UV projects throughout his career, authoring papers and making

Continued to page 6

ABOUT OUR PRESIDENT-ELECT [Continued]



**President-Elect
Paul Swaim, P.E.**

presentations on UV disinfection for drinking water, wastewater, and reuse applications.

From his 18 years of experience, Paul's expertise includes water treatment process selection, treatability (bench and pilot scale) testing, conventional water treatment, GAC applications, treatment for emerging contaminants, UV disinfection, and advanced oxidation. Paul's UV project experience includes several of the first drinking water UV

disinfection applications in the USA and Canada, several of the world's first municipal applications of UV-hydrogen peroxide advanced oxidation, and several of the largest drinking water UV disinfection projects in North America.

In 2005, Paul was lead author for the American Water Works Association (AWWA)/American Society of Civil Engineers, "Water Treatment Plant Design, Fourth Edition, Chapter 29 – UV Disinfection." He also co-developed a full-day course for AWWA on UV disinfection, delivering the course multiple times in the US, Canada, and Puerto Rico over the last six years. Recently, Paul was a contributing author of AWWA's, "Selecting Disinfectants in a Security-Conscious Environment."


Goals for the Future of the IUVA In His Own Words...

First of all, I am thrilled and honored to serve the IUVA. This organization has been built on the shoulders of many hard-working, dedicated individuals with a true common passion for using UV to improve public health and the environment. Building on this, current President, Bertrand Dussert, has initiated several efforts that will move the IUVA forward.

During my term as President, my goal will be to keep the IUVA growing as a vital, thriving organization that forms strong partnerships with related organizations and that effectively shares knowledge on the use of UV to protect public health and the environment worldwide.


So far as "President-Elect," it has been very exciting for me to get involved in the strategic planning effort initiated by Bertrand Dussert, Linda Gowman, Guus Ijpelaar, and others. We have identified a slate of programs to implement that I believe will yield benefits for the IUVA in growing our numbers, influencing the industry, and providing value to our members. You will be hearing more about these programs soon! I am particularly interested in increased efforts to engage the end-users of UV and in developing a plan to address the key technical UV issues facing the industry.

UV disinfection may not be the brand new technology du jour anymore, but it is and will continue to be one of our best options to create sustainable solutions for our communities. The future of the IUVA continues to be bright. I look forward to working with all of our members and to many more great accomplishments in our future together.




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The following are some items of note from IUVA Member Announcements:

Neotec UV opens Los Angeles Office

www.neotecuv.net

Neotec UV manufacturer of UV disinfection systems announced that they have opened an office in Los Angeles to expand in the North American region and to the worldwide market.

Neotec also announced the installation of a 16 MGD (60,000 m³/d) capacity open channel UV system in Paju WWTP in Korea, with testing scheduled to be completed by 20 December 2009. Additionally, their in-line chamber type system for shipboard ballast water treatment is currently in the process of being certified by the International Maritime Organization (IMO) and has already been installed in ships for 21st Century Shipbuilding Company.

Open Channel UV Systems Debut at WEFTEC

www.aquionics.com

At this year's WEFTEC, Aquionics introduced its new OpenLine Series of open channel UV treatment systems for the secondary wastewater market. The OpenLine is designed to treat secondary wastewater flows over a wide range of flows and UV transmittances and employs a new type of low-pressure, high-output (LPHO) amalgam lamp stated to deliver a more stable output over its operating life. Bill Decker, president of Aquionics stated, "It offers a neatly packaged solution that is pre-engineered for wastewater applications."

Aquionics also launched its new AF-3 Series of closed-vessel UV systems, which also employs high-efficiency LPHO amalgam lamps. Validation work for the AF-3 Series in accordance with the US EPA UV Disinfection Guidance Manual (UVDGM) has been completed. Aquionics is part of the Fluid Technology Division of Halma.

UV Pure Technologies to Supply Kinetico, Inc. with Residential Systems

www.kinetico.com

UV Pure Technologies is providing Kinetico-branded UV systems to Kinetico Incorporated, Newbury, OH. Kinetico chose UV Pure to develop and produce Kinetico-branded UV water purification systems to its own engineering specifications, and UV Pure developed the systems exclusively for Kinetico using UV Pure's patented and advantaged Crossfire Technology®. The product line includes a 12 GPM residential system and a 12 GPM NSF/ANSI 55 Class A system for regulatory jurisdictions that require it. Kinetico will launch its UV product line to its dealers in North America, and subsequently, it will be rolled out to its global distribution network in nearly 100 countries.

Dr. Ashish Mathur joins UltraViolet Devices Sparks Technology Division

www.uvdi.com

UltraViolet Devices, Inc. (UVDI) is a manufacturer and supplier of UV products for both air, surface and water disinfection, and Sparks announced the addition of Ashish Mathur, Ph.D as their new Senior Molecular Filtration Applications Engineer.

Dr. Mathur brings over 22 years of industry experience to UVDI. He received his doctorate and master's degrees in fiber and polymer sciences from Cornell University. His most recent position before joining UVDI was Vice President of Research and Technology for Ahlstrom Filtration.

Calgon Carbon to supply UV system to treat Boston drinking water

<http://www.calgoncarbon.com>

Calgon Carbon Corporation announced today that it has been selected by the Massachusetts Water Resources Authority (MWRA) to provide an ultraviolet disinfection system for the John Carroll Water Treatment Plant in Marlboro, Massachusetts.

The Calgon UV system, scheduled to be delivered in June 2012, will treat up to 450 million gallons of drinking water per day. Earlier this year, the company was awarded a contract to supply similar UV reactors for the treatment of San Francisco's drinking water.

CH2M HILL VP Linda Macpherson Named WaterReuse Person of the Year

http://www.ch2m.com/corporate/news_room/news_story.asp?story_id=547

CH2M HILL announced that Linda Macpherson was named a WaterReuse Person of the Year by the WaterReuse Association and the Clovis Water Reuse Facility, designed, built and operated by the firm received the WaterReuse Award of Merit.

The awards were presented during the 24th WaterReuse Annual Symposium in Seattle. The WaterReuse Association is a nonprofit organization that advances the beneficial and efficient use of water resources through education, sound science, and technology. Macpherson and Eric Rosenblum with the City of San Jose were each named WaterReuse Person of the Year. The Clovis Water Reuse Facility was among five other reuse projects receiving the Award of Merit.

The Clovis facility is an innovative design-build-operate water reuse project developed by CH2M HILL and commissioned by Clovis, Calif., to relieve the demand on underground and surface water supplies. It will provide recycled water for irrigation, especially as the region's population continues to grow. The nearly \$40 million facility was completed in February 2009. The 2.8 million gallons per day plant uses low-pressure, high-output ultraviolet lamps for disinfection that require one-third the amount of energy compared to other ultraviolet options. Use of the membrane bioreactor process provides the opportunity for enhanced automation, reduced facility size and superior treatment performance.

Additionally, the Cannibal™ sludge reduction system will lower the amount of biosolids significantly, and this is the largest application of the technology to date in California. CH2M HILL OMI will operate the facility for 10 years.

The Clovis facility has also been recognized with the Environmental Business Journal Business Achievement Award, a Global Water Award from the International Desalination Association and Global Water Intelligence and an Excellence in Environmental Engineering Award from the American Academy of Environmental Engineers.

NEWS FROM IUVA

IUVA 5th World Congress – A Look Back in Photos:



Event Location, Dam Square, Amsterdam, The Netherlands



IUVA President 2007-2009, Linda Gowman, Ph.D., P.Eng.



Welcome Reception, From Left to Right: Jim Bolton, Ph.D., Prof. Jim Malley, Ph.D., President Bertrand Dussert, Ph.D.



IUVA Executive Director, Paul Overbeck



Cheers!!!



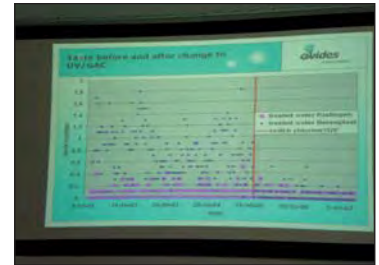
Plenary Speakers, Dr. Joop Kruithof & Prof. Don Bursill



From Left to Right: Dr. Margarete Bucheli, Diana Schoenberg and Prof. Dr. Regina Sommer, World Congress Technical Committee Chair



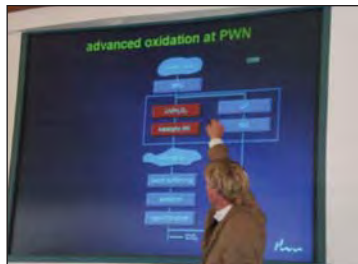
Thank you to our Regulatory Workshop Speakers



Evides waster taste feedback from customers: before and after UV... what an improvement!



Taking photos on our technical tour, at Evides in Berenplaat



Our tour concludes in Heemskerk, with PWN – presented by our host, Bram Martijn...



...with a tour of the beautiful facility.

**5th World Congress
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Chair - Prof. Dr. Regina Sommer, Medical University Vienna
 Dr. Andreas Kolch, HYTECON GmbH
 Dr. Joop C. Kruithof,
 Wetsus Centre for Sustainable Water Technology
 Prof. Dr. James P. Malley, Jr., University of New Hampshire

5th UV World Congress Proceedings are available on CD ROM for \$75 plus shipping. Please contact Diana at dianas@iuva.org to order.

**5th World Congress Local Organizing /
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Dr. Joop C. Kruithof,
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 Dr. Guus Ijpelaar, Royal Haskoning

5th World Congress Award Winners:

UV Engineering Project of the 2008 Award
 Orange County Water and Sanitation District for their
 Groundwater Replenishment (GWR) System

**IUVA 2008-2009 UV Light Award for Volunteer
Recognition**

Christopher Schulz, CDM - IUVA Treasurer

UV Lifetime Achievement Award

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Phillips www.philips.com/uvpurification

Siemens www.siemens.com/iuva

UV-technik www.uvtechnik.com

Aquafine UV www.aquafineuv.com

Trojan Technologies www.trojanuv.com

Viqua www.viqua.com

We are pleased to introduce the new IUVA Executive Operating Committee and Board of Directors elected during the 5th UV World Congress in Amsterdam:



Bertrand W. Dussert, Ph.D.



Paul Swaim, P.E.



Linda Gowman, Ph.D., P.Eng.



Guus F. Ijpelaar, Ph.D.



Christopher Schulz, P.E.

President Bertrand W. Dussert, Ph.D.Siemens Water Technologies Corp.
President-Elect Paul Swaim, P.E.CH2M HILL
Immediate Past Pres. Linda Gowman, Ph.D., P.Eng.Trojan Technologies Inc.
Secretary Guus F. Ijpelaar, Ph.D.Royal Haskoning
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We Thank our 2008-09 IUVA Workshop, Conference and World Congress Organizers

NWRI-IUVA Water Reuse Workshop (Orlando) – Jeff Mosher, Gary Hunter and Andy Salveson
 Cryptosporidium Inactivation Workshop (London, UK) – Andreas Kolch
 WQA-Aquatech UV Technology Workshop (Chicago) – Bruce Laing
 North American Conference on UV and Ozone Technologies (Boston) – Linda Gowman and Jeff Neemann
 UV in Water, Wastewater and Reuse Workshop (Singapore) – Rongjing Xie
 UV Session at 19th Ozone World Congress (Tokyo) – Kumiko Oguma
 5th UV World Congress (Amsterdam) – Linda Gowman
 European UV Regulatory Workshop (Amsterdam) – Andreas Kolch and Margarete Bucheli

Please Welcome our New IUVA Members (June – November):

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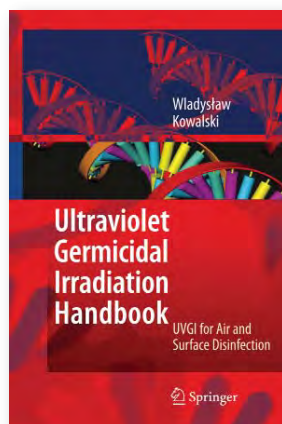
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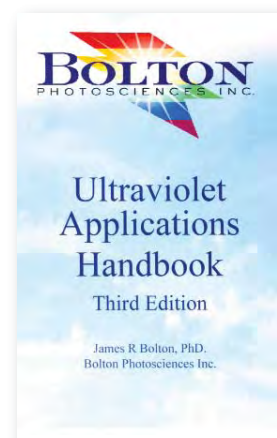
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PUBLICATIONS

We are pleased to announce that two of our members have published new or updated books on Ultraviolet Science and Technology.



Both books will be available through the IUVA. A separate order form with Table of Contents will be e-mailed to all members and posted on the IUVA website in 2010.



The following are interesting media items that may effect the UV Industry

2010 will feel Full Stimulus Boost for Water per Analyst

www.jmsonline.com/jms

The impact on water industry companies on most of the federal stimulus spending on water/wastewater infrastructure will be felt in 2010, financial analysts at investment firm Janney Montgomery Scott (JMS) wrote in a November 24 report.

After the current recession has run its course, growth rates in the municipal water and wastewater industry will resume during the next two to three years at their previous "catch-up" growth rates of 2 to 2-1/2 times the rise in gross domestic product, according to JMS. The report noted that \$30 billion to \$40 billion in annual funding is needed to fix the huge backlog in improvements of aging water infrastructure. The report also noted that "stimulus funding support hardly fills local demand."

