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LIFT TECHNOLOGY SCAN
Open Call for Innovative Technology Submissions
PROGRAM APPLICATION
ATTACHMENT A: COVER SHEET

APPLICANT CONTACT INFORMATION:

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Title: co-founder, Manager			
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TECHNOLOGY PROVIDER INFORMATION:

Organization: Pellucid Water LLC	**Year Established:** 2014	**# of Employees:** 2
Owner or Head of Organization: Dr. Sorin Manolache and Mark Raabe		
Organization Website: www.pellucidwater.com		

TECHNOLOGY INFORMATION:

Name of Technology Being Submitted: Pellucid Water Cold Plasma

Brief Technology Description (400 characters or less [about 1-2 sentences] for use on LIFT website and related materials):
Pellucid Water designs cold plasma reactors for water decontamination and disinfection. Contaminants are removed from solution through aggregation and precipitation: organics (e.g. solvents, lubricants and pharmaceuticals); and inorganic contaminants (e.g., phosphorus, water hardness, heavy metals and other salts).

Technology Development Level (Scale of 1-6, see instructions): 1

Technology Topic Area (pick up to 3 total; use 2 X's [XX] to indicate your #1 choice):

☐ Biosolids to Energy	☐ Energy Conservation	☐ Other Resource Recovery*
☐ Biosolids Upgrading	☐ Energy Production	☐ Primary Treatment
☐ Carbon Diversion	☐ Filtration	☐ Secondary Treatment (Activated Sludge)
☐ Collection Systems	☐ Intelligent Water Systems	☐ Stormwater BMPs
☐ Decentralized Systems	☐ Decision Support Tools	☐ Stormwater Green Infrastructure
☐ Desalination	☐ Sensors	☐ Thickening and Dewatering
☐ Brine Concentrate Management	☐ MBR and MABR Systems	X X Water Reuse
☐ Digestion	☐ Nutrient (N or P) Removal	☐ Direct Potable Reuse
X Disinfection	☐ Nutrient (N or P) Recovery	
	Odor Control	

X **Other (Write-In)** tertiary treatment; e.g., removal of complex organic compounds

*Other Resource Recovery in this instance applies to resources besides nutrients, energy, or water

The authorized signature below indicates your Organization's acceptance into the Water Environment & Reuse Foundation's ("WE&RF's) Technology Scan Program, a function of WE&RF's Leaders Innovation Forum for Technology ("LIFT"), and to the following terms and conditions:

1. WE&RF will submit your Application for review before a committee of experts, LIFT Program participants and/or WE&RF Subscribers who will engage in discussions and determine possible subsequent steps including potential pilots, demonstrations, testing/evaluation and or implementation of the technology.
2. You agree to release WE&RF, its employees, representatives, officers, trustees and agents from any liability for any damage, demand, cause of action or claim resulting or arising from the review of your Technology Scan Application.
3. You agree to indemnify, defend and hold WE&RF harmless from all liability which may arise or occur during or following the Application review. Your indemnification will include all WE&RF employees, agents, officers, trustees and representatives and includes payment of WE&RF damages, costs, expenses and attorney fees.
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I have read the foregoing Release and Indemnity Agreement, all terms and conditions set forth above, and sign in my capacity as a duly authorized representative of my organization. I also hereby state that the information in this application is accurate and complete to the best of my knowledge

BY: ___Pellucid Water LLC___________________
Company Name

_______________________________________ DATED: _______________________
Signature

____Sorin O. Manolache_________________________
Printed Name, Title

Note: The following are responses to ten (10) questions contained in the LIFT-Link Technology Scan. Text highlighted in blue responds to follow-up questions from the Review Committee. Appendices are located on separate web pages and accessed by clicking on the various Appendix hot buttons located throughout the text.

1. Company Background

Pellucid Water LLC was formed in 2014 as a partnership between Dr. Sorin Manolache and Mark Raabe. The company designs commercial reactors using a proprietary cold plasma technology. The reactors remove chemicals from solution through aggregation and precipitation.

The technology has its origins in research conducted by Dr. Manolache over the past 30 years at the University of Wisconsin – Madison (UW) and Petru Poni Institute for Macromolecular Chemistry in Romania. While at the UW, Dr. Manolache conducted research at the Center for Plasma-Aided Manufacturing (CPAM), investigating an innovative technology called Dense Medium Plasma (DMP) for decontamination and disinfection of water – see **Appendix 2**. After incorporation, this technology was further advanced and a commercial prototype, continuous flow, Pellucid Water cold plasma (PWCP) reactors developed – see **Appendix 3** and **Appendix 7**.

Pellucid Water is a member of The Water Council and one of six companies awarded a grant under the 2014 Batch II business accelerator program, called The BREW (Business, Research and Entrepreneurship in Wisconsin). Pellucid Water was a finalist in the 2015 Wisconsin Governor's Business Plan Contest and finalist in the 2015 Wisconsin Innovation Awards.

