Basics of UV Disinfection Systems and Validation Methods

Ernest (Chip) R. Blatchley III, Ph.D., P.E., BCEE

Ernest (Chip) R. Blatchley III is a Professor in the School of Civil Engineering and in the Division of Environmental & Ecological Engineering at Purdue University. Professor Blatchley teaches and conducts research in the area of Physico/Chemical Processes of Environmental Engineering, with particular emphasis on disinfection systems. Research within the Blatchley group has focused on UV-based systems, and has been important in the development of fundamental photochemical reactor theory. The Blatchley group and collaborators have developed numerical and experimental methods for measurement of the behavior of UV systems.

The Blatchley group has been active in the area of swimming pool chemistry for roughly five years. The focus of work in this area has been on defining the basic chemistry of DBP formation and control in swimming pools. Recent and ongoing research in the Blatchley group addresses the effects of UV-based treatment on water and air chemistry in chlorinated, indoor pools.

Abstract

UV photoreactors are used in aquatics facilities to promote disinfection and to improve water chemistry. However, the design of UV systems for these applications is often based on empiricism, rather than science. The basic characteristics of UV reactors are reviewed, including fundamental principles of photochemistry and reactor theory. These basic principles also form the basis reactor design protocols.

At present, three general methods of reactor characterization and validation are available for UV systems: Biodosimetry, Lagrangian Actinometry, and Computational Fluid Dynamics-Intensity Field (CFD-I) models. The basic characteristics of these three methods of reactor analysis are presented, along with a discussion of the strengths and weaknesses of each method. Some recommendations regarding UV system design and validation are also presented.

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World Aquatic Health Conference
Seattle, WA
13 October 2011

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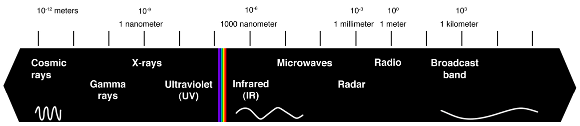
UV Myths (or at least unproven hypotheses) from the Internet

- "UV reduces risk of cancer"
- "Depending on the type of chloramine, different wavelengths are required for the photolysis process such as:
  - Monochloramine - 245 nm
  - Dichloramine - 297 nm
  - Trichloramine - 260 & 340 nm"
- "UV disinfection is a purely physical process; organisms can not become resistant to it as they have to chemicals like chlorine."

Outline

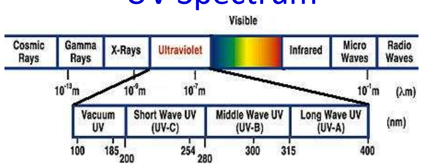
- Introduction/Definitions
- Laws of Photochemistry
- Photochemical Kinetics: UV Dose = Master Variable
- Effects of UV in Chlorinated Pools
- UV System Types
- Reactor Analysis and Validation
- Uncertainty in UV Design for Pools
- Chlorination + UV
- Future Work

Electromagnetic Spectrum



http://blog.widen.com/blog/the-color-space/call-me-mr-biv-v1

UV Spectrum



UV Range	Wavelengths (nm)	Applications
UVA	315-400	Sunburn, “Blacklight”
UVB	280-315	Sunburn, Germicidal
UVC	200-280	Germicidal, Photochemistry
Vacuum UV	100-200	High-Energy Applications

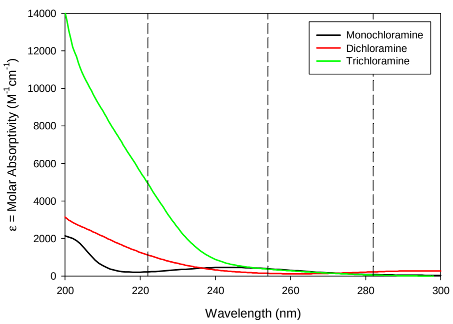
Photochemistry Basics

- Laws of Photochemistry:
  - First Law (Grotthus-Draper): Target Molecule Must Absorb Radiation
  - Second Law (Stark-Einstein): Absorbed Radiation Must Have Sufficient Photon Energy to Break or Form a Chemical Bond
- Photon Energy Depends on Wavelength
  - Shorter wavelengths have higher energy
- Bond Energy Often Similar to Photon Energy Within Ultraviolet (UV) Spectrum