House Passes Chemical, Water Security Legislation to strengthen security at America's chemical plants and drinking water, wastewater facilities

<http://transportation.house.gov>

The House of Representatives passed, by a vote of 230 to 193, the Chemical and Water Security Act of 2009. The bill strengthens security at America's chemical plants and drinking water and wastewater facilities by establishing risk-based and reasonable security standards for these critical assets. H.R. 2868 reauthorizes the Department of Homeland Security's (DHS) Chemical Facility Anti-Terrorism Standards (CFATS) program, which is slated to expire October 2010, and improves the program in many ways, according to the Committee on Energy and Commerce. It also authorizes the US Environmental Protection Agency (EPA) to establish similar security programs for drinking water and wastewater facilities.

A key feature of the Chemical and Water Security Act of 2009 requires the riskiest chemical facilities, drinking water facilities and water treatment works to assess and, when appropriate, implement methods to reduce the potential for and consequences of a terrorist attack.

Both bills contain a provision allowing government to require chemical facilities, including water and wastewater facilities, to use what a regulator perceives as being a safer chemical or process, known as inherently safer technology (IST). The chemical causing most concern at water treatment facilities is chlorine.

Singapore Reuse Systems stay in the News

<http://www.greentechmedia.com/articles/read/sewage-to-drinking-water-singapore-shows-the-way>

It was reported in November that another system for turning wastewater into drinking water for an island development in Singapore was set to go on line.

The Global Water modular system was delivered in March and put through testing by the project's developers and Singapore officials.

It is located at a new ferry terminal on Pulau Seringat, a man-made island adjacent to Singapore southeast of the island of Sentosa in the Singapore Strait. The development is planned to accommodate up to 1,500 people, including permanent residents and guests at two luxury hotels.

US\$2bn Stimulus for Drinking Water a Small Portion of Total Activity

www.mcilvaineconomy.com

Some 900 projects with \$2.0 billion in stimulus support are moving forward. But they represent a small portion of the total activity in municipal drinking water. Some of the recent project updates in the McIlvaine North American Public Water Plants and People testify to the larger scale of activity. A few include:

- Austin, TX approved a \$508 million water treatment plan to avoid a crisis.

- Rhode Island officials announced recently the awarding of an unprecedented

\$135 million in low-cost loans to 32 communities to increase drinking-water supplies/develop new pipelines and treatment facilities to reduce water pollution.

- The city of Pasco, TX needs to invest more than \$28 million over six years on its water treatment and distribution systems to meet regulatory requirements.

- Switching Waukesha, WI's water supply to Lake Michigan rather than groundwater wells would cost \$56 million in initial construction costs.

- Colorado Springs, CO utilities master plan calls for \$500 million in water treatment expenditures.

- The proposed Fullerton Water Plant in Baltimore, MD would cost \$360 million

Lunar Water Found - When will we treat it?

http://www.nasa.gov/mission_pages/LCROSS/main/prelim_water_results.html

NASA's recent "bombing" of the moon has revealed the presence of water in the crater Cabeus, near the moon's South Pole, according to a November 13 NASA statement.

NASA said in its statement that regions of the moon that are permanently in shadow, like the Cabeus crater, could hold a key to the history and evolution of the solar system, much like an ice core sample taken on Earth reveals ancient data. Water and other compounds also represent potential resources that could sustain future lunar exploration.

Continued to page 14

New Stormwater Rule Feedback Requested

<http://cfpub.epa.gov/npdes/stormwater/rulemaking.cfm>

The EPA proposed a survey to help strengthen stormwater regulations and reduce stormwater discharges from newly developed and redeveloped sites.

The agency said in a press release that it plans to propose a rule to control stormwater from newly developed and redeveloped sites, and to take final action no later than November 2012.

In support of this rulemaking, the EPA is proposing to require three different groups to complete questionnaires about current stormwater management practices: 1) the owners, operators, developers, and contractors of newly and redeveloped sites; 2) the owners and operators of municipal separate storm sewer systems; and 3) states and territories.

The draft survey would require detailed information about stormwater management and control practices, local regulations, and baseline financial information. The proposed survey will be open for public comment for 60 days following publication in the *Federal Register*.

EPA orders chemical testing for endocrine disruptors

<http://www.epa.gov/endo>

The EPA issued the first test orders for pesticide chemicals to be screened for their potential effects on the endocrine system with the Endocrine Disruptor Screening Program (EDSP) Tier 1 screening for the first group of 67 chemicals. The agency will start issuing test orders between Oct. 29, 2009, and Feb. 26, 2010.

The data generated from the screens will provide information to help the agency identify whether additional testing is necessary, or whether other steps are necessary to address potential endocrine disrupting chemicals. Testing, conducted through the agency's Endocrine Disruptor Screening Program, will eventually expand to cover all pesticide chemicals, the agency said in a press release. The agency will review the responses, evaluate the data, determine the potential of endocrine interaction, and whether additional testing is necessary to guide further regulation.

Catalunya Plans Future Indirect Potable Reuse

The Catalan water agency (ACA) has developed plans to have 275,000m³/d of indirect potable reuse capacity available for use in situations of extreme water shortage by 2020. The move is unprecedented for Spain, and follows recent uncertainty over the long-term viability of the country's desalination programme.

ACA has commissioned the Catalan water research institute (ICRA) to study the indirect potable use of wastewater treated by filtration, UV and chlorination at the Baix Llobregat WWTP and then pumped into the Llobregat river before potabilisation. The recycled water coming from the Baix Llobregat plant is being analysed according to 150 different parameters to assure that it reaches sufficient quality for potable use.

Once ICRA has issued its final report on the quality of the recycled water, the Catalan government public health department will take a decision on whether or not to authorise its emergency use for human consumption.

EPA Releases Guide to Help Scientists Understand Children's Exposure to Pollutants

<http://cfpub.epa.gov/ncea/CFM/recordisplay.cfm?deid=199243>

The US Environmental Protection Agency released a user-friendly document to help risk assessors understand how children are exposed to pollution. The document, titled "Highlights of the Child-Specific Exposure Factors Handbook," serves as a quick-reference guide to the more comprehensive "Child-Specific Exposure Factors Handbook".

Spain Risking Fines over Failure to Treat Wastewater

<http://ec.europa.eu/geninfo/query/resultaction.jsp?userinput=Spain%20wastewater>

The European Commission is sending Spain a final written warning for failing to implement a court ruling on the treatment of waste water in the area of Playa de la Motilla in the Valencia region. Under the Urban Waste Water Directive urban areas with more than 10,000 inhabitants are required to have adequate collection and treatment systems. Larger towns and cities across the European Union are required to collect and treat their urban waste water under the EU Urban Wastewater Treatment Directive.

US Congress boosts rural water funding

www.awwa.org/publications/StreamlinesArticle.cfm?itemnumber=51298

The US House and Senate recently agreed on an agriculture appropriations bill for fiscal year 2010 that gives rural water and wastewater programs more than the regular FY 2009 appropriation and more than what the Obama Administration had requested, the American Water Works Association's (AWWA) Streamlines.

According to AWWA, here's what the bill, HR 2997, appropriates for rural water and waste programs:

- Rural Utilities: Rural Water and Waste Disposal Program — \$568.7 million
- Environmental Quality Incentives Program — \$1.18 billion
- Water quality research — \$12.6 million
- Natural Resources Conservation Services — \$887.6 million.

The \$568.7 million for the Rural Water and Waste Disposal Program Account includes \$70 million for water and wastewater programs for Native American tribes and the Hawaiian Home Lands. It also includes \$19.5 million for technical assistance to rural water and wastewater systems, including \$15 million for the National Rural Water Association circuit rider program — a significant boost from FY 2009, when \$11.5 million was appropriated for that program.

EPA to begin new evaluation of Atrazine

<http://ec.europa.eu/geninfo/query/resultaction.jsp?userinput=Spain%20wastewater>

The US Environmental Protection Agency announced the agency's intent to launch a comprehensive new evaluation of atrazine, one of the most widely used agricultural pesticides in the United States, to determine its effects on humans.

EPA said it will evaluate the herbicide's potential cancer and non-cancer effects on humans, and will include in the new study "the most recent studies on atrazine and its potential association with birth defects, low birth weight, and premature births." The goal of

the evaluation, which will include the review of atrazine residues in public drinking water systems, is to help the agency decide whether to revise its current risk assessment of the herbicide and whether new restrictions are necessary to better protect public health.

According to the EPA, the agency's plan calls for a September 2010 presentation of its evaluation, at which time the agency will seek peer review. Atrazine is listed as a primary drinking water contaminant by the EPA. The agency now sets the maximum contaminant level (MCL) of atrazine in drinking water at 3 parts per billion (ppb) (3 micrograms per liter).

New EPA list of drinking water contaminants for regulatory consideration

<http://www.epa.gov/safewater/ccl/ccl3.html>

Emerging contaminants (ECs) such as pharmaceuticals and hormones, as well as disinfection byproducts, natural elements and pesticides, are among the substances on the US Environmental Protection Agency's (EPA) newly released list of potential future drinking water contaminants. These regulatory "contaminant candidates" are known or anticipated to occur in public water systems and may require regulation.

The EPA initially considered approximately 7,500 potential chemical and microbial contaminants. Rocket-fuel chemical perchlorate and the chemical used to make Teflon®, perfluorooctanoic acid (PFOA), are on the final CCL 3, the third list of its kind produced by EPA in recent years. In all, the CCL 3 includes 104 chemicals or chemical groups and 12 microbiological contaminants, including

E. coli. Other contaminants on the list include pesticides, herbicides, disinfection byproducts, pharmaceuticals, chemicals used in commerce, waterborne pathogens and algal toxins.

According to an agency statement, the EPA will make regulatory determinations for at least five contaminants in accordance with the Safe Drinking Water Act. For those CCL 3 contaminants that lack sufficient information for a regulatory determination by 2013, EPA will encourage research to provide the information needed.

Toxins Trickle through OH Debris Landfills

http://www.columbusdispatch.com/live/content/local_news/stories/2009/09/14/landfills.ART_ART_09-14-09_A1_5DF24GE.html?sid=101

An Ohio Environmental Protection Agency investigation has found the suspected carcinogens arsenic, benzene and vinyl chloride, as well as toxic levels of lead, in the water trickling through the rubble at 30 debris landfills it inspected. Debris landfills, home to old concrete, bricks and lumber, operate without plastic liners and extensive pollution monitoring and collection systems that are required at Ohio's 41 licensed municipal landfills.

Of the state's 55 debris landfills, 30 have waste-collection systems, ponds or pumps that make it possible to draw water. At each of these surveyed landfills, officials found as many as 29 pollutants at levels exceeding safe drinking water limits, pollution standards or both, the article said.

New York Times Exposé on Contaminated US Drinking Water

http://www.nytimes.com/2009/09/13/us/13water.html?_r=2

An estimated 1 in 10 Americans have been exposed to drinking water that contains dangerous chemicals or fails to meet a federal health benchmark in other ways, an investigation by *The New York Times* has found.

"Those exposures include carcinogens in the tap water of major American cities and unsafe chemicals in drinking-water wells. Wells, which are not typically regulated by the Safe Drinking Water Act, are more likely to contain contaminants than municipal water systems," the report said. It notes that many who consume dangerous chemicals through their drinking water do not realize it because "most of today's water pollution has no scent or taste."

The *Times* said its research included the review of "hundreds of thousands of water pollution records" from all 50 states and the US Environmental Protection Agency (EPA) obtained through Freedom of Information Act requests, as well as from more than 250 interviews with state and federal regulators, water-systems managers, environmental advocates and scientists. The *Times* compiled a national database of water pollution violations "that is more comprehensive than those maintained by states or the EPA," the report said.

The *Times* says its research shows that 40 percent of the nation's community water systems violated the Safe Drinking Water Act at least once last year. "Those violations ranged from failing to maintain proper paperwork to allowing carcinogens into tap water. More than 23 million people received drinking water from municipal systems that violated a health-based standard," the report said.

Turning Stormwater into Drinking Water

<http://www.csiro.au/news/Turning-stormwater-into-drinking-water.html>

Australia's Commonwealth Scientific and Industrial Research Organization (CSIRO) scientists have bottled 'Recharge', pure drinking water that was once stormwater.

The water was captured in the City of Salisbury, on the Northern Adelaide Plains in South Australia. It was stored under Salisbury in a porous limestone aquifer 160m below ground.

The stormwater was first treated by passing it through a reed bed or wetland to allow particle settling. It was then injected via wells into a limestone aquifer for storage and months of natural slow filtration through the aquifer. For extra safeguard and aesthetic quality the water was aerated, filtered through an activated carbon filter and it underwent microfiltration and ultraviolet disinfection.

After recovery the water was rigorously tested in National Association of Testing Authorities (NATA) accredited laboratories. 'Recharge' complies with the same health standards as tap and bottled water.