2. Key Personnel

Principals:

Sorin Manolache, PhD, is a plasma chemist and chemical engineer, formerly employed as a research scientist at UW-Madison. Dr. Manolache is the manager of research and development. See **Appendix 1** for resumes.

Mark Raabe is a civil and environmental engineer with experience as a regulator, researcher and consultant in the water sector. Mr. Raabe is the interim manager for sales and marketing, and provides engineering support. See **Appendix 1** for resume.

Advisory Board:

Kurt Raabe, CPA (brother to Mark) has 35 years of accounting, financial and operating experience at paper mills of Georgia Pacific, Sher Plastics Co., and beverage company Diageo, PLC. Mr. Raabe provides business and financial support.

Tim Casper, attorney at Murphy Desmond S.C. is a trial lawyer and member of Murphy Desmond's Business Start-Up/Entrepreneur group. Mr. Casper provides advisory services in business start-ups and contracts.

Matthew Frank, attorney at Murphy Desmond S.C. previously served as Secretary of the Wisconsin Department of Natural Resources. He maintains a practice in environmental law, renewable energy and sustainability. Mr. Frank provides advisory services regarding regulatory issues.

3. Technology Description

Current methods of water decontamination are based on the use of chemical agents, ion exchangers, bioreactors, catalysts, or membrane-based systems. The application of PWCP does not require any additional biological agents, materials or consumables. PWCP uses only the internal chemistry of the water and its contaminants.

The PWCP electrical discharge creates a highly reactive environment by producing positively and negatively charged particles and free radicals – see **Appendix 12** on electric discharge regimes. These interact initially on the organic molecules. Selective bonds are broken and functional groups added that induce aggregation of the organic molecules into macromolecular / supramolecular (macro/supra) structures, similar to the branches on a tree (see Figure 3.1). When the macro/supra structures reach a critical size, they become unstable in solution, form a flocculent, and precipitate from solution. See **Appendix 11** on plasma chemistry methods.

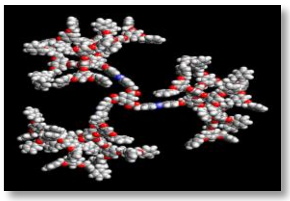

Figure 3.1. Supramolecular structures.

The inorganic portion of the chemical matrix is removed as a secondary process. Inorganic chemicals are attached to the macro/supra structure either chemically or physically trapped. Concurrently, biological organisms are destroyed by the effect of cold plasma on their structural membranes and disruption of the membrane due to the chemical changes of the environment. Organisms are then removed from solution through chemical bonding or entrapment in the macro/supra structure.

3.1 What problem does it solve?

Three critical issues exist with respect to water:

1. replacement of aging water and wastewater treatment infrastructure;
2. compliance with new water quality regulations; and
3. growing shortages of freshwater.

Pellucid Water provides solutions to all three issues through application of PWCP: an innovative form of cold plasma technology that kills and removes bacteria and viruses, and precipitates molecules, biomolecules and ions from solution. These chemical resources are then more readily available for recovery/reuse.

3.2 What is the value proposition?

PWCP provides value to the end user by decreasing the cost of water treatment and increasing the capabilities and efficiencies of water treatment systems. The major attributes of this technology are summarized below:

SIMPLICTY: PWCP uses a simpler approach to water treatment through use of plasma chemistry for removal of chemicals from solution and disinfection. PWCP uses only an electrical discharge that minimally affects the chemical matrix, and targets physical properties that result in their precipitation. Conventional technologies use chemical agents (e.g., alum), biological organisms (e.g., biofilters), filter media (e.g., membranes) and ion exchangers.

VERSATILITY: PWCP removes organic as well as inorganic chemicals from solution. It can also be used concurrently for disinfection. Conventional technologies are specialized in their application; thus, a series of processes are required for similar treatment.

EFFICIENCY: PWCP has a highly reactive chemistry and consistent performance. Whereas, conventional biofilters have comparatively low efficiency and their performance can vary with external conditions. The efficiency of chemical polymers and ion exchangers is similarly dependent on replacement of consumables or recharging.

NO WASTAGE: PWCP does not produce any added wastes. Conventional technologies such as chemical polymers combine with the chemicals in the water, and filter media must be recharged through backwashing. Both methods create secondary wastes.

LOW ENERGY: PWCP ionization occurs at low energy levels and marginally affects chemicals in solution, inducing aggregation, flocculation and precipitation. Conventional technologies such as biofilters and membranes have comparatively large electrical power requirements.

COST: PWCP reduces overall treatment costs when compared with conventional technologies because consumables include electrical power only. Infrastructure costs are reduced because of the multiple and simultaneous treatment capabilities of cold plasma. Cold plasma is a more cost effective technology, because it is more versatile and more efficient than conventional technologies.