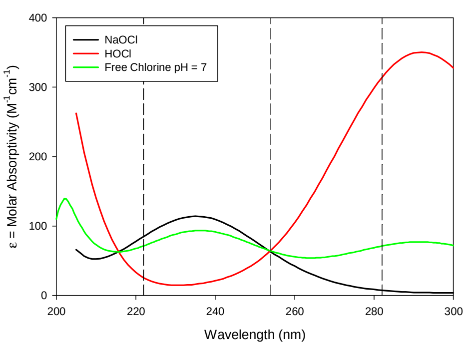
Laws of Photochemistry: Implications

- Photochemical Reactions Favored by:
  - Strong absorbance by target molecule
  - High intensity
- Absorbed UV Radiation Can Promote Reactions
- Photochemical Reactions Demonstrate Wavelength Dependence

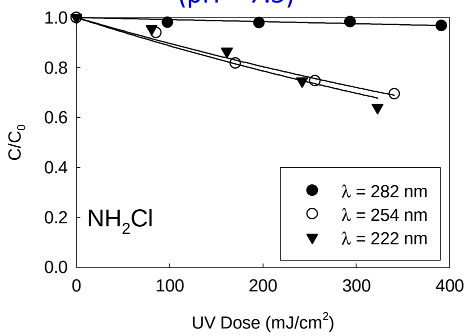
UV Absorbance Spectra: Inorganic Combined Chlorine (NH_2Cl, $NHCl_2$, NCl_3)



UV Absorbance Spectra: Free Chlorine ($HOCl + OCl^-$)

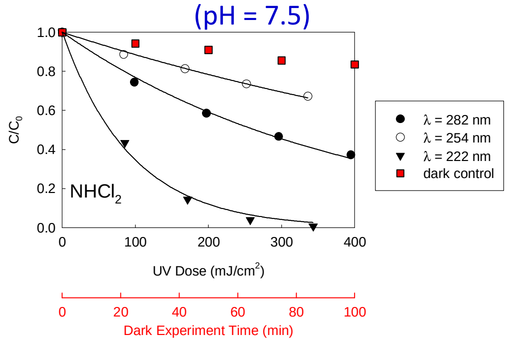


UV Photodegradation of Monochloramine (pH = 7.5)



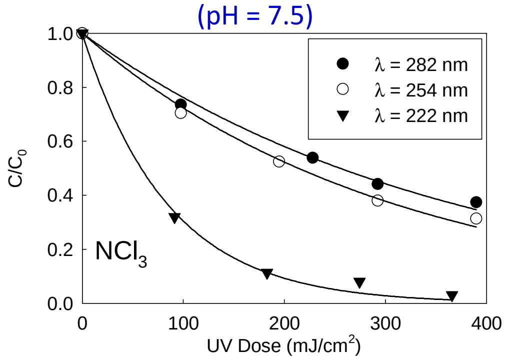
Li, J. and Blatchley III, E.R. (2009) "UV Photodegradation of Inorganic Chloramines," *Environmental Science & Technology*, **43**, 60-65.

UV Photodegradation of Dichloramine (pH = 7.5)



Li, J. and Blatchley III, E.R. (2009) "UV Photodegradation of Inorganic Chloramines," *Environmental Science & Technology*, **43**, 60-65.

UV Photodegradation of Trichloramine (pH = 7.5)



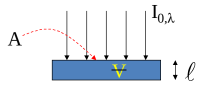
Li, J. and Blatchley III, E.R. (2009) "UV Photodegradation of Inorganic Chloramines," *Environmental Science & Technology*, **43**, 60-65.