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A Kinetic Model for the Degradation of Natural Organic Matter During the Ultraviolet Hydrogen Peroxide Advanced Oxidation Process

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ABSTRACT

A completely dynamic, kinetic model was developed to predict the degradation of chromophoric natural organic matter (CNOM) and H_2O_2 during the UV/ H_2O_2 . Model parameters were estimated numerically by optimizing fitting to experimental results obtained with a "synthetic water" using Suwannee River NOM. The reaction rate constant for the reaction between hydroxyl radicals ($\bullet OH$) and NOM was estimated at $1.14E4 \text{ L mg}^{-1} \text{ s}^{-1}$, in close agreement with past literature reports. The reaction rate constant for the reaction between $\bullet OH$ and CNOM was estimated at $3.08E8 \text{ L mol}^{-1} \text{ s}^{-1}$. Considering the change in CNOM helped improved prediction of H_2O_2 degradation but the model still under predicted experimental measurements. This discrepancy is hypothesized to be due to the model's neglect of the reaction between H_2O_2 and carbon-centered radicals, formed when $\bullet OH$ react with NOM.

Key Words: Ultraviolet; Hydrogen peroxide; Natural organic matter; Advanced oxidation; Drinking water treatment; Kinetic model

INTRODUCTION

A number of models have been presented to characterize the ultraviolet (UV) plus hydrogen peroxide (H_2O_2) advanced oxidation process, termed UV/ H_2O_2 (1-4). Some of these models applied the assumption of pseudo steady-state hydroxyl radical ($\bullet OH$) concentration while others consider all species dynamic, including radicals. Existing models incorporate the $\bullet OH$ scavenging potential of natural organic matter (NOM) while few model the transformation of NOM. Those that do consider changes in NOM primarily target the mineralization of NOM and so, do not address its partial degradation under practical operation conditions.

In commercial drinking water UV/ H_2O_2 applications, the oxidation conditions (i.e., fluences and/or H_2O_2 concentrations) are not strong enough to mineralize NOM. Instead, significant partial oxidation of NOM takes place, leading to changes in water characteristics that in turn affect process efficacy and water quality (5,6). For example, the reduction in the absorbance of water at 254 nm UV leads to an increase in the photolysis of H_2O_2 , thereby increasing the rate of $\bullet OH$ production.

The focus of this research has been the development of a model that predicts partial degradation of NOM by incorporating a surrogate parameter, the absorbance of 254 nm UV, representing structural transformation of NOM (from aromatic to aliphatic) attributable to $\bullet OH$ attack. The portion of NOM that absorbs at 254 nm has been defined as chromophoric natural organic matter (CNOM). The

model treats all species (including radicals) under non-steady state conditions and predicts system parameters, such as components' concentration and absorbance trajectory.

MATERIALS AND METHODS

Experiments were conducted using "synthetic waters" in which isolated Suwannee River NOM (SRNOM) (International Humic Substances Society) was added to MilliQ water. UV/ H_2O_2 treatment was performed using a low pressure high output lamp (Trojan Technologies) housed in a collimated beam apparatus. Experiments were conducted at different irradiation times, initial H_2O_2 concentrations, and NOM concentrations (conditions presented in Table I).

A calibrated radiometer (IL1700, sensor SED240 for 254 nm, International Light Inc.) was used to determine the incident photon fluence rate following the actinometry method given by (7). TOC was measured using a Sievers 900 TOC analyzer. The degradation of CNOM was monitored using a spectrophotometer (Cary 100, Varian Inc.). H_2O_2 concentration was measured by reaction with iodide catalyzed by molybdate (8). The scavenging rate of the NOM was determined by competition kinetics with the $\bullet OH$ probe 4-chloro-benzoic acid (pCBA), which was measured by HPLC (Waters 600-MS) with Waters 996 photodiode array detector and Supelcosil LC-18 column.

The following system of equations was used to model the reactions (Table II) of UV/H₂O₂ system:

$$[1] \frac{d[H_2O_2]}{dt} = k_{a,H_2O_2,254} H_2O_2 \cdot OH [H_2O_2] - k_2 [\bullet OH][H_2O_2] - [H_2O_2] - k_3 [\bullet OH][HO_2^-] - k_7 [O_2^{\bullet -}][H_2O_2] - k_{10} [HO_2^{\bullet}][H_2O_2] - k_6 [\bullet OH]^2 + k_8 [O_2^{\bullet -}][HO_2^{\bullet}] + k_9 [HO_2^{\bullet}]^2$$

where

$$[2] k_{a,H_2O_2} = \frac{E_p^z \epsilon_{H_2O_2} [1 - 10^{-aZ}] \times 1000}{aZ}$$

In Equation [2], E_p^z is the incident photon fluence rate (Es cm⁻² s⁻¹) and Z is the pathlength (2.95 cm).

$$[3] a = [H_2O_2] \epsilon_{H_2O_2} + CNOM$$

In Equation [4], a is the total water absorption coefficient at 254 nm (cm⁻¹), $\epsilon_{H_2O_2}$ was the decadic molar absorption coefficient of H₂O₂ at 254 nm (19.6 M⁻¹ cm⁻¹) and CNOM was adsorption coefficient of chromophoric NOM which, by definition, only absorbed at 254 nm.

$$[4] [HO_2^-] = \frac{K_a [H_2O_2]}{[H^+]}$$

$$[5] \frac{d[\bullet OH]}{dt} = -k_2 [\bullet OH][H_2O_2] - k_3 [\bullet OH][HO_2^-] - k_4 [\bullet OH][HO_2^{\bullet}] - k_5 [\bullet OH][O_2(\bullet-)] - [(2k) 6[\bullet OH]_2 - k_{OH,TOC9Hsystem}$$

$$[6] \frac{d[O_2^{\bullet -}]}{dt} = k_4 [\bullet OH][HO_2^{\bullet}] - k_5 [\bullet OH][O_2^{\bullet -}] - k_7 [O_2^{\bullet -}][H_2O_2] - k_8 [HO_2^{\bullet}] - 2k_9 [HO_2^{\bullet}]^2 - k_{10} [HO_2^{\bullet}][H_2O_2] + k_2 [\bullet OH][H_2O_2] + k_3 [\bullet OH][HO_2^-]$$

$$[7] [HO_2^{\bullet}] = \frac{[H^+][O_2^{\bullet -}]}{K_{a2}}$$

$$[8] \frac{d[pCBA]}{dt} = -k_{OH,pCBA} [\bullet OH][pCBA]$$

$$[9] \frac{dCNOM}{dt} = -k_{OH,CNOM} [\bullet OH]CNOM$$

All the reaction rate constants (Table II) were given except for $k_{OH,CNOM}$ and $k_{OH,TOC9Hsystem}$. These two parameters were numerically estimated by maximum likelihood estimation.

RESULTS AND DISCUSSION

The experimental results from UV/H₂O₂ treatment of SRNOM synthetic water are given in Figure 1. Using this experimental data and the set of model expressions given above, the two unknown rate parameters $k_{OH,CNOM}$, and $k_{OH,TOC9Hsystem}$, were estimated simultaneously using maximum likelihood estimation. Given as lines in Figure 1 are model predictions using the estimated rate parameters.

Scavenging of hydroxyl radical by natural organic matter

The observed rate of degradation of pCBA increased with increasing the initial H₂O₂ concentration (Figure 1). As an increase in H₂O₂ yielded a greater concentration of $\bullet OH$, the increase in the degradation of the pCBA was expected. Further, as TOC was increased, there was a reduction in the observed rate of degradation of pCBA. Again, this was expected as a greater concentration of NOM would lead to greater scavenging of $\bullet OH$ by NOM, in turn reducing observed rate of degradation of pCBA.

From the parameter estimation, the reaction rate constant for the reaction between $\bullet OH$ and TOC, $k_{OH,TOC9Hsystem}$, was estimated at 1.14E4 L mg⁻¹ s⁻¹. Literature reports for $k_{OH,TOC9Hsystem}$ for SRNOM fractions and isolated NOM originating from different sources are presented in Table II. The $k_{OH,TOC9Hsystem}$ estimated in this study for SRNOM agreed reasonably well with literature reports for $k_{OH,TOC9Hsystem}$ for fulvic and humic fractions of SRNOM. The estimated value, 1.14E4 L mg⁻¹ s⁻¹, was within error of the value reported by Westerhoff et al. (9) for SRNOM fulvic acid using pulse radiolysis with competition kinetics and direct transient growth (1.33±0.2 E4 L mg⁻¹ s⁻¹). Slightly higher were the



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values for SRNOM humic acid reported by Goldstone et al. (10) using γ -radiolysis with competition kinetics ($1.9 \pm 0.05 \text{ E4 L mg}^{-1} \text{ s}^{-1}$). About three-fold the value estimated in this study were the values reported by Goldstone et al. (10) for SRNOM fulvic acid ($2.7 \pm 0.05 \text{ E4 L mg}^{-1} \text{ s}^{-1}$) and by Westerhoff et al. (11) for SRNOM fulvic acid ($3.08 \text{ E4 L mg}^{-1} \text{ s}^{-1}$) using ozonation with competition kinetics. This variation between reported $k_{\bullet\text{OH},\text{TOC}9\text{Hsystem}}$ values demonstrates that estimation of the parameter is subject to the method used for $\bullet\text{OH}$ production (i.e. ozonation, UV/ H_2O_2 , pulse radiolysis, γ -radiolysis, or nitrate-induced solar driven photolysis), as well as the type of NOM employed (i.e., aquatic isolate, fulvic or humic isolates). Yet, it is apparent that $k_{\bullet\text{OH},\text{TOC}9\text{Hsystem}}$ has been estimated to fall within a range from roughly 1E4 to $4\text{E4 L mg}^{-1} \text{ s}^{-1}$ (Table III). The $k_{\bullet\text{OH},\text{TOC}9\text{Hsystem}}$ estimated in this work lies within this range.

Degradation of chromophoric natural organic matter

It was observed that as the initial H_2O_2 concentration was increased, the observed rate of degradation CNOM increased. As discussed earlier, an increase in H_2O_2 would

yield a greater concentration of $\bullet\text{OH}$ thereby increasing the degradation of CNOM. From parameter estimation, $k_{\bullet\text{OH},\text{CNOM}}$ was estimated at $3.04\text{E8 L mol}^{-1}\text{s}^{-1}$. Future research will present the ability of the model, using the two parameters estimated for synthetic water, to predict changes in CNOM for natural waters.

Prediction of the change in CNOM is deemed important since in the UV/ H_2O_2 system CNOM is often the major absorber of photons. Any change in CNOM would have an impact on water absorption coefficient, a (Equation [3]), the photolysis of H_2O_2 (Equation [2]), and subsequently the concentration of $\bullet\text{OH}$. A reduction in CNOM would lead to greater absorption of photons by H_2O_2 thus improving photolysis and $\bullet\text{OH}$ production. Therefore, it was clear that by considering the change in CNOM, prediction of H_2O_2 degradation would be more accurate.

Hydrogen peroxide degradation

Interestingly, the observed rate of degradation of H_2O_2 was not greatly affected by the change in TOC. That is, about 20% degradation of H_2O_2 was observed for all three concentrations of TOC. Also, the model did not accurately

Figure 1: Experimental results (points) and model predictions (lines) for pCBA, CNOM, and H_2O_2 for synthetic water treated by UV/ H_2O_2 are varying levels of TOC, initial H_2O_2 concentration, and irradiation time.

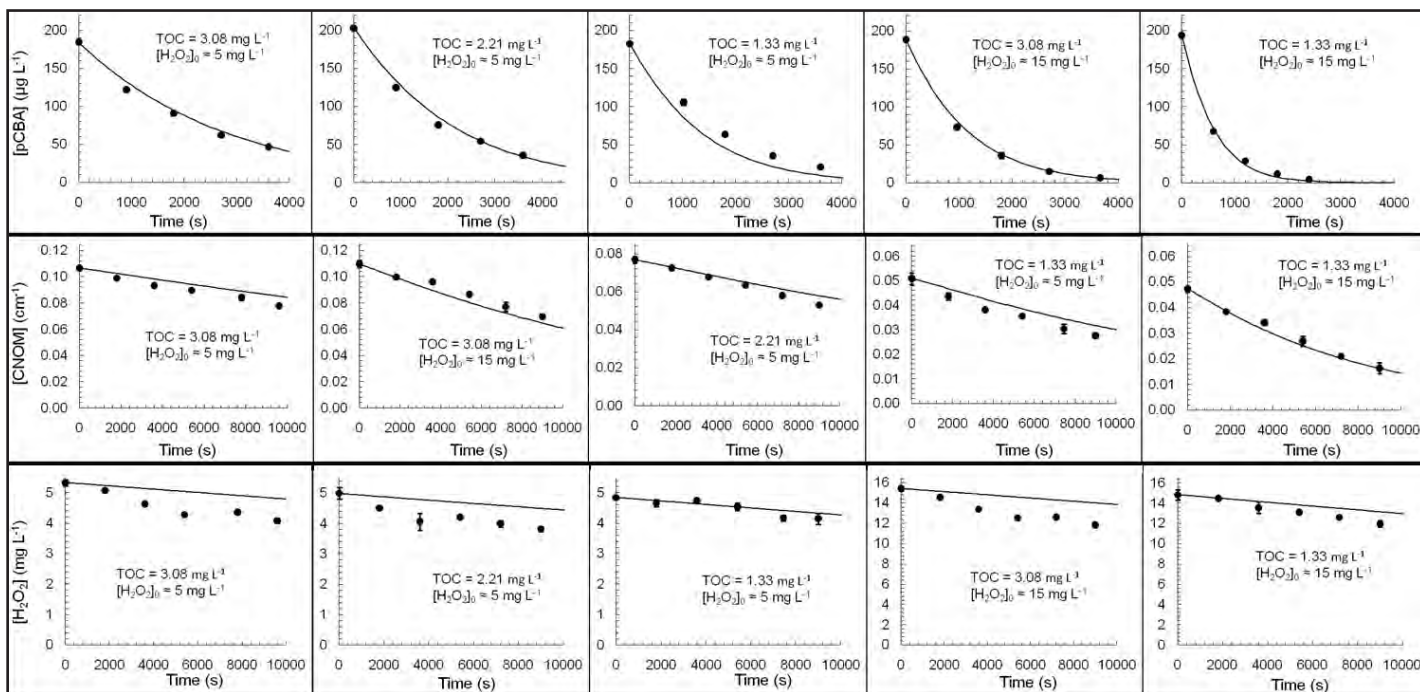


Table I. Experimental conditions for UV/ H_2O_2 treatment of synthetic water

NOM Source	Suwannee River
Total organic carbon (mg L^{-1})	1.33, 2.21, 3.08
A254 (cm^{-1})	0.049, 0.065, 0.108
Irradiation time (min)	0, 30, 60, 90, 120, 150
Initial H_2O_2 concentration (mg L^{-1})	5, 15