RESOURCE RECOVERY & REUSE: PWCP creates opportunities to utilize the resources contained in the water, and the water itself. Chemical compounds removed from solution can then be recovered and either recycled or reused as value-added products. Likewise, water can be recycled or used for new purposes. Conventional treatment processes are constrained because chemicals either cannot be recovered; are altered by the addition of added chemistry (i.e., polymers) or biological degradation; or are lost through respiration or volatilization.

3.3 What is its impact potential for the water sector?

The aggregate impact of the attributes of PWCP is potentially transformative. This is due to the fundamental science upon which PWCP is based.

3.4 What is innovative about the technology? PWCP uses chain reactions initiated by plasma, whereas conventional technologies specifically target each contaminant molecule. From the standpoint of efficiency, this can be compared with a proficient pool player who strikes a ball that knocks 5 other balls in pockets simultaneously, instead of shooting at each ball individually. PWCP uses low energy electrical discharges that aggregate molecular structures, and acts on the entire chemical matrix simultaneously. This contrasts with conventional technologies that require high energy inputs in the forms of chemicals, electrical power, mechanical devices, etc. – each acting only on a portion of the chemical matrix.

Current technologies that are widely used for water decontamination and disinfection have existed for decades; some have existed since the early 20th century. Advances since that time have increased their efficiency; however, the underlying chemistry remains the same. This underlying 'classical chemistry' governs the efficiency of the process methods and their potential for transformative change.

Transformational changes that are sought in the water sector will not occur until the water treatment industry moves beyond classical chemical methods. There is a nascent movement in this direction by companies like Pellucid Water; however, the momentum that exists by current technologies, and the reluctance by industries (and municipalities) to adopt innovative technologies, are major impediments to transformational change.

PWCP is based on 'plasma chemistry' rather than classical chemistry. Plasma chemistry is a very reactive chemistry that can be applied to a broad base of water quality problems. PWCP treats the whole chemistry concurrently using only an electrical discharge. Thus, its application has potential to greatly reduce the infrastructure that is currently used (consisting of multiple treatment technologies in a process system) and greatly reduce operational costs by eliminating the use of chemical and biological agents.

Application of plasma chemistry is also potentially transformational in applications where classical chemistry is limited, logistically untenable, or not feasible. An example is the application of PWCP for precipitation of complex organic compounds from solution – see **Appendix 8**. The vast number and classes of these compounds is beyond the capability of a single treatment process based on classical chemistry. However, plasma chemistry reacts with all organic compounds.

3.4.1 Are there competing technologies in the marketplace, and if so how does this compare to them?

There are various private companies and public institutions that are developing water treatment technologies using cold plasma. These technologies employ *advanced oxidation* as the plasma mechanism. The table below compares these technologies with the *branching* mechanism employed by PWCP.

	Tubular Plasma Reactor	DMP WaPR	DMP	Hydrox	Independent Moving Discharges in Plasma Reactor
Developer	Symbios Techologies, Inc.	Orbital Tech. Corporation	CPAM, UW - Madison	Japan	Pellucid Water, LLC
Treatment	Advanced oxidation	Advanced oxidation	Advanced oxidation	Advanced oxidation	Macro/Supra molecular particle aggregation
Final products	CO_2	CO_2	CO_2	CO_2	Separable particles
Configuration	tubular	Stationary electrodes	disc	Stationary electrodes	Moving discharges
Electrodes	Parallel actuated	NA	Parallel actuated	NA	Independent actuated
Water conductivity range	Low	Low	Low	NA	Low to High
Flow range demonstrated	Not specified	Very low	Batch type, 200 mL	Batch type	100 – 1000 gal/day on a portable device

Symbios Technologies is the only company other than Pellucid Water that markets a cold plasma reactor for direct application to water. The following is a detailed review of Symbios Technologies' technology and comparison with PWCP technology:

- **Background:** Symbios has its origins in research conducted by D. Sorin Manolache (now at Pellucid Water) et al. at the University of Wisconsin Center for Plasma-Aided Manufacturing (CPAM). The Office of Naval Research (ONR) contracted with CPAM to investigate the application of Dense Medium Plasma (DMP) for use in disinfection of gray water on Navy ships. At that time, Dr. Derek Johnson was an intern employed with ONR on this project. A copy of the reactor was sent to ONR under this contract.
- **Colorado State University:** Dr. Johnson worked with Dr. David Dandy (faculty in the Chemical & Biological Engineering Dept.) at Colorado State University (CSU) in development of a *tubular*

plasma reactor (TPR). Symbios' website states that commercialization of TPR technology is a collaboration between Symbios and CSU.

- **NSF sponsorship**: The Symbios website states that the company has had a close relationship with NSF since 2011, when it was awarded a Phase I SBIR grant, which supported initial development of TPR. NSF continued support in 2013 by awarding a Phase II SBIR grant and a supplemental grant called Technology Enhancement for Commercial Partnerships (for electrode advancements to the TPR).