Photochemical Kinetics

$$\Phi_\lambda = \frac{\textit{number of moles consumed or produced}}{\textit{number of einsteins}_\lambda \textit{ absorbed}}$$

$$v_\lambda = \frac{-d[T]}{dt} = I_{a,\lambda}\Phi_\lambda$$

$$I_{a,\lambda} = I_{0,\lambda}A\left(1 - 10^{-\varepsilon_\lambda[T]\ell}\right)$$



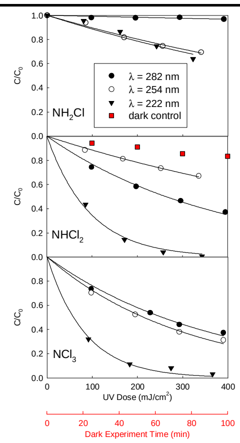
$$\textit{when } \varepsilon_\lambda[T]\ell \ll 1, I_{a,\lambda} \approx \frac{I_{0,\lambda}A(2.303 \cdot \varepsilon_\lambda[T]\ell)}{V}$$

$$\therefore \lim \ell \to 0, v_\lambda = \frac{-d[T]}{dt} = 2.303 \cdot I_{0,\lambda}\varepsilon_\lambda[T]\Phi_\lambda = k_\lambda I_{0,\lambda}[T]$$

$$\frac{[T]}{[T]_0} = exp\left(-k_\lambda I_{0,\lambda}t\right)$$

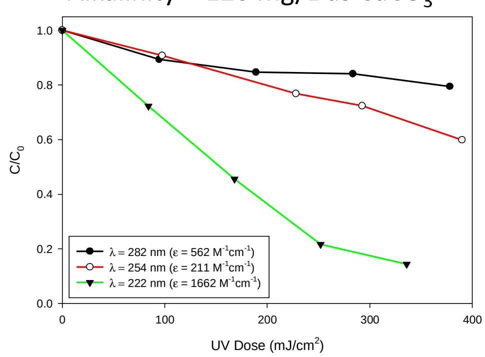
Dose = I·t

UV Photodegradation of Inorganic Chloramines (pH = 7.5)



Li, J. and Blatchley III, E.R. (2009) "UV Photodegradation of Inorganic Chloramines," *Environmental Science & Technology*, **43**, 60-65.

CH_3NCl_2 Photodecay; pH = 7.5 Alkalinity = 120 mg/L as $CaCO_3$



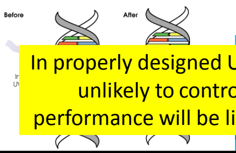
UV Systems in Pools: Photochemistry + Chlorination (Disinfection)

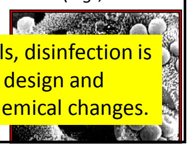
UV Disinfection

- Damage to DNA, Proteins
- Broad-Spectrum Antimicrobial Agent
- Effective Against Bacteria, Protozoa
- Limited Effectiveness Against (Some) Viruses

Chlorine Disinfection

- Damage to Cell Membranes, Enzymes, etc.
- Broad-Spectrum Antimicrobial Agent
- Effective Against Bacteria, Viruses
- Minimal Effectiveness Against Protozoa (*e.g.*, *Crypto*)





In properly designed UV systems in pools, disinfection is unlikely to control. Overall system design and performance will be limited by photochemical changes.

UV Systems in Pools: Photochemistry + Chlorination (Chemistry)

UV System

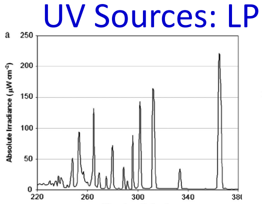
- Photolysis of Susceptible Bonds
  - NCl
  - NO
- Chemistry is Not Completely Defined

Chlorination

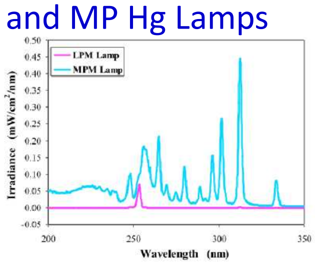
- Common Reaction Types:
  - Chlorine Substitution
  - Oxidation
  - Hydrolysis
- Chemistry is Not Completely Defined

UV and Chlorine Work Together to Alter Pool Chemistry

UV Sources: LP and MP Hg Lamps



From: Lakretz *et al.* (2011) *Biofouling*, **27**, 3, 295-307.