Table II. Series of reactions and corresponding rate constants for kinetics model

Reaction	Rate constant	Reference
1 $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\cdot\text{OH}$	$\Phi^{H_2O_2, \cdot OH} = 0.5$ (primary quantum yield)	(12)
2 $\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2\cdot^- + \text{H}_2\text{O} + \text{H}^+$	$k_2 = 2.7\text{E}7 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
3 $\cdot\text{OH} + \text{HO}_2^- \rightarrow \text{O}_2\cdot^- + \text{H}_2\text{O}$	$k_3 = 7.5\text{E}9 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
4 $\cdot\text{OH} + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k_4 = 6.6\text{E}9 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
5 $\cdot\text{OH} + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k_5 = 8.0\text{E}9 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
6 $\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$	$k_6 = 5.5\text{E}9 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
7 $\text{O}_2\cdot^- + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2$	$k_7 = 0.13 \text{ L mol}^{-1} \text{ s}^{-1}$	(14)
8 $\text{O}_2\cdot^- + \text{HO}_2\cdot + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH}^- + \text{O}_2$	$k_8 = 9.7\text{E}7 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
9 $\text{HO}_2\cdot + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k_9 = 8.6\text{E}5 \text{ L mol}^{-1} \text{ s}^{-1}$	(15)
10 $\text{HO}_2\cdot + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{H}_2\text{O} + \text{O}_2$	$k_{10} = 3.7 \text{ L mol}^{-1} \text{ s}^{-1}$	(14)
11 $\text{H}_2\text{O}_2 \leftrightarrow \text{H}^+ + \text{HO}_2^-$	$k_{a1} = 10^{-11.6}$	(16)
12 $\text{HO}_2\cdot \leftrightarrow \text{H}^+ + \text{O}_2\cdot^-$	$k_{a2} = 10^{-4.8}$	(16)
13 $\cdot\text{OH} + \text{pCBA} \rightarrow \text{products}$	$k_{\cdot\text{OH}, \text{pCBA}} = 5\text{E}9 \text{ L mol}^{-1} \text{ s}^{-1}$	(17)
14 $\cdot\text{OH} + \text{TOC} \rightarrow \text{products}$	$k_{\cdot\text{OH}, \text{TOC}} = ? \text{ L mg}^{-1} \text{ s}^{-1}$	
15 $\cdot\text{OH} + \text{CNOM} \rightarrow \text{products}$	$k_{\cdot\text{OH}, \text{CNOM}} = ? \text{ L mol}^{-1} \text{ s}^{-1}$	

Table III. Literature reported values for $k_{\cdot\text{OH}, \text{TOC}9\text{Hystem}}$

NOM Source	$k_{\cdot\text{OH}, \text{TOC}9\text{Hystem}}$ ($\text{L mg}^{-1} \text{ s}^{-1}$)	Determination Method	Reference
Suwannee River NOM Isolate	1.14E4	UV/H ₂ O ₂ : competition kinetics	Present work
Suwannee River Fulvic Acid	(1.33±0.2)E4	Pulse radiolysis: competition kinetics and direct transient growth	(9)
Suwannee River Fulvic Acid	3.08E4	Ozonation: competition kinetics	(11)
Suwannee River Fulvic Acid	(2.7±0.04)E4	γ-radiolysis: competition kinetics	(10)
Suwannee River Humic Acid	(1.9±0.04)E4	γ-radiolysis: competition kinetics	(10)

predict H₂O₂ degradation, under predicting the actual concentrations (**Figure 1**). Similar to the UV/H₂O₂ models presented in the literature, the model presented here assumed photolysis to be the primary pathway for H₂O₂ degradation. If this assumption were to be correct, an increased TOC would lead to slower degradation of H₂O₂ since TOC increase would lead to higher CNOM and subsequently the water absorbance. This would result in additional screening of UV and a reduction in the number of photons absorbed by H₂O₂.

This limitation was to some extent addressed in our model which included the change in water absorbance which affects the modelling of H₂O₂ degradation. Despite improving model predictions to some extent, the model developed here, as have past models, under predicted H₂O₂ degradation. Higher observed degradation of H₂O₂ is hypothesized to be due to H₂O₂ reaction with carbon-centred radicals that are formed when $\cdot\text{OH}$ reacts with

NOM. Future research is clearly needed to define expressions to more accurately predict H₂O₂ degradation during UV/H₂O₂ advanced oxidation of water in which NOM is present.

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ULTRAVIOLET DISINFECTION SOLUTIONS

Approach for Achieving Sustainable Operation of the 2-bgd Catskill/Delaware UV disinfection Facility

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ABSTRACT

Recent advances in testing methods are being applied to the validation of NYC's Catskill/Delaware UV equipment. These advanced methods will allow the full scale facility to operate in a more sustainable manner with up to 50% reduction in operating power requirements (and corresponding reduction in carbon dioxide emissions) and savings of over \$1 million annually.

Key Words: UV disinfection, Dyed microspheres, Validation, Sustainable

INTRODUCTION

The design of the Catskill/Delaware UV disinfection facility commenced in 2001, concurrent with the development of the Long Term 2 Enhanced Surface Water Treatment Rule (LT2). The intent of the LT2 is to ensure protection of public health, particularly regarding infection by *Cryptosporidium*. The New York City Department of Environmental Protection (NYCDEP) has specifically undertaken the design and construction of the Catskill/Delaware UV facility in order to meet the requirements of LT2. At the time of design and validation testing, the LT2 was not final, nor was the UV Disinfection Guidance Manual (UVDGM), which prescribes the validation protocol. Therefore, not only was the design criteria for the UV facility conservative, but also the validation testing because NYCDEP wanted to ensure that the UV facility would meet the requirements of the rule when finalized. Essentially, the conservative design criteria and validation testing impacted the applied dose and capacity of the UV equipment, both of which directly affect the size of the UV units and therefore the footprint of the UV disinfection facility. NYCDEP is currently conducting additional validation testing with dyed microspheres (DMS) and other advanced surrogates, allowing for increased certainty of the applied dose, while reducing the power required to achieve proper disinfection by over 18,500 kWhrs per day – enough energy to power nearly 1,000 homes. This paper presents the results of the validation testing and the approach the City of New York is taking to ensure a sustainable operation of the Catskill/Delaware UV Disinfection Facility.

BACKGROUND

NYCDEP is implementing UV disinfection in the Catskill/Delaware Water Supply System in compliance with the United States Environmental Protection Agency's (USEPA) Filtration Avoidance Determination (FAD) – the UV facility is scheduled to be online in 2012. UV disinfection in combination with chlorine disinfection, which is currently in place, provides a multiple disinfection barrier against bacteria, viruses, and protozoa like *Cryptosporidium* and *Giardia*. The Catskill/Delaware system is required under LT2 to provide disinfection for 2-log inactivation of *Cryptosporidium*, 3-log inactivation of *Giardia* and 4-log inactivation of viruses. The doses required by LT2 to achieve inactivation of *Cryptosporidium* are shown in Table I. The Catskill/Delaware system is conservatively designed to achieve a 3-log inactivation of *Cryptosporidium* with UV disinfection alone, a 3-log inactivation of *Giardia* through a combination of UV and chlorine disinfection and 4-log inactivation of viruses with chlorine disinfection.

Table 1: Experimental conditions for uv/h₂O₂ treatment of synthetic water

Regulatory Dose Requirement (mJ/cm ²)	Log Inactivation of <i>Cryptosporidium</i>		
	2.0	2.5	3.0
	5.8	8.5	12

USEPA Approach to Validation

In order to effectively and safely verify the effectiveness of UV equipment and establish the disinfection effectiveness, referred to as the reduction equivalent dose (RED), testing (i.e. validation) is required and furthermore is mandated by the LT2. Surrogate organisms are typically used because there are inherent dangers and challenges of validating equipment with the target organism, in the case of Catskill/Delaware – *Cryptosporidium*. However, using a surrogate results in inherent differences compared to the target organism – mainly because the target organism and the surrogate organism exhibit different sensitivities to UV light. The validation protocol set forth in the UVDGM accounts for these differences through the RED bias factor to ensure the RED achieved correlates properly to the required UV dose – as set forth in the LT2 – for the target organism.

Until recently, the surrogate microbe MS2 was the industry standard in the United States for establishing disinfection effectiveness through validation testing of a UV unit. The general consensus in the United States was that MS2 was easier to work with and the best surrogate to conservatively estimate the disinfection efficacy for larger capacity (i.e., greater than 5 mgd) UV units – despite the use of other types of surrogates for validation testing in Europe, like *Bacillus subtilis*. Only recently (i.e., post-2005) have other, more efficient surrogates such as Q-beta and T1 been identified and used for validating UV equipment in the US. The 2003 USEPA Draft UVDGM established guidelines for an RED approaching 40 mJ/cm² for 3-log inactivation of *Cryptosporidium*. Therefore, an RED of 40 mJ/cm² was selected as the design criteria for the Catskill/Delaware UV facility design. However, the final UVDGM, issued in 2006, changed how the RED bias was calculated and the manual permitted validation with surrogates other than MS2, such as Q-beta, which exhibits a sensitivity towards UV light that is more similar to *Cryptosporidium* and therefore, could significantly reduce the RED bias of a UV unit. In order to do so, the RED bias and other uncertainties encountered during a validation are calculated and incorporated into an overall ‘uncertainty factor of validation’ or what is referred to as the Validation Factor. To ensure the regulated dose is achieved, the following equation is applied:

Required Regulated Dose ≤	Validated RED	[1]
	Validation Factor (VF)	
Whereas, $VF = RED_{bias} \times (1 + U_i)$		
$U_i = \text{Uncertainty of Validation (\%)}$		

More recently, advances have been made in the application of chemical actinometry, which uses non-biological surrogates, such as DMS, to provide a greater understanding of the treatment characteristics of a unit.

Lagrangian Actinometry

Researchers at Purdue University, led by Professor Ernest R. Blatchley III of the School of Civil Engineering, developed a method known as Lagrangian actinometry (LA) that allows direct measurement of the dose distribution. (Shen, *et al.*,

2005; Blatchley, *et al.*, 2006) The actinometry process uses dyed microspheres that correlate dose measurement at a physical scale to that of an individual microorganism. The microspheres, which have size and density characteristics similar to the target organism, mimic the trajectories of individual microorganisms in actual treatment settings. The dye undergoes a photochemical reaction when exposed to UV radiation, yielding a stable, fluorescent compound that can be easily and accurately differentiated from the non-fluorescent parent compound (**Figure 1**). The fluorescence measurements are carried out in a flow cytometer, an instrument that can develop accurate fluorescence measurements for thousands of microspheres in a matter of minutes. Methods for characterization of a UV unit by DMS is similar to the methods with biological surrogates and consist of introducing a population of DMS upstream of a UV unit and collecting effluent samples for analysis of fluorescence among the captured microspheres. The significant benefit of DMS is that by measuring the actual dose distribution delivered by a UV unit, the RED bias is eliminated and therefore the Validation Factor can be significantly reduced through increasing the certainty of the delivered dose.

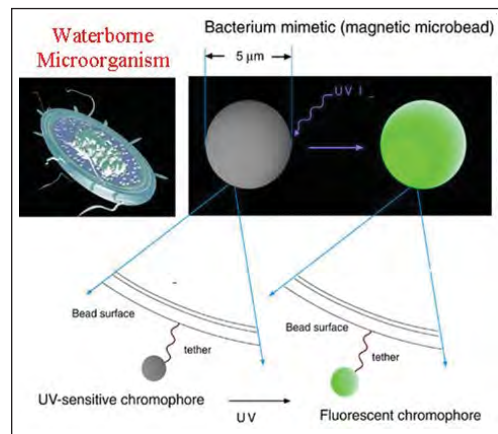


Figure 1: Representation of the Dyed-Microspheres Actinometry Process

Catskill/Delaware UV Unit Selection

As no UV units with capacities greater than 20 mgd were commercially available, the NYCDEP undertook a novel equipment selection and procurement process to ensure the best UV units would be used for the Catskill/Delaware UV Facility. The NYCDEP procured a single UV unit from two UV system suppliers - and validated both at the New York Validation and Research Center of New York. The validation was conducted by HydroQual Inc. and was performed according to the UV Disinfection System Validation Work Plan which was prepared based on the Draft UVDGM and provided to the New York State Department of Health (NYSDOH) for approval prior to the validation. The details of procurement and testing were reported by Valade, *et al* (2005).