  [Note: NSF did not fund a Phase I SBIR application by Pellucid Water, despite references regarding the differences between Symbios' and PWCP technologies. NSF reviewers did question the difference between PWCP and a Phase I grant awarded by NASA to Orbitec for design of a continuous flow cold plasma reactor (which was unsuccessful). However, no reference was made to prior funding by NSF of research on cold plasma by Symbios.]

- **TPR:** This is an adaptation of DMP technology developed at CPAM and patented by the Wisconsin Alumni Research Foundation (WARF). However, rather than a rotating disk as a basis for the design, TPR uses a rotating tube. See page 315, Figure 3, of the publication entitled *Development of a Tubular High-density Plasma Reactor for Water Treatment* at URL **https://pdfs.semanticscholar.org/c428/11ac90b20de0c051bda373ee05996c2feeb3.pdf**.

- **Plasma Chemistry Mechanisms:** Research at CPAM investigated more efficient methods of *advanced oxidation* using plasma. This was the basis of research using DMP. Advanced oxidation is one of three plasma chemistry mechanisms, as shown **Appendix 11**. The other mechanisms are *branching* and *crosslinking*.

- **Pellucid Water's Cold Plasma (PWCP)**: Pellucid Water advanced DMP technology by moving away from *advanced oxidation* and instead targeting *branching* as a preferred mechanism for water treatment, using plasma to assemble macromolecular / supramolecular structures. This mechanism can be applied for water decontamination and disinfection of liquids, and for functionalization of organic molecules.

- **Comparison of TPR with PWCP**: The following are major differences between these technologies:

  1. **Energy Requirements – current level:** TPR requires high current to create plasma discharges. Multiple pins are connected to a single electrode but mainly one pin fires at any one time. [Note: The pins cannot be balanced because they are connected to the same electrode.] This increases the potential for the plasma discharge to enter the regime of 'hot plasma'. Hot plasma discharges may result in the creation of nanoparticles that are dispersed from the pins. Furthermore, hot plasma discharges will result in high maintenance, because the pins will require frequent replacement.

     PWCP discharges use multiple electrodes that are balance, with each firing independently of other electrodes in the reactor. This allows for greater control of the discharge, preventing hot plasma discharges; much less use of energy; and much greater efficiency in delivery of plasma to the water.

  2. **Energy Requirements – oxidation:** TPR targets each organic and inorganic molecule, and breaks bonds (where possible) using oxygen. This requires large amounts of energy. The Symbios website states that compressed air is used to generate the plasma.

     PWCP does not target each organic and inorganic molecule, and it does not destroy the molecules through oxidation. Rather, it breaks selective bonds and adds functional groups that result in aggregation of the molecules through chain reactions and branching. This requires much less energy. Compressed air is not required.

3. **Conductivity:** TPR use of multiple pins results in high surface area. Discharges will occur when the conductivity is relatively low, but becomes problematic when conductivity increases. Higher energy inputs will then be required to generate discharges, with most lost in conduction (heating).

   PWCP is applicable to a broad range of effluents because the discharge uses higher frequency AC and reduces the conductivity lost. [Note: The advantage of AC discharges over DC is that insufficient time exists to fully polarize the liquid.] Thus, much less energy is required, and potential problems are avoided that are associated with high-energy electrical discharges.

4. **Decontamination – organics:** According to the Symbios website, TPR destroys "many" organic compounds. This limitation applies to complex organic compounds that are resistant to oxidation, and therefore cannot be removed from solution. Thus, TPR is likely not a suitable platform to address the problem of Chemicals of Emerging Concern (CECs) that was discussed in the White Paper to EPA – see **Appendix 8**.

   PWCP is applicable to all organic compounds because it does not remove chemicals from solution through oxidation. Rather, it aggregates them into macromolecular / supramolecular structures.

5. **Decontamination – inorganics:** TPR is not marketed as a treatment method for removal of inorganic compounds – no reference to inorganics is made on the Symbios website. Oxidation of inorganic compounds and ions change their state; however, most of them remain soluble at low concentrations.

   PWCP removes inorganic compounds and ions from solution in a secondary process, where they attach to macromolecular / supramolecular structures chemically or are physically trapped. They are then removed from solution through flocculation and precipitation together with the organic chemistry.

6. **Disinfection:** TPR destroys micro-organisms through the creation of hydrogen peroxide. This process results in acidification of the water.

   PWCP destroys micro-organisms through denaturing of the membrane (requiring much less energy than TPR); formation of hydrogen peroxide at low concentrations is also possible. PWCP does not result in acidification of the treated water.

7. **Scaling:** The Symbios website states that TPR is "[r]eadily scalable, from a small size to skids of multiple reactors deployed in parallel to process 7,000 bbl/day or more…". The potential for scaling TPR to much larger flow rates is limited due to engineering constraints; specifically, water must pass through the narrow gap between the tube and the reactor chamber. [Note: Scaling to high flow rates will likely result in high capital and operating costs, because multiple reactors would be required.]