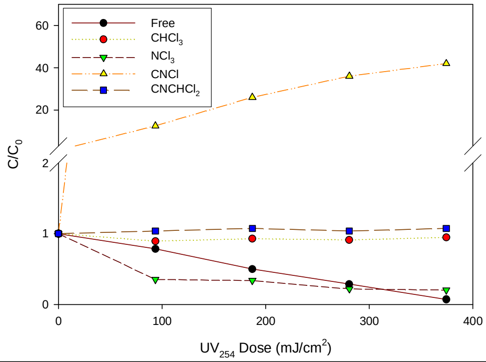


From: Koutchma (2010) *Proceedings of SPIE-The International Society for Optical Engineering*, Volume 7789, DOI: 10.1117/12.860259.

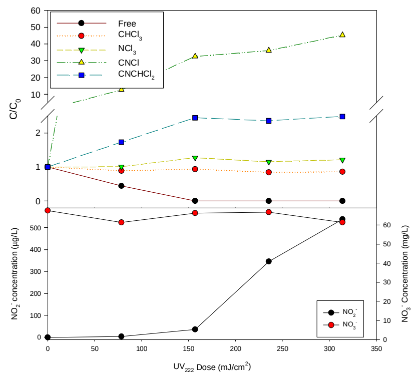
- LP Lamps
  - Monochromatic (λ=254 nm)
  - Low output power
- MP
  - Polychromatic (200 < λ < 400 nm)
  - High output power

Short Wavelength UV Can Open Up Some Reaction Pathways

UV_{254} Irradiation of Pool Water



UV_{222} Irradiation of Pool Water



Dose = Master Variable

(*Particle-Specific Basis*)

$$Dose = \int_0^{\tau} I(t)\, dt$$

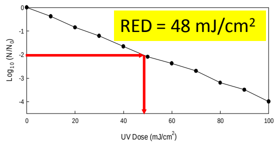
- Exposure Time
- Intensity Field
- Intensity History
- Particle Trajectory

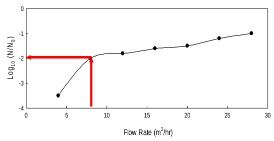
All UV Reactors Deliver a Distribution of Doses. The Dose Distribution Governs Reactor Performance. Reactor Validation Methods Focus on Measurement of Delivered Dose.

Conventional Method: Biodosimetry

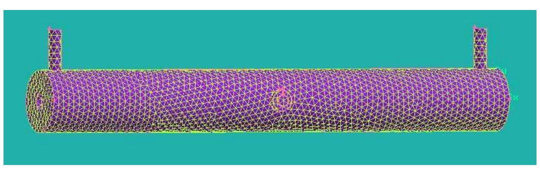
"Reduction Equivalent Dose" (RED)

- Measure Dose-Response Behavior with Collimated-Beam
- Measure Inactivation on Flow-Through System
- Equate Inactivation to "Reduction Equivalent Dose" by Comparison with Collimated-Beam Data