The selected design capacity for the UV units was 40 mgd largely due to validation testing facility limitations; at the

time, the largest validation facility had a test capacity of 20 mgd. The design UV transmittance (UVT) selected was 87%, which represents the 5th percentile of historical Catskill/Delaware water quality UVT data. Validation testing was performed in 2005 to ensure the UV units selected were able to provide the required dose at the design flow and UVT. While both UV units met the design requirements and delivered a nominal dose of 40 mJ/cm², the NYCDEP selected Trojan Technologies Inc. as the sole-source supplier based on a life cycle cost analysis.

UV Facility Description

Each Trojan UV unit is a stainless steel pressure vessel and contains arrays of low pressure high output (LPHO) lamps mounted in a cross flow configuration and is outfitted with UV intensity sensors. A UV unit (**Photo 1**) contains 210 LPHO UV lamps mounted inside the unit but is capable of containing up to 240 lamps. For operational purposes the 210 lamps in the UV unit are separated into three banks and the unit was validated to operate with 90, 150, or 210 lamps online. Each lamp is protected by a quartz sleeve.

The UV Facility contains four UV modules for the Catskill/Delaware water supply. Each UV module is connected to a separate raw water header and consists of 14 UV units for a total of 56 UV units within the UV Facility. Each of the 56 UV units was designed to treat 40 mgd at the design conditions of 87% UVT, achieving the maximum design capacity of 2,020 mgd for the UV facility, with five standby UV units available, equivalent to 10% UV unit redundancy at the maximum design capacity. Each process train consists of an upstream isolation butterfly valve and magnetic flow meter, UV disinfection unit, and a downstream butterfly control/isolation valve.



Photo 1: Installation of UV Lamp Sleeves in Catskill/Delaware UV Unit

Catskill/Delaware Validation

Validation testing of the Trojan UV unit conducted in 2005 was performed with both MS2 and Q-beta as surrogates. A large set of data set for the Trojan unit was established over a wide range of operating conditions. Flows between 20 and 60 mgd and UVT's of 85, 90 and 95% were used. In order to allow efficient operation of a UV unit over the wide

range of flow and UVT, the number of lamps in operation was also varied. Nearly 100 discrete operating points were evaluated in order to develop a robust operating range of the Catskill/Delaware UV unit. As part of the initial testing of the Trojan UV unit, testing using dyed microspheres was conducted during the preliminary development of the Lagrangian Actinometry testing procedures.

Based on the current requirements of NYSDOH to achieve an RED of 40 mJ/cm², the maximum Validation Factor that would be allowed to ensure the regulated dose is achieved is 3.33 based on Equation 1.

$12 \text{ mJ/cm}^2 \leq$	40 mJ/cm ²
	Validation Factor
Maximum Validation Factor based on 40 mJ/cm ² MS2 Requirement	≤ 3.33

At the time of the development of validation protocol for the Catskill/Delaware UV unit, significant investigations were on-going into alternate validation surrogates that more closely represent the dose response characteristics of *Cryptosporidium*. (Clancy, 2004) The most significant benefit of using a surrogate that more closely mimics the dose response of the actual target organism (i.e. *Cryptosporidium*) is that a reduction in the RED bias will be achieved and therefore a reduction in the Validation Factor that must be applied to the validated dose to ensure the appropriate regulated dose is achieved. As input power to a UV unit is directly proportional to delivered dose, reducing the Validation Factor of a UV unit allows less power to be used to achieve a specific regulated dose, as the certainty of the validation results has been increased. (Fallon, 2007) If a Validation Factor is reduced by 50 percent, the resulting power required to achieve the same regulatory log inactivation of a target organism will be reduced by a corresponding 50 percent. This would result in significant operating cost savings for utilities without adversely impacting public health.

Due to the success of these early tests, NYCDEP is currently undertaking additional validation testing that will provide a validation dataset using DMS, as well as additional data for T1 as the surrogate, across the full operating range tested in 2005. The benefits to New York City of using these additional surrogates are presented below.

Results of Catskill/Delaware Validation

Validation factors were calculated for MS2 and Q-beta, based on the validation testing of the Trojan UV unit in 2005. Factors were also estimated for DMS as only limited data was available from the 2005 testing. The DMS Validation Factors were estimated using similar uncertainty values as the MS2 and Q-beta results. Although the validation factors developed for the biological surrogates vary with the target log inactivation and UVT, conservative estimates are provided herein for discussion purposes. At the

design UVT of 87%, the estimated Validation Factors are:

	2-log	3-log
MS2	2.77	2.42
Q-beta	2.11	1.77
DMS	1.20	1.20

Because these validation factors are significantly lower than the maximum required by the current 40 mJ/cm² RED requirement, more efficient and sustainable operation of the UV unit could be achieved while still meeting and exceeding the federal regulations (i.e., the LT2). **Table II** details the power required to operate the Trojan UV unit at various flow rates for 3-log *Cryptosporidium* inactivation levels, and 91% UVT (the average historical Catskill/Delaware UVT), and the same end of lamp life conditions as the basis of design, which is 91 percent of the new lamp output.

Table II: Power required for 3-log *Cryptosporidium* Inactivation with Catskill/Delaware UV Unit

Q (mgd)	Power Required per Unit (kW)			
	MS2	QB	DMS	40 mJ/cm ²
20	14.53	12.30	9.93	17.34
40	21.02	17.79	14.36	29.98
60	31.19	26.39	17.82	41.85

Evaluation of UV Unit Capacity Impact on Capital Cost

The layout of the Catskill/Delaware UV Facility is based on a UV unit capacity of 40 mgd, resulting in a sizeable footprint and capital cost exceeding \$1 billion. Theoretically, using higher capacity UV units would have resulted in a smaller footprint and a corresponding reduction in the capital cost. The theoretical UV unit treatment capacity was calculated based on MS2 and Q-beta validation data (**Table III**). Validation data from the Trojan unit shows that 3-log inactivation of *Cryptosporidium* can theoretically be achieved with flow rates of at least 80 mgd and 2-log inactivation can be achieved for flows well in excess of 90 mgd. These results are based on testing with Q-beta as the surrogate following the UVDGM procedures. A capacity of 60-mgd per unit would allow for a reduction to 10 units per module from the design of 14 units per module, resulting in a significant reduction in footprint from the current design.

Theoretically a capacity of at least 80 mgd can be achieved with the Trojan unit as configured while still maintaining greater than 3-log inactivation of *Cryptosporidium*, although validation testing has not been performed at this flow rate and would need to be conducted to achieve regulatory approval. This would allow for a reduction to 9 units per module and an even greater reduction in the footprint of the facility.

Even higher capacities could be achieved by using DMS as the validation surrogate. **Table IV** provides theoretical

Table III: Performance Characteristics of Catskill/Delaware UV Unit for MS2 and Q-beta Validation Surrogates

Flow (mgd)	Validated RED (mJ/cm ²)	MS2				Q-beta				Duty Units Required	Units per Module**	Headloss (in.)
		Validated Dose* (mJ/cm ²)		Validated: Regulated Dose Ratio†		Validated Dose* (mJ/cm ²)		Validated: Regulated Dose Ratio†				
		2-log	3-log	2-log	3-log	2-log	3-log	2-log	3-log			
40	42.5	15.3	17.6	2.75	1.28	20.1	24.0	3.46	2.00	51	14	14.5
50	34.2	12.3	14.1	2.13	1.03	16.2	19.3	2.79	1.61	41	12	21.2
60	28.6	10.3	11.8	1.78	0.86	13.5	16.1	2.33	1.34	34	10	29.0
70	24.6	8.9	10.2	1.53	0.74	11.6	13.9	2.01	1.16	29	9	38.0
80	21.6	7.8	8.9	1.34	0.65	10.2	12.2	1.76	1.02	26	8	48.2
90	19.3	7.0	8.0	1.20	0.58	9.1	10.9	1.57	0.91	23	7	59.7

* Validated dose = RED/VF; †Validated:Regulated Dose Ratio Values greater than 1.0 meet regulatory requirements

Table IV: Performance Characteristics of Catskill/Delaware UV Unit for DMS Validation Surrogate

Flow (mgd)	Validated RED (mJ/cm ²)	DMS				Duty Units Required	Headloss (in.)
		Validated Dose* (mJ/cm ²)		Validated: Regulated Dose Ratio†			
		2-log	3-log	2-log	3-log		
40	42.5	35.4	35.4	6.11	2.95	51	14.5
50	34.2	28.5	28.5	4.91	2.37	41	21.2
60	28.6	23.8	23.8	4.11	1.99	34	29.0
70	24.6	20.5	20.5	3.54	1.71	29	38.0
80	21.6	18.0	18.0	3.10	1.50	26	48.2
90	19.3	16.1	16.1	2.77	1.34	23	59.7
100	17.4	14.5	14.5	2.50	1.21	21	72.3
110	15.8	13.2	13.2	2.28	1.10	19	86.1
120	14.5	12.1	12.1	2.09	1.01	17	101.2
130	13.5	11.2	11.2	1.93	0.93	16	117.4
140	12.5	10.4	10.4	1.80	0.87	15	134.8

* Validated dose = RED/VF; †Validated:Regulated Dose Ratio Values greater than 1.0 meet regulatory requirements

treatment capacities of the UV unit based on extrapolation of the existing validation data.

Although the Trojan UV units could, theoretically, be rated for up to 120-mgd and still achieve 3-log inactivation credit, the headloss at flow rates higher than 50 mgd is substantial, exceeding the design criteria of 18 inches, and not feasible for Catskill/Delaware. As only 18-inches of head is available to be lost through the UV units at the maximum flow plant flow rate of 2,020-mgd; this headloss is equivalent to a flow rate of approximately 46 mgd through the Trojan UV unit. Therefore, only a minimal reduction in the number of UV units could be achieved. Furthermore, as with most UV facilities, the hydraulic elements of the facility, which enable water to flow to and from the UV equipment, represent the largest portion of the capital cost of a facility and more than 80% of the Catskill/Delaware facility capital costs. Therefore, significant capital cost savings would not be realized by increasing the capacity of the units.

The benefit of lower Validation Factors for the Catskill/Delaware UV Facility is that the operation of the UV units could be performed with fewer lamps on-line and therefore lower power consumption, thereby reducing operational costs as compared to the MS2 Validation Factors.

Evaluation of Validation Surrogate Impact on Catskill/Delaware UV Operations

Under the requirements of LT2 and the UVDGM, there is no prescribed minimum Validation Factor that the installed equipment must have. However, NYSDOH has currently imposed a minimum RED of 40 mJ/cm², which essentially requires that the Validation Factor for the Catskill/Delaware UV equipment be 3.33. The Catskill/Delaware equipment meets this requirement at the original design capacity of 40-mgd, but the lower Validation Factors that are allowed under the federal guidance would allow for significant reductions in the number of lamps required to achieve the Catskill/Delaware UV disinfection requirements and consequently a corresponding reduction in the power usage and UV unit consumables (e.g., ballasts, lamps, sleeves, sensors, etc.). Additionally, with fewer lamps required to achieve the required level of disinfection, the Facility could be operated with fewer UV units in service under many conditions, thereby requiring a lower number of UV units to be cleaned each month and reducing the volume of cleaning chemicals required. The reduction in power, consumables and cleaning chemicals will directly result in reduced operating costs and carbon footprint of the facility, thereby providing for a more sustainable operation of the Catskill/Delaware UV facility.

The power requirement, the number of UV units and lamps in operation and the associated operating costs were calculated based on the MS2, Q-beta and DMS using the UVDGM protocols, as well as the current 40 mJ/cm² requirement, in order to evaluate the impact of the validation surrogate on the Catskill/Delaware operations. Operating costs were developed based on expected average monthly plant flows and water quality for the initial year of

operation (2012) and future operation (2045) (Figure 2). All costs are reported 2009 dollars.