   PWCP is much more suited to scaling because the design of the reactor does not have these engineering constraints; specifically, the electrical discharge is not dependent on maintaining a gap between a stationary and rotating electrode. Scaling of PWCP simply requires matching the amount of cold plasma delivered to the water to the chemical matrix and flow rate.

8. **Footprint:** The size of the TPR reactor will increase with scaling, due to the design, engineering constraints, electrical power requirements, and oxygen demand.

   PWCP reactor has a small footprint that does not increase proportionally with scaling, because engineering constraints do not exist, electrical requirements are low, and compressed air is not required.

9. **Resource recovery:** TPR does not create opportunities for revenue generation through resource recovery and reuse, because the organic and inorganic molecules are changed or destroyed through oxidation.

   PWCP aggregates the organic and inorganic molecules into macromolecular / supramolecular structures that are removed from solution through flocculation and precipitation. These structures are stable (i.e., they will not resolublize) and compounds that were toxic in solution are rendered nontoxic as a precipitate (e.g. acrylic monomers are toxic but some polymers are used in dentistry). [Note: CO_2 can be one of the end products in advanced oxidation, which is a greenhouse gas.]

4. Technology Applications

4.1 What is the best application(s) for this technology?

PWCP is most suited to removal of chemicals from solution. Cold plasma acts on the entire chemical matrix within a water sample. Therefore, its potential is for all applications where the objective is to remove chemicals from solution (and concurrently for disinfection). The benefits derived will depend on the specific application.

4.2 Does it integrate into existing systems?

PWCP can be integrated into existing secondary treatment systems to provide tertiary treatment; i.e., to improve removal efficiencies of organic and inorganic compounds (e.g., phosphorus), and to remove compounds that do not respond to secondary treatment (e.g., complex organic compounds). PWCP could also be used in place of secondary treatment, because it reacts with the entire chemical matrix simultaneously, as well as provides disinfection.

4.3 Is it completely new and stand alone?

PWCP is a new platform for water treatment. It is a 'stand alone system' for the removal of chemicals from solution and for disinfection. The PWCP reactor can be designed for specific water quality objectives and integrated in an overall process system.

4.3.1 Is this technology similar to electrocoagulation?

Pellucid Water cold plasma (PWCP) technology is typically associated with other cold plasma technologies that incorporate *advanced oxidation* as the plasma mechanism, and with electrocoagulation. Research conducted by Dr. Sorin Manolache while a research scientist at the University of Wisconsin, Center for Plasma-aided Manufacuring (CPAM), investigated the application of Dense Medium Plasma (DMP) as a more efficient *advanced oxidation* process – see **Appendix 2**. However, after leaving CPAM and forming Pellucid Water, Dr. Manolache began development of cold plasma reactors that use *branching* rather than *advanced oxidation* as the plasma mechanism. A comparison of major attributes of PWCP (using *branching*) versus electrocoagulation is found in **Appendix 4**, Table 4.1.

4.4 Is it intended to enhance or replace?

PWCP could be used to enhance existing water treatment systems. For example, it could be used as a tertiary treatment system to remove organic and inorganic chemicals from an existing secondary treatment facility. However, this does not utilize the full potential (and realize the full financial benefits) of PWCP, because it is not being applied to the full chemical matrix of the effluent entering the treatment facility. PWCP could instead provide tertiary treatment while at the same time replace existing secondary treatment technologies that remove chemistry from solution and provide disinfection.

4.4.1 Is it possible to share a basic schematic of the technology – i.e., how this would integrate into a plant?

The schematic of a water treatment process system using PWCP technology depends on the application. The following design elements are common to each application:

- **Contact between plasma and effluent:** The length of time required will depend on: 1) the amount of plasma required to aggregate the chemistry into a flocculent; 2) the rate of plasma delivered; and 3) the amount of chemistry in the effluent. The contact time is determined through tuning of the reactor and bench tests, using a sample of the effluent. The required contact time is achieved through use of a *contact tank* where one or more PWCP reactors are used to recirculate the effluent.
- **Sedimentation:** A vessel is required to allow the flocculent to aggregate and precipitate. The amount of time required will be based on the chemical matrix of the effluent and tuning of the reactor. The plasma discharges can be designed to place charges on the flocculent particles to accelerate aggregation. Tuning of the PWCP reactor will be conducted in conjunction with bench tests to determine the precipitation time required.
- **Solids Capture / Dewatering:** PWCP is a technology for aggregation of dissolved chemistry and disinfection. It is not a technology for separation of the precipitate from water. In some applications, a process system using PWCP will require a solids recovery/dewatering technology as part of the process system. In other applications, a solids recovery technology may not be required.