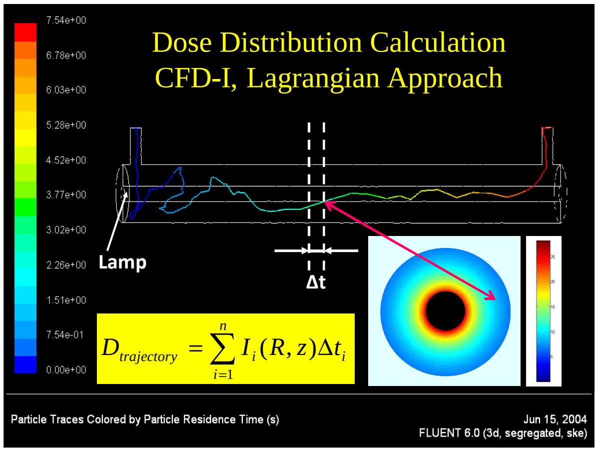


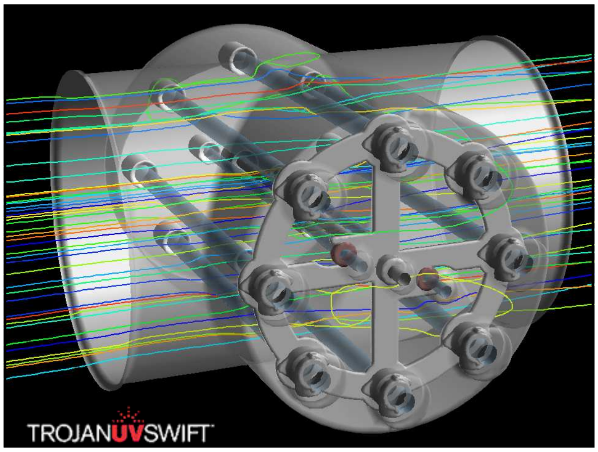


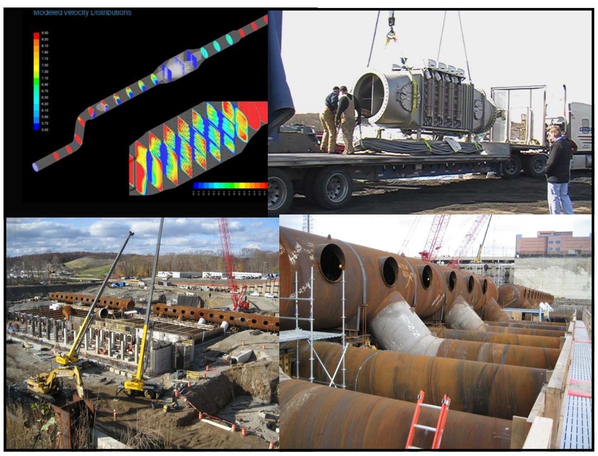
Flow Field Simulation: Computational Fluid Dynamics (CFD)



Dose Distribution Calculation CFD-I, Lagrangian Approach

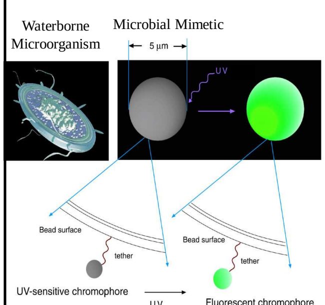






Dyed Microspheres: Lagrangian Actinometry

Blatchley *et al*. (2006) "Dyed Microspheres for Quantification of UV Dose Distributions: Photochemical Reactor Characterization by Lagrangian Actinometry," *J. Environmental Engineering, ASCE*, 132, 11, 1390-1403.



- Particle mimics microorganism size, specific gravity, ∴ trajectory
- Linked UV-sensitive chromophore (*S*)
- Becomes fluorescent under UV irradiation (*P*)
- Bead fluorescence intensity (FI) is correlated to UV dose received.
- FI measured by flow cytometry

UV Reactor Validation: Approach

- Identify Target Contaminants
  - Microbial Pathogens
  - Chemicals
- Identify Limiting Factor (Chemistry)
- Define Dose Requirement (40, 60, 80 mJ/cm^2 ???)
- Apply Validation Method(s)

UV Validation: Methods (Details in Next Presentation)

Biodosimetry

- Long History of Use
- Familiarity
- Widely Applied
- Difficulty with Translation from Challenge Organism to other Targets

Lagrangian Actinometry

- Measurement of Dose Distribution
- Results Translate to All Photochemical Targets
- Standardized Method Available

CFD-I

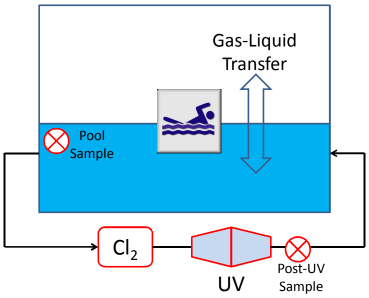
- Simulation of Dose Distribution
- Results Translate to All Photochemical Targets
- Mathematical Complexity

Uncertainty in UV Design for Pools

- Current Designs Based on Empiricism
- Design Dose = 40, 60, 80 mJ/cm^2 ???
- Effects of UV Systems on Water (and Air) Chemistry are Incompletely Defined
- Lack of Industry-Wide Treatment Standards
- Effects of Lamp Type
  - LP
  - MP

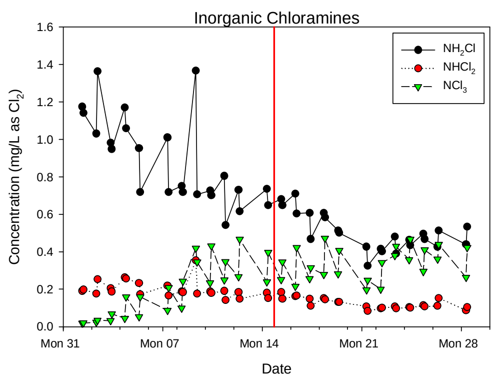
•Design Dose?
•Which?