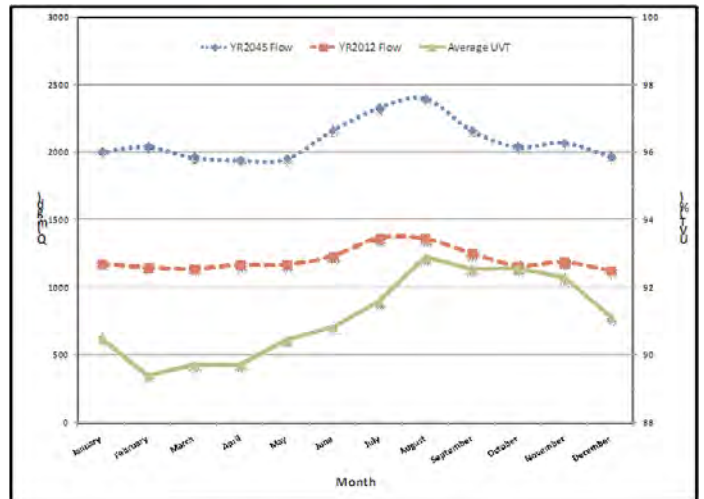


Figure 2: Average UVT and Flow Rates for Years 2012 and 2045

For the Catskill/Delaware facility, the requirement for using an RED of 40 mJ/cm² (based on MS2) in lieu of applying the USEPA recommended protocols will cost an additional \$165,000 in electric power costs in the first year of operation alone. The costs savings would increase to \$280,000 and \$380,000 if Q-beta or DMS were used, respectively, and nearly double by the year 2045 (Figure 5). Although significant power savings could be achieved through use of one of the advanced surrogates, other

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operational savings would be realized as well. As less power is required to achieve the required level of disinfection, fewer UV unit consumables such as lamps, sleeves and ballasts would be required. In addition, as fewer UV units

would need to be on-line in order to achieve disinfection of the plant flow, cleaning of few reactors each month we need to be performed each month, thereby reducing the volume of cleaning chemical consumed. The estimated annual operating costs (including power) based on the

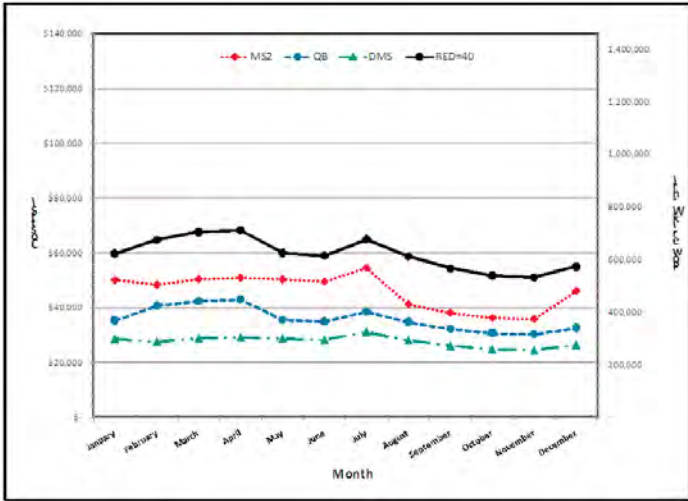


Figure 3: Monthly Power Costs for Various Surrogates – Year 2012 (in Year 2009 dollars)

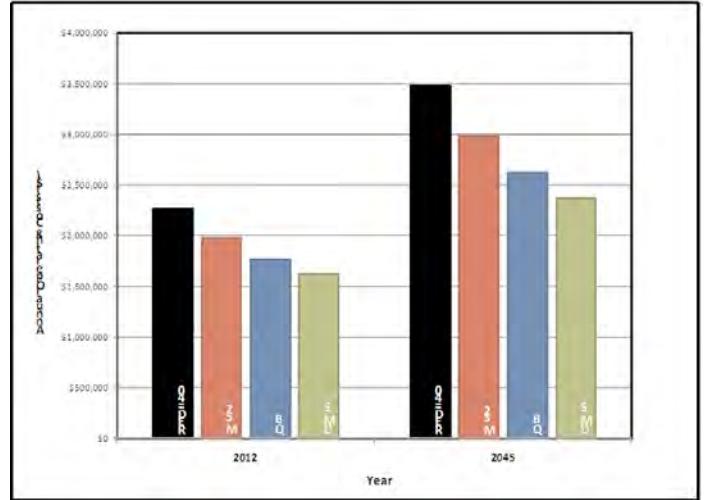


Figure 6: Annual Operating Costs (in Year 2009 dollars)

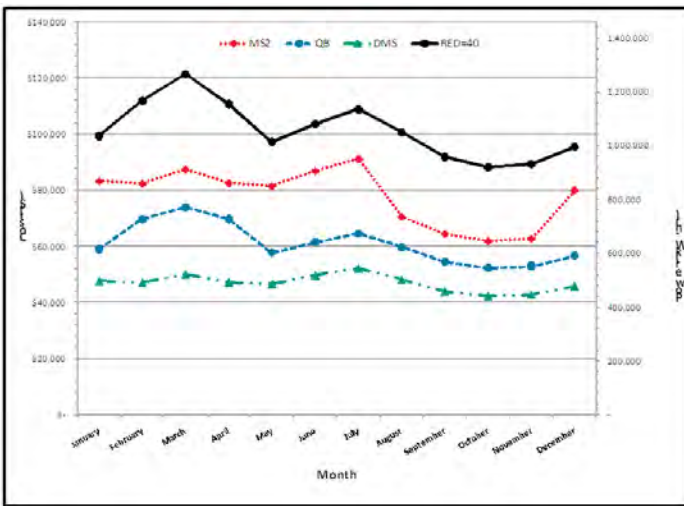


Figure 4: Monthly Power Costs for Various Surrogates – Year 2045 (in Year 2009 dollars)

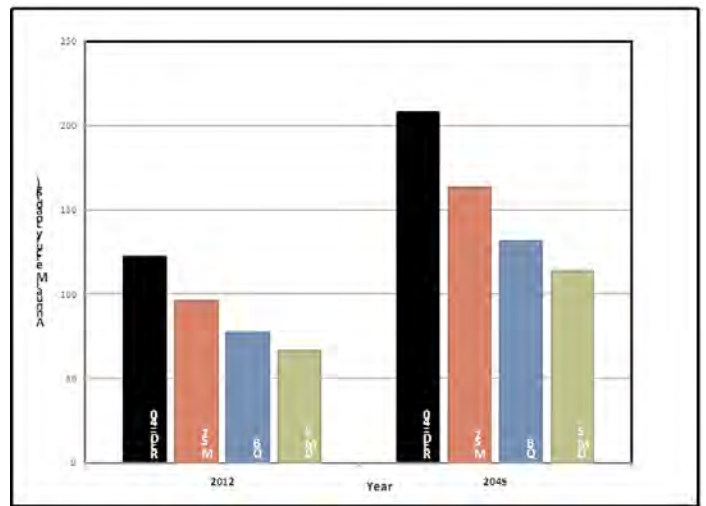


Figure 7: Annual Mercury Consumption

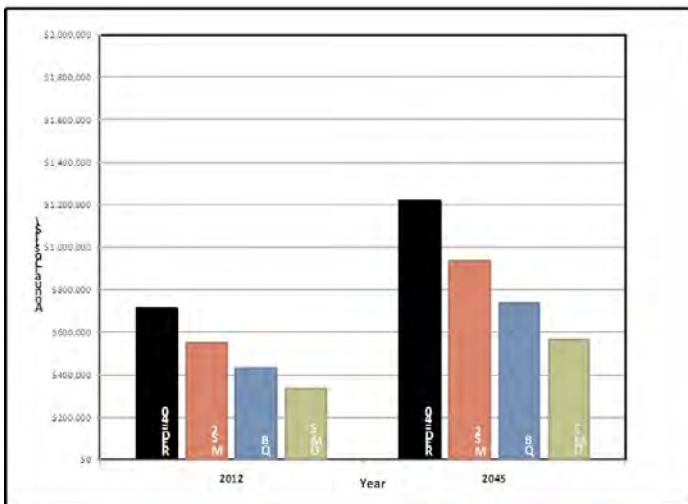


Figure 5: Annual Power Costs (in Year 2009 dollars)

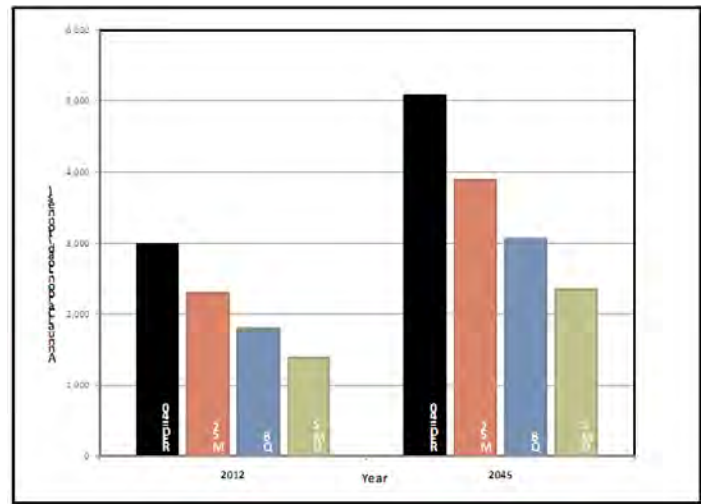


Figure 8: Annual Carbon Loading

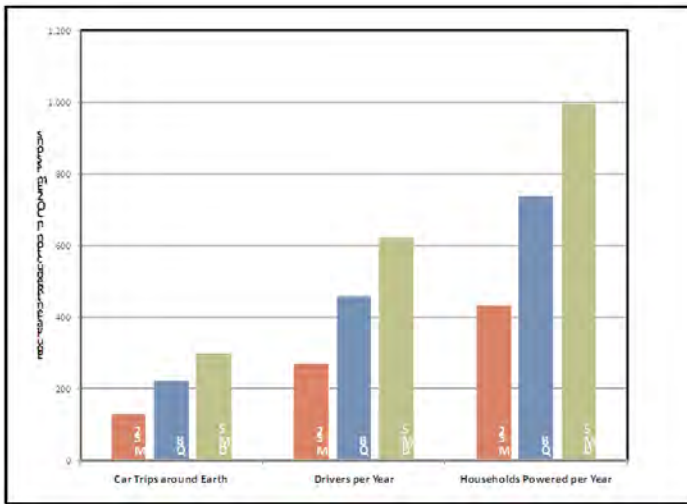


Figure 9: Annual Carbon Emissions Equivalents

various validation protocols are summarized in **Figure 6** for the initial year of operation (2012), as well as in the future (Year 2045).

An annual operating savings of at least \$250,000 would be realized in the first year of operation by using the USEPA recommended protocols in lieu of the 40 mJ/cm² requirement, even if MS2 was used as the surrogate. With dyed microspheres, the savings in the first year of operation would increase to over \$600,000 and be over \$1 million by the year 2045.

Although cost savings is a significant factor, the benefits to using the advanced surrogates go beyond simple economics. By reducing the power requirements for achieving full disinfection, significant reductions in the environmental and carbon footprint of the Catskill/Delaware facility can be achieved, without compromising public health in the slightest. The reduction in power requirements will reduce the number of lamps consumed by the facility. As the UV lamps contain mercury, reducing the number of lamps consumed will reduce the amount of mercury used in the facility (**Figure 7**). Reductions of between 21 and 45 percent can be achieved through use of the USEPA recommended guidelines instead of the required 40 mJ/cm² RED. By reducing the number of lamps used the potential for release of mercury into the environment through accidental lamp breakage would also be significantly reduced.

Although reducing the potential for mercury release will help the environment, the greatest impact on the environment that the use of advanced surrogates will have is through a reduction in the facility's carbon footprint (**Figure 8**). As shown above, the use of DMS will reduce the electrical power requirement of the facility by as much as 1.2 MW-hrs per year, which is enough electricity to power nearly 1,000 homes in New York State (**Figure 9**). This reduction in power use would have the same impact of carbon emissions in New York if 619 cars were to be removed from the roadways. The resulting carbon emissions that will be caused by the additional electricity required to

power the Catskill/Delaware UV units based on a 40 mJ/cm² RED requirement compared to an RED based on MS2 or DMS is equivalent to driving a car around the earth 129 or 297 times every year, respectively

CONCLUSIONS

Significant advancements have been made in the understanding of UV disinfection validation testing surrogates over the past five years. Use of these advanced surrogates such as Q-beta or dyed microspheres would allow for a more sustainable operation of New York City's 2-bgd Catskill/Delaware UV Facility. Reduction in annual power usage would exceed 1.2 MW-hr, enough electricity to power nearly 1,000 homes, and save up to \$1 million per year in operating costs. Furthermore, the use of these surrogates will have a positive impact to the environment by lowering the risk of mercury contamination, as well as the carbon footprint of the facility.

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Effect of UV Radiation on the viability of Cyanobacteria (Blue-green algae)

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ABSTRACT

Cyanobacteria can pose problems in reservoirs and source water supplies due to production of taste and odour compounds and toxins. Copper sulphate has commonly been used as an algicide to control cyanobacterial growth but due to the adverse environmental impact of copper it has been banned in some countries and has this led to research into alternative methods. The use of UV irradiation has been suggested as one such alternative. The current study tested the effect of UV irradiation on a naturally occurring cyanobacterial population with results showing potential for its use as a control agent.

INTRODUCTION

Blooms of cyanobacteria or blue-green algae are an important issue for the water industry because of their ability to impart compounds such as tastes, odours and toxins to drinking water supplies. The problems that these micro-organisms cause will vary depending upon the season, and the characteristics of the reservoir or source water supply due to differences in climate, geology and chemistry of the water body. The two main taste and odour compounds of concern are geosmin and 2-methylisoborneol (MIB) which produce earthy-musty odours and which are a significant problem due to their low threshold of detection by humans (approximately 10 ng/L). Some cyanobacteria also produce toxins which can be generally characterised as hepatotoxins, that affect liver function, or neurotoxins that affect the nervous system. Understandably, water managers are concerned by the presence of cyanobacteria in source waters and algicides have long had a role in their control. Copper sulphate has been the algicide of choice and has generally been regarded as effective, economical and safe for operators to use, however, copper use is banned in many countries and is increasingly being regarded less favourably in others. This is due to the recognition of its adverse environmental impacts on the aquatic ecosystem and this has led to research into alternative control methods (Burch et al, 2001). A number of alternatives are available in the market place but most have not had rigorous and scientifically valid testing.