The schematics for four separate types of applications are discussed below:

- **Municipal WWTF, tertiary treatment only**

  Interest has been expressed by various municipalities in the possible application of PWCP as a tertiary treatment system to reduce residual phosphorus concentrations (to comply with new water quality regulations). Bench studies (previously discussed in the LIFT application) indicate that PWCP is highly efficient in reducing phosphorus concentrations. [Note: The mechanism used is to bind the phosphorus to residual organic molecules in solution; thus, additional treatment of organics occurs simultaneously.]

  The tertiary system will require a contact tank and sedimentation tank. The precipitate could be discharged to the secondary clarifier, where the sediment may act to enhance sedimentation within the vessel.

  This application uses only a portion of the capability of PWCP to treat municipal effluent; however, municipalities are typically reluctant to make major modifications to their secondary WWTF because these facilities are bonded. However, the tertiary treatment system may nonetheless be designed to expand its application so the municipality may reduce operational costs of the secondary WWTF. For example: Bench tests conducted for design of the tertiary system could be conducted on the effluent from the secondary WWTF before disinfection rather than after disinfection. PWCP is a strong disinfectant; thus, use of PWCP in a tertiary system could result in decommissioning of the existing disinfection system (e.g., chlorination and dechlorination). This would result in a reduction in the operating costs of the secondary WWTF, and may not require significant changes in the overall design of the tertiary system.

- **Municipal WWTF, secondary and tertiary treatment**

  The discussion of PWCP technology in the LIFT application identified PWCP as a technology that reacts with the chemical and biological matrixes simultaneously. Thus, PWCP could be applied as a replacement for conventional secondary treatment and thereby avoid the added cost of a separate tertiary treatment system.

  The major components of a process system based on PWCP technology include the following:

  - primary clarifier
  - PWCP contact tank (multiple tanks would facilitate ease of operation/maintenance)
  - secondary clarifier
  - solids recovery/dewatering

- **Municipal WWTF, pre-treatment of sludge before an anaerobic digester**

  Vendors who supply equipment for dewatering sludge from *activated sludge* systems have inquired whether PWCP can be used as a pretreatment for anaerobic digesters. PWCP disinfects water by denaturing the cell membrane of organisms. This would make the organic compounds within the membrane more readily available for digestion by anaerobic bacteria within the digester. [Note: Studies have yet to be conducted to validate this thesis.]

  This application will require a contact tank before the inlet of the anaerobic digester. No further infrastructure is anticipated because sedimentation is not required.

  PWCP could also be used for treatment of the digestate, to remove residual dissolved chemistry. This will require a contact tank and a sedimentation tank. The solids could be sent to the secondary clarifier of the WWTF.

  If PWCP is used for secondary/tertiary treatment, there would not be any sludge produced from an *activated sludge* system (because *activated sludge* is unnecessary to remove organic compounds from solution). The precipitate from the secondary clarifier could potentially be sent to the anaerobic digester without pretreatment (i.e., without PWCP treatment and dewatering, assuming the solids/water ratio is acceptable). It should be noted:

- **Organic loading:** The amount of organic material recovered in the secondary clarifier will be larger because biological decomposition is not part of the WWTF.

- **Energy production**: The amount of energy generated from anaerobic digestion will be larger, due to the increase in the volume of organic solids removed from solution and quality of the feedstock (i.e., a larger percentage of organic compounds are available for digestion).

- **Questions:** Research has not been conducted on the fate of precipitate produced by PWCP from treatment of municipal effluent. Questions exist regarding whether anaerobic bacteria are capable of decomposing the macro-molecular and supra-molecular structures produced by PWCP. Pellucid Water has discussed this with various universities as a potential area of research; however, funding for this research has not been secured. [Note: The scope of this research could also include the fate of PWCP precipitate when exposed not only to anaerobic bacteria, but also aerobic bacteria (where a WWTF does not have an anaerobic digester). This study would provide important data regarding the mechanism used in decomposition of the precipitate and the rates that both organics and nutrients become available for production of methane or for uptake of nutrients by plants.]

- **Industrial WWTF, treatment of wastewater in the manufacture of fiber composites**

  Certain industrial processes that incorporate PWCP may potentially greatly reduce the production of wastewater, or even eliminate it entirely. An example was cited in the LIFT application, where a Pellucid Water reactor is being employed by a company that is developing a cellulosic composite with hydrophobic properties. Pellucid Water conducted bench tests using effluent generated from their wet-processing system. The wastewater contained residual dissolve organics (i.e., lost cellulosic fiber) and residual chemicals. Application of PWCP resulted in functionalization of the surface chemistry of the cellulosic fiber and subsequent bonding of the residual chemistry. The cellulosic fiber precipitated and floated to the surface. Later research conducted by the company indicated that the precipitate could be used as filler in the production of new hydrophobic cellulosic fiber. Thus, full utilization of inputs (fiber and chemistry) is realized, and the water can be recycled in a closed system.