Effects of UV and Chlorine in Combination

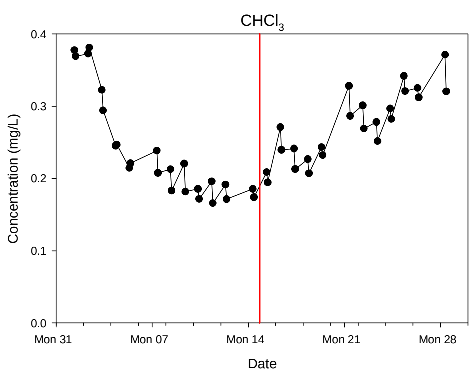


- Continuous recirculation
- Chlorination and UV on each pass
- Volatile compounds escape to gas phase
- Both processes affect water and air chemistry

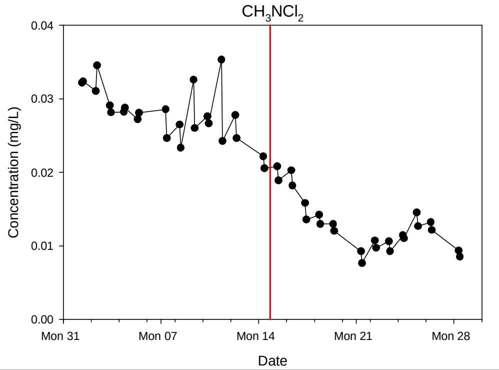
Before and After Inclusion of UV (1)



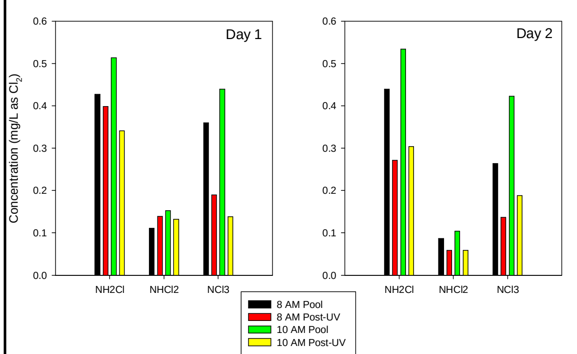
Before and After Inclusion of UV (2)



Before and After Inclusion of UV (3)



Inorganic Chloramines: Pool Water and Post-UV



Effects of Rechlorination (1)

Effects of Rechlorination (2)

Effects of UV-Based Treatment on Water and Air Chemistry in Chlorinated, Indoor Pools (1)

- Project Period = 2011-2014
- Field Experiments
  - Year 1: Control (no UV)
  - Year 2: LP UV
  - Year 3: MP UV
  - Measure Water and Air Chemistry
- AP Chemistry Students at Local High School(s)

Effects of UV-Based Treatment on Water and Air Chemistry in Chlorinated, Indoor Pools (2)

- Laboratory Experiments
- UV/Chlorination of Model Compounds
  - Amino Acids
  - Creatinine
- Kinetics and Mechanisms of Relevant Reactions

Effects of UV-Based Treatment on Water and Air Chemistry in Chlorinated, Indoor Pools (3)

- Effects of UV on Disinfection Byproducts (DBPs) in Pools
- Target Compounds
  - Free and Combined Chlorine
  - NO_3^-/NO_2^- (MP UV Systems)
  - Chlorinated Nitriles
    - UV Enhances Production
    - Chlorine Needed for Formation and Decay
  - Nitrosamines
    - Known to be formed efficiently in pools
    - UV is known to be effective for control
    - Effects in pools essentially undefined
- Results to Serve as Basis for UV System Design in Pools

Data from WLHS Study