Ultraviolet (UV) radiation is used widely in the treatment of water and wastewater treatment for destruction of a range of pathogens including bacteria, protozoa and viruses. A

number of studies have indicated that the physiological processes in cyanobacteria affected by UV-B and UV-A radiation include growth, pigmentation, photosynthetic oxygen production, motility, nitrogen uptake and phycobiliprotein composition and (Hädar D, 1984; Wu *et al.*, 2005) Cyanobacteria have developed a number of mechanisms to reduce the damaging effects of UV radiation which include light driven repair of UV-damaged DNA, accumulation of detoxifying enzymes and antioxidants, and synthesis of UV protectants such as mycosporine-like amino acids and scytonemin (Ehling-Schulz and Scherer, 1999; Sinah and Hädar, 2008). The sensitivity of cyanobacteria to UV can vary within and between species (Patnaik *et al.*, 1993).

However, while cyanobacteria may have protective mechanisms against UV radiation it has been suggested that both direct and indirect exposure of cyanobacteria and algae to UV-radiation can control their growth (Bin Alam et al, 2001). Gjessing and Kallqvist 1991 showed that UV-irradiation of water containing humic substances inhibited the growth of the green algae *Selenastrum capricornutum* and exhibited a residual effect lasting several weeks. They explained that photon-initiated interactions of humic substances and other chemicals in the water resulted in the formation of oxidizing reagents such as the hydroxyl radical which provided the algicidal activity. Work in Japan with laboratory grown cultures of the common problem cyanobacterium *Microcystis aeruginosa* showed that exposure to a UV-dose of 75 mJ cm⁻² was lethal and a smaller dose of 37 mJ cm⁻² prevented growth for 7 days. These UV doses are within range of conventional high pressure UV-lamps used for water disinfection (~40 mJ cm⁻²).

Bin Alam *et al* (2001) indicated that as an alternative to copper sulphate, boats equipped with UV-lamps are being used in some eutrophic lakes in Japan to control algal growth. This is potentially an attractive treatment option as it does not involve harmful chemical addition.

This study describes a preliminary investigation into the effect of artificially generated UV on a natural cyanobacterial population in Torrens Lake, South Australia, during a bloom that occurred in March 2007. The test was designed to treat the cyanobacteria in the lake water containing a natural population to account for the effects of resistance to UV radiation that wild cyanobacteria may have and any natural properties of the water that could reduce UV effectiveness.

MATERIALS AND METHODS

Water samples containing a natural mixed population of the cyanobacteria *Planktothrix mougeotii* and *Microcystis aeruginosa* were collected from the Torrens Lake in March, 2007. The test design involved the exposure of small volumes (7mL) of lake water with cyanobacteria in shallow open dishes (5cm Petri dish) to UV radiation at 256nm using a collimated UV beam at 3 doses: 40, 80 and 120 mJ cm⁻². This spanned the exposure levels recommended by WHO (2004) to remove bacteria (7 mJ cm⁻²), viruses (59 mJ cm⁻²) and protozoa (10 mJ cm⁻²) from drinking water. The collimated beam apparatus housed a low pressure UV (LP-UV) lamp which was calibrated using an IL1400 (UV Process Supply Inc.) radiometer. The UV light entered the suspension with a near zero degree angle of incidence and was homogeneous across the surface area. UV dose delivered to the suspension was calculated using measurements of incident UV intensity, exposure time, suspension depth, and the absorption coefficient of the suspension. The absorption co-efficient of Torrens Lake water was determined using a UV-Vis spectrophotometer to be 0.692 cm⁻¹ at 254nm. The suspension was slowly mixed using a magnetic stirrer and bar to ensure uniformity of exposure to UV. To achieve exposure doses of 40, 80 and 120 mJ cm⁻² the lake water samples were exposed for 7 min 11 s, 14 min 22 s and 21 min 32 s respectively.

The viability of cyanobacteria was determined 24 hours after UV exposure by a technique involving microscopic examination and cell counting and the use of activity stains which give an indication of cell damage and viability. The stains used were Fluorescein diacetate (FDA) and Propidium iodide (PI). FDA passes through cell membranes and is hydrolysed by intracellular esterases of healthy cells to produce fluorescein (a fluorescent product) which exhibits a green fluorescence when excited with blue light. PI only passes through the membranes of dead or dying cells and stains DNA in the cells an orange colour. "Total Cell" number was measured using a Sedgewick-Rafter counting chamber and microscope. The proportion of viable cells expressed as a percentage was measured after treatment with vital stains using a Lund Cell counting chamber and fluorescent microscopy. "Viable Cell" number was then

determined using percentage of living cells and the "Total Cell" number.

Each exposure was performed in triplicate. Controls were included which consisted of lake water samples held in experimental set-up (stirred in dishes) for the same time periods as the exposed cell suspension but without exposure to UV. A single control was included for each dosage and an average determined from the combined value. This removes any effect from variables other than UV exposure on cell numbers and viability.

After exposure, the cell suspensions were transferred to 50mL centrifuge tubes and incubated at 25°C in a controlled environment cabinet under artificial illumination of 30 μmol photons m⁻²s⁻¹ of photosynthetically active radiation (PAR) with light/dark cycle of 12h:12h for a period of 24 hours to reproduce conditions similar to that experienced in the environment.

ANOVA was used to determine a significant (p<0.05) difference between total cell numbers and total viable cell numbers (STATISTICA®).

RESULTS AND DISCUSSION

Figure 1 shows the effect of 40, 80 and 120 mJ cm⁻² of UV radiation at 254nm compared to the control on total cell number and viable cell number of *P. mougeotii*, and *M. aeruginosa* 24 hours after exposure.

There was no significant (p<0.05) decrease in the total number of *M. aeruginosa* cells 24 hours after cell suspensions were exposed to UV radiation at all three doses compared to the control (Figure 1A). All the cells present were viable after exposure to 40 and 80 mJ cm⁻² i.e. there was no significant difference between total cell numbers and total viable cell numbers (p>0.05). However, at the highest irradiance of 120 mJ cm⁻² the number of viable cells for *M. aeruginosa* was significantly lower than the control and the other two UV exposures (p<0.05).

The viability of *P. mougeotii* was extremely low i.e. approximately 10 % of the total cells present were shown to be viable at all three exposures (Figure 1B). It would appear that exposure to UV radiation at the doses tested made the cell membrane leaky which allowed propidium iodide to penetrate and stain the DNA and so indicate that the cell



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was dead. However, the cell membrane still retained enough integrity to preserve its shape, and so appeared as a whole cell in the total cell count. Cell numbers would be expected to decrease over time as the membrane starts to breakdown.

Results suggest that *M. aeruginosa* was more resistant to the negative effects of UV than *P. mougeotii*.

CONCLUSIONS

The results of this preliminary trial have shown that exposure to UV radiation at 254nm has a significant effect on the viability of natural populations of cyanobacteria but appears to vary between cyanobacterial types. For example, the viability of *M. aeruginosa* cells was still high even after exposure at 120 mJ cm⁻² compared to cells of *P. mougeotii* which showed a significant reduction in viability at an exposure of 40 mJ cm⁻². This is not surprising as *M. aeruginosa* (Figure 2) form large spherical colonies where cells located in the middle would be protected from incident radiation by surrounding cells. *P. mougeotii* are free-floating long chain filamentous cyanobacteria (Figure 3) making them an easy target for UV radiation. The current study has shown that the effect of UV radiation and its use as a cyanobacterial control method warrants further investigation.

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Figure 1: The effect of UV on the viability of natural populations of cyanobacteria 24 hours after exposure. The figure shows numbers of total and viable cells of **A**; *Microcystis aeruginosa*, and **B**; *Planktothrix mougeotii*, in a Torrens Lake water sample 24 hours after exposure to UV irradiation (254nm) at doses of 0, 40, 80 and 120 mJ cm⁻²

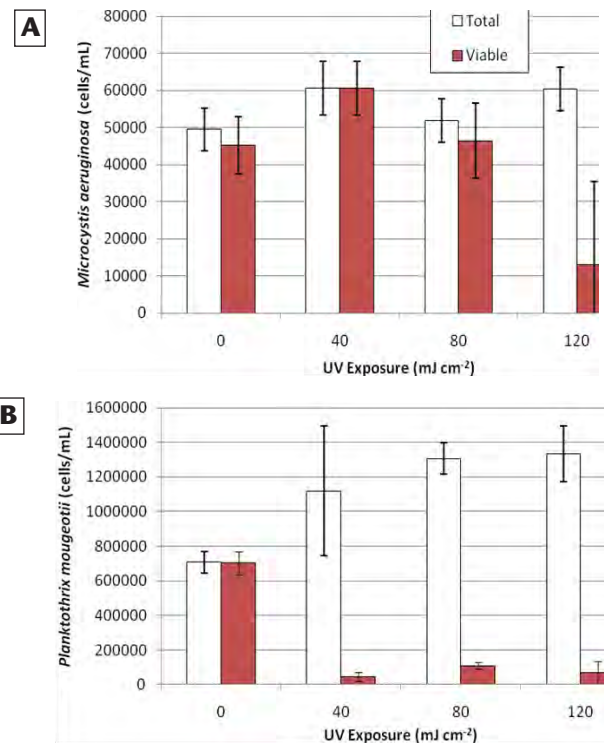


Figure 2: Colony of *Microcystis aeruginosa* from Torrens Lake.

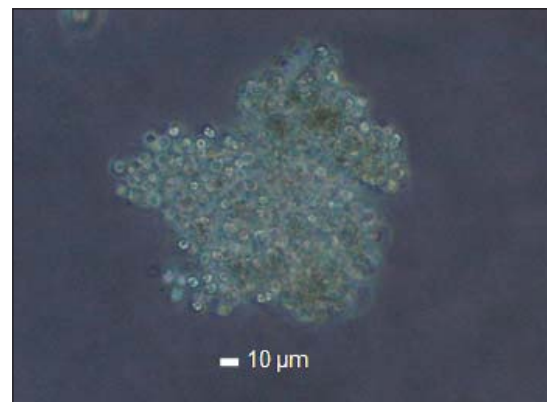
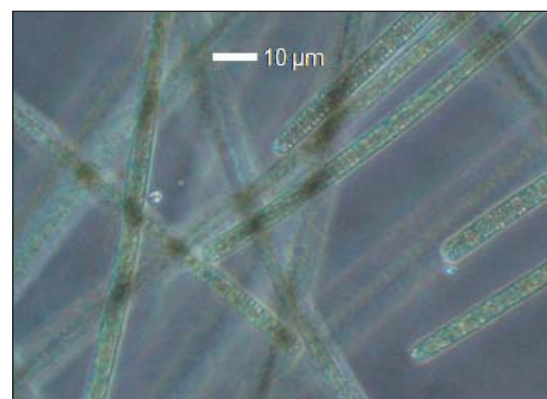


Figure 3: Filaments of *Planktothrix mougeotii* from Torrens Lake.



Novel UV LED Advanced Oxidation System for Disinfection and Removal of Organic and Heavy Metal Contaminants in Water

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ABSTRACT

A novel technology is described, suitable for point of use (POU)/point of entry (POE) water purification systems, that uses a dual wavelength UV LED system to excite a fixed-substrate photocatalyst. This advanced oxidation process rapidly mineralizes organic and inorganic contaminants in water without the chemicals, consumables, toxic waste, pressure drop, or water wastage of traditional solutions. With a self-cleaning fixed photocatalytic substrate, uniform LED illumination, and extremely high surface area, the system is inherently compact, lightweight, scalable, and low-maintenance. The process combines photolysis, germicidal disinfection, photocatalysis, and photo-adsorption to effectively eliminate many contaminants in water without creating any waste stream. Reported tests confirm successful disinfection of Raoultella Terrigena bacteria and MS2 phage virus, removal of heavy metals including arsenic and lead, and the elimination of a wide range of organic chemicals from water, including phenol, MTBE, and PCE.

Key words: Photocatalysis; Advanced oxidation; LED; Titanium dioxide; Point of use; Photoreactor; Water purification.

INTRODUCTION

A number of technologies are available to remove known, regulated toxic contaminants in the production of municipal drinking water. However, US Environmental Protection Agency regulates fewer than 0.1% of the approximately 100,000 industrial chemicals in worldwide use (1), and the World Health Organization offers guidelines for a comparable fraction of organic chemicals (2). Unregulated organic contaminants found in US municipal drinking water sources include detergents, pharmaceuticals, herbicides, petrochemicals, and fire retardants (3). For example, within the past year pharmaceuticals have been reported in over twenty water supplies for major US cities (4).