  This application of PWCP requires only a contact tank. Sedimentation is not required; rather, the treated effluent (both sediment and clear water) is simply circulated back to the wet-process tank.

4.5 Is there a retrofit aspect?

Retrofitting existing water and wastewater treatment facilities with PWCP reactors may not be feasible in all instances. Where an existing treatment facility has exceeded its design life and must be replaced, retrofitting is feasible. Also, retrofitting may not be economically feasible when considering the cost associated with servicing municipal bonds that finance existing infrastructure.

4.6 Is its applicability across "all" systems / configurations or select systems or is it exclusively a "green field" technology?

PWCP is applicable across all treatment systems for removal of chemicals from solution and disinfection.

4.6.1 What are the byproducts of this process?

Cold plasma discharges using *branching* is a fundamentally different mechanism from discharges using *advanced oxidation*. Branching results in aggregation of chemicals within the organic and inorganic matrix into macro-molecular and supra-molecular structures. Whereas, advanced oxidation disaggregates the chemicals, which can lead to the formation of byproducts that are chemically different than their parents.

The structures produced by PWCP are stable (i.e., they will not resolublize) and compounds that were toxic in solution are rendered nontoxic as a precipitate.

5. Technology Performance and Benefits

- **Performance Goal:** Removal of chemicals from solution and disinfection using cold plasma technology.
- **Claims of this Technology:** Plasma chemistry is fundamentally a better platform for water treatment than classical chemical methods used by current water treat technologies.
- **Expected Results:** Use of PWCP will result in savings in infrastructure and recurring costs derived from:
  1. treatment of the whole chemical matrix and disinfection concurrently;
  2. a broader range in applications;
  3. higher range of efficiency; and
  4. elimination of chemicals, biological agents or membranes.

In addition, land requirements are reduced because PWCP requires a small footprint when compared with existing technologies.

6. Testing and Demonstration Results to Date

Date	Scale	Type	Location	Duration	Data
2004	Bench	research	University of WI	4 years	see **Appendix 2**
2014	Bench	research	Pellucid Water	2 years	see **Appendix 3**
Jan. 2015	Bench	paper mill	central WI	2 weeks	see **Appendix 5**
Jan. 2015	Bench	municipal WWTF	Whitewater, WI	1 week	see **Appendix 6**
2016	Pilot	wood composite	USDA, Madison, WI	unknown	see **Appendix 9** & **Appendix 10**
2016-2017	Pilot	paper mill	northeast WI	unknown	see **Appendix 9**
2016 - 2017	Pilot	industrial wastes	Waukesha, WI	unknown	see **Appendix 9**

6.1 Since submitting the LIFT application, provide an update on pilots being developed.

Pellucid Water identified three planned pilot-scale treatment systems using PWCP reactors for the following applications: water treatment and manufacture of new cellulosic composites with hydrophobic properties; water treatment and enhanced manufacture of existing cellulosic (i.e., paper) composites; and mobile industrial wastewater treatment.

Since submittal of the LIFT application, progress has been made toward development of a pilot-scale system for water treatment and production of new cellulosic composites – previously described in Appendix 9. The updates include the following:

- Pellucid Water sold a PWCP reactor to an unnamed party for research purposes. Their objective is development of hydrophobic cellulosic composite materials for the consumer market. PWCP is used for both treatment of the wastewater and manufacture of the composite.
- This party recently notified Pellucid Water of their intent to purchase one or more larger PWCP reactors for a pilot-scale facility. This facility is currently being designed and is expected to be constructed in early 2017.

Pellucid Water recently began collaboration with a potential licensee called CORNCOB, Inc. (**http://www.corncobinc.com/**) to apply PWCP technology in their innovative filtration system for separation of both dissolved and suspended solids down to sub-micron sizes. A PWCP reactor would be integrated into their existing pilot-scale treatment system, and tests conducted using effluents of market interest.

7. Papers, Publications, and Proceedings

Dr. Manolache et al. published various technical papers and patents on the application of Dense Medium Plasma (DMP), using *advanced oxidation* as a cold plasma mechanism for water decontamination, disinfection and production of nanoparticles. The following is a list of selected technical papers. Abstracts of the first three technical papers are located in **Appendix 13**. [Note: A complete list of publications is available upon request.]

Research conducted by Dr. Manolache at Pellucid Water on development of continuous flow cold plasma reactors using *branching* as a cold plasma mechanism has not been published.