While some of these contaminants may eventually be regulated, the evolution to regulation is a time-consuming process requiring development of monitoring and removal technologies and community implementation of these technologies. In addition, up to 5% of regularly tested municipal water samples may contain coliform bacteria and up to 10% of water samples may contain lead at concentrations exceeding the US EPA action level without raising alarm. As a result of these factors, drinking water will typically include contaminants for 20 years or more before the contaminants are regulated and their full health effects are known. Today, the available technologies are

either impractical or ineffective for removing a broad range of contaminants from municipal or other water sources at point of entry/use:

- Filtration, including granular activated carbon, removes a moderately wide range of contaminants but requires monitoring and filter replacement to assure continuous performance, and saturated filter elements require regeneration or disposal.
- Reverse Osmosis typically wastes much more water than it purifies, and although it effectively removes inorganic minerals, it also removes those which are desirable for taste. It also fails to remove many soluble organic contaminants including some pharmaceuticals, petroleum byproducts, pesticides and herbicides.
- UV Germicidal Irradiation (UVGI) from lamps is an effective disinfectant, but monitoring, cleaning, and pre-filtration are required to assure germicidal performance.
- Advanced Oxidation Processes, including ozonation and UV-activated hydrogen peroxide, require production and storage of toxic chemicals and are therefore generally impractical in smaller-scale, point of entry/use applications.

Small-scale water purification applications require cost-effective, robust and non-selective processes and products for disinfection and removal of organic and heavy metal contaminants without added chemicals and/or frequent filter changes. **Table I** highlights the gaps in meeting this need with available technologies, and shows that the puralytic process herein reported can reduce chemical use, improve the reduction of organic contaminants, reduce maintenance, and extend the breadth of contaminants covered while achieving significant environmental benefits when compared to existing technologies.

Table I: Advantages/deficiencies of available technologies for point of use or other small-scale water purification applications.

Technology	Property									
	Germicidal Effectiveness	Organics Removed	Heavy Metals Removed	No Toxic Waste Stream	Water Conserved	Scalable to POU/POE	No Chemicals Added	Infrequent Service Req'd	Solar Power Practical	
Chlorination	****	*	-	****	*****	*	-	*	-	
UV Germicidal	*****	*	-	****	*****	*****	*****	***	-	
Carbon Filtration	**	*	**	*	*****	*****	*****	**	-	
Reverse Osmosis	**	**	* ⁺	*	*	*****	*****	***	-	
Ozonation	****	****	-	**	*****	*	-	*	-	
UV/Peroxide	****	****	-	**	*****	*	-	*	-	
Puralytic Process	****	****	***	****	*****	*****	*****	****	*****	

PURALYTIC PROCESS PHOTO-CHEMISTRY

The puralytic process reported herein involves four light-activated processes – photolysis, photoadsorption, germicidal irradiation, and photocatalytic oxidation. Each of these processes is wavelength and intensity dependent, and has relative advantages for specific contaminant removal, but all work synergistically in the puralytic process.

- **Photolysis.** Photolysis is the direct absorption by a contaminant molecule of photons with sufficient energy to directly dissociate chemical bonds. Shorter wavelengths are more energetic, and therefore more effective.

- **Photoadsorption.** While anatase TiO₂ is already an excellent medium for contaminant adsorption, under exposure to UV light it becomes an even more aggressive adsorber, and can also photoreduce and photodeposit certain contaminants. Compounds involving noble metals and non-noble heavy metals with favorable redox potentials have been shown to photodegrade (5) into molecular components, photoreduce into less toxic forms, and then photodeposit onto the catalyst. The surface area of the puralytic photocatalyst is sufficient to allow this to

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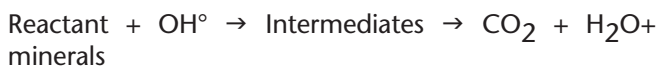
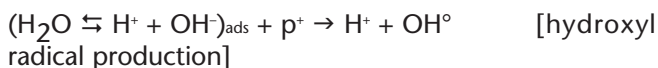
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occur for several years without system performance degradation.

- **Germicidal Irradiation.** Ultraviolet germicidal irradiation with mercury lamps is a well-established process for sterilizing pathogens. For germicidal applications, the 250-280 nm wavelength band is effective at disrupting the DNA of microorganisms. Monochromatic radiation within this band, such as the 254 nm radiation from a low-pressure mercury lamp, sterilizes microorganisms, but a band of wavelengths above 265 nm would be even more effective (6) and reduce dark repair of DNA (7). Higher-pressure mercury and xenon lamps produce broadband radiation – inefficient for disinfection or for activating a semiconductor photocatalyst. Moreover, UV lamp sources are fragile, and mercury lamps in particular are environmental hazards. More robust and efficient sources with optimized spectral output are preferred for germicidal systems.
- **Photocatalytic Oxidation.** Photocatalytic oxidation (PCO) by a photo-activated semiconductor photocatalyst has been actively studied (8-11) as an advanced oxidation process applicable to water purification. This process offers non-selective degradation of organic contaminants in water into simpler and less toxic compounds, and ultimately into inorganic ions, CO₂ and water. PCO involves the absorption of energetic photons by the semiconductor and the subsequent production of hydroxyl radicals at the semiconductor surface. Anatase TiO₂ is a particularly effective semiconductor photocatalyst in converting light into hydroxyl radicals – a more powerful oxidizing agent than ozone and twice as powerful as chlorine, with sufficient energy to completely mineralize organic contaminants. The critical reaction pathway is:



However, cost-effective production of sufficiently high photocatalyst surface area in contact with water, and delivery of enough energetic photons to the semiconductor to activate it, has proven difficult. Systems employing UV-activated TiO₂ slurries have been demonstrated to be effective in breaking down most organic contaminants (10-11), but require complicated, expensive systems for management of the slurry material. An order of magnitude increase in surface area and a significant improvement in mass transport is needed to enable smaller scale POU/POE PCO systems.

Optimized illumination sources are also needed for cost-effective water purification systems. At low UV intensities, below approximately 1 sun (about 2-3 mW/cm² below

400nm), production of hydroxyl radicals by UV-illuminated anatase TiO₂ photocatalyst is known to be linearly proportional to the UVA intensity, while the production of hydroxyl radicals has been reported (8-9) to increase sub-linearly at higher UVA intensities. Most research to date has been done with lamps illuminating a slurry. These lamps have typically been low pressure Hg lamps emitting at 254nm or Hg “black light” lamps emitting in the UVA band near 370 nm with limited optical flux and efficiency. An optimized, more photon efficient optical solution is needed for PCO systems.

In the puralytic process, the PCO process parameters are optimized to meet the requirements discussed above:

- The UVA intensity is as large as possible without exceeding the range of linear proportionality between intensity and hydroxyl radical production.
- The source photon energies are just above the semiconductor band gap to be efficiently absorbed by the semiconductor. UVA photons with wavelengths in the 360-390 nm range are preferred for production of hydroxyl radicals by anatase TiO₂ (band-gap near 388 nm) – photons with longer wavelengths are not strongly absorbed and those with shorter wavelengths waste their excess energy in heating the semiconductor.
- The photocatalyst is applied to a transparent substrate increasing both surface area and mass transport compared to slurry systems.
- UV LEDs are used for illumination to avoid the issues associated with lamp technologies.

PHOTO-REACTOR TECHNOLOGY

Reported herein is a patent pending advanced oxidation process technology and photoreactor with improved photocatalytic oxidation performance, improved germicidal performance, and identification of synergies resulting from combining optimized UVA and UVC wavelengths for water purification. This technology processes water in a single pass, flow-through system, without the bypass water flow and resulting water waste stream required for membrane filter systems. This technology also does not require addition of chemicals, nor does it require activated carbon filters needing frequent replacement.

This reactor technology was developed based on a novel, extremely-high-surface-area anatase TiO₂ semiconductor photocatalyst on glass wool. The specific surface area of this new photocatalyst is more than ten times that of the typical Degussa P25 slurries used and reported in prior photocatalytic research studies. Because this photocatalyst is stationary on the glass wool substrate within the reactor, turbulence in water flow through the wool promotes significant mass transfer improvement compared with a slurry reactor without a significant pressure loss through the reactor. Moreover, the production rate of hydroxyl radicals with this technology is up to ~20 times greater than has been reported for slurry reactors. Thus, this novel

photocatalyst provides for photodegradation rate improvements through improved mass transfer and higher rates of hydroxyl radical production than have been possible with photocatalyst slurries.

Another advantage of this high photocatalyst surface area is the improved photoadsorption and photodeposition of heavy metals from contaminated water onto the photocatalyst without a corresponding reduction in PCO activity. This novel photoreactor and technology have been shown to effectively photo-reduce and photo-adsorb heavy metals, particularly lead, arsenic, selenium, uranium, and mercury.

Tests to determine saturation levels for these metals (marked by reduction of photocatalytic activity) are ongoing, but are predicted to be in excess of several years at municipal water contamination levels.

To activate the photocatalyst, an LED source with optimized wavelengths and intensities was developed to efficiently produce hydroxyl radicals on the semiconductor surface. This allows treating water at flow rates over 1 liter per minute, efficiently removing >99% of most organic materials and heavy metals while also achieving full disinfection. A photograph of the photocatalyst in water inside an LED-illuminated reactor is shown in **Figure 1** below.



Figure 1: Interior of photo-reactor showing UV LED illuminated photocatalyst immersed in water.

TEST METHOD

A dual wavelength photoreactor was constructed with variable contaminant concentrations, flow rates, photocatalyst density, and illumination intensity. A diagram of the system is shown in **Figure 2** below.

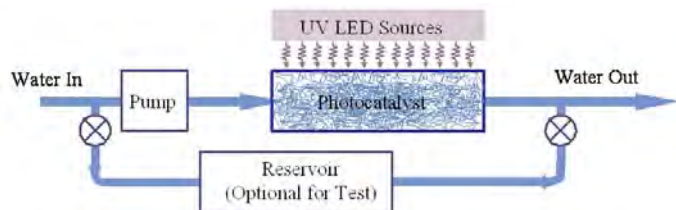


Figure 2: Schematic of test set-up for evaluating Puralytics reactor and process.

Water with controlled contaminant levels was introduced into the reactor via a peristaltic pump, and samples from the resulting output stream were tested at different points in time. Organic contaminants were tested by gas chromatography/mass spectrometry at an external water testing facility, or by use of a Total Organic Carbon meter. Pathogens were tested in an EPA Biosafety Level 2 Laboratory using both Type 1 and Type 2 water. Heavy metals were measured using cyclic voltammetry or tested by an external laboratory. Control tests were done with illumination off, with individual wavelengths acting alone, and with all illumination sources on. A reservoir was included in the test reactor system to allow recirculation as a diagnostic tool.

RESULTS

Four different photo-activated processes were identified in the test results that contribute to the overall results – photoadsorption, photolysis, photocatalysis, and germicidal sterilization. Depending on the contaminant compound, these processes have varying contributions. For heavy metals, photocatalytic reduction of the metals contributes to photoadsorption onto the mesh. For certain organic molecules, photolysis is a significant contributor to photodegradation. However, photocatalysis is the principal photodegradation process for organics, effectively removing >90% of all materials tested at flow rates of 1 liter per minute independent of starting concentration. Degradation rates of organic contaminants generally follow the predicted Langmuir Hinshelwood degradation curves, but at much higher degradation rates than previously reported. Figure 3 below shows reactor-normalized results for some of the contaminants tested in this study.

The tests also show that the PCO process acts to reduce the population of microorganisms in treated water through multiple kill mechanisms, and that the dual wavelengths act synergistically to achieve a higher kill rate. **Figure 3** on the opposite page shows that significant germicidal results are achieved with UVA illumination alone. Note that these UVA germicidal rates are more than an order of magnitude greater than reported with slurry systems (14). With modest added UVC illumination flux in the reactor, 4-log reduction of viruses and 6-log reduction of bacteria is readily achieved (not shown).

CONCLUSIONS

A novel water treatment system has been demonstrated that incorporates a photo-activated advanced oxidation process. This new AOP process combines an improved high-surface-area, stationary substrate photocatalyst system and optimized LED sources to achieve unprecedented performance on a broad range of contaminants in a low maintenance, self cleaning system. The technology allows the potential for scaling the reactor capacity and performance for different requirements in POU/POE commercial, residential, and industrial water purification applications. Addition of a UVC germicidal process within

the photoreactor synergistically increases the disinfection and photolysis performance of the treatment system.

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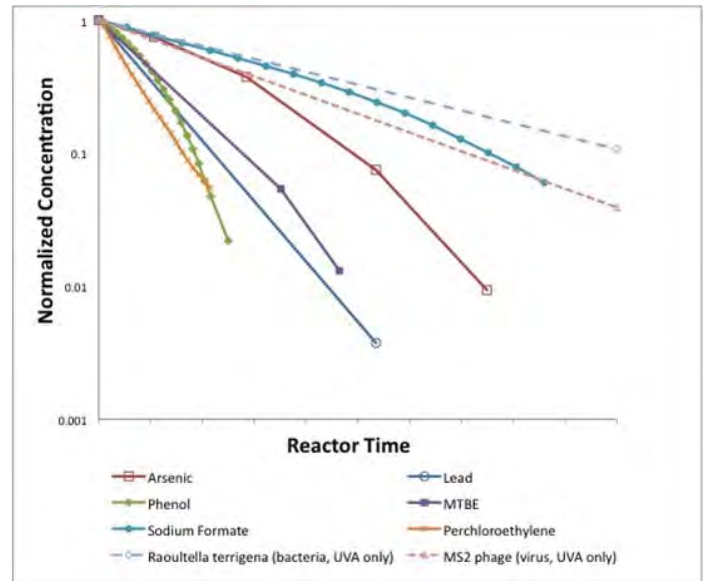



Figure 3: Observed Puralytics process contaminant removal.

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