1. **S. Manolache**, E. B. Somers, A. C. L. Wong, V. Shamamian and F. Denes, Dense Medium Plasma Environments: A New Approach for the Disinfection of Water, *Environmental Science and Technology* 18, 3780 – 3785 (2001).
2. D. C. Johnson, V. A. Shamamian, J. H. Callahan, F. S. Denes, **S. O. Manolache** and D. S. Dandy, Treatment of methyl tert-butyl ether contaminated water using a Dense Medium Plasma Reactor: A Mechanistic and kinetic investigation, *Environmental Science and Technology* 37, 4804 – 4810 (2003).
3. **S. Manolache**, V. Shamamian and F. Denes, DMP Plasma-Enhanced Decontamination of Water of Aromatic Compounds, *Journal of Environmental Engineering* 130(1), 17 – 25 (2004).
4. Method for Disinfecting a Dense Fluid Medium in a Dense Medium Plasma Reactor, F.S. Denes, **S.O. Manolache**, A.C.L. Wong, and E.B. Somers, 06/15/2004, *US 6749759 B2*.
5. F. S. Denes, **S. Manolache** and H. Jiang, Dense Medium Plasma Environments Used for the Synthesis of Nanoparticle Systems and Structural Modification of Liquid Media, *J. Photopolymer Sci. Technol.* 26(4), 513 – 527 (2013).
6. H. Turkoglu Sasmazel, **S. Manolache**, M. Gumusderelioglu, Functionalization of PET fabrics by water/O_2 plasma for biomolecule mediated cell cultivation, *Plasma Processes and Polymers* 7(7), 588 – 600 (2010).
7. H. Turkoglu Sasmazel, **S. Manolache**, M. Gumusderelioglu, Water/O2 plasma assisted treatment of PCL membranes for biosignal immobilization, *Journal of Biomaterials Science: Polymer Edition* 20(7-8), 1137-1162 (2009).
8. Y. Ma, **S. Manolache**, F. Denes, J. Cho, and R. Timmons, Surface Modification of Rutile TiO_2 by Submerged Arc for Improved Photoreactivity, *Journal of Materials Engineering and Performance* 15(3), 370-375 (2006).
9. F. Denes and **S. Manolache**, Macromolecular Plasma-Chemistry: an Emerging Field of Polymer Science, *Progress in Polymer Science* 29(8), 815-885 (2004).
10. Colloidal Nanoparticles and Apparatus for Producing Colloidal Nanoparticles in a Dense Medium Plasma, F. S. Denes, **S. O. Manolache** and N. Hershkowitz, 10/05/2010, *US 7807112 B2*

8. Intellectual Property Status

Pellucid Water is in the process of applying for a provisional patent on its commercial prototype, continuous flow, cold plasma reactor.

9. Technology Development Level

Based on the criteria for the TDL scale, Pellucid Water has completed Level 1 for many applications of its cold plasma technology. However, in regard to the Technical Readiness Level (TRL) scale, for some applications Pellucid Water has completed Level 6.

Pellucid Water has yet to conduct pilot-scale testing with any current industrial or municipal water or wastewater treatment facility. However, various pilot-scale systems are in the planning stage – see **Appendix 9**.

10. Technology Next Steps Needed / Desired

Pellucid Water is advancing its technology by identifying applications that are achievable based on its current level of technical development and readiness. This is defined as waste streams having a flow rate less than 100,000 gallons/day and low to high concentration of chemicals within its matrix. Applications that have a greater flow rate will require additional R&D to scale the technology. [Note: Scaling is not limited by the underlying science. The PWCP reactor must be engineered to deliver sufficient amounts of cold plasma to achieve the desired water quality objective.]

The most immediate commercial application is for industrial effluents where the flow rates are within its present capabilities. However, Pellucid Water continues to advance its R&D in scaling its technology to higher flow rates. Pellucid Water has applied to various federal government agencies to support its R&D, particularly in regard to scaling and demonstration of commercial feasibility through construction of pilot-scale systems. However, no grants have been obtained presently. Based on evaluation of the White Paper (see **Appendix 8**), EPA representatives recommended that testing and evaluation be conducted at EPA's Technology & Evaluation Facility. Pellucid Water submitted a Phase I proposal to the 2017 EPA-SBIR program and 2017 NASA-SBIR. , and is currently in discussion with NASA for possible testing and evaluation.

Municipal and private water and wastewater treat facilities have expressed interest in this technology; however, no party has expressed interest in supporting its commercialization through demonstration at a pilot-scale.

10.1 Any reason the development of this technology has been so delayed?

Historically, research in cold plasma was conducted in the gas phase. Dr. Sorin Manolache began his career in Romania investigating applications initially in the gas phase and then expanded into non-aqueous liquids (i.e, called *Dense Medium Plasma*) – i.e., liquids that have low conductivity. He moved to the United States in 1990's and joined scientists at the University of Wisconsin, where a Center for Plasma-aided Manufacturing (CPAM) had been formed with a grant from the National Science Foundation. While at CPAM, he developed applications of cold plasma for direct application to aqueous solutions, rather than through the gas-water interface. This application was based on *advanced oxidation*. [Note: The design of the research reactor developed at CPAM is the basis of the cold plasma reactor marketed by Symbios Technologies.]

The research priorities at CPAM were not in development of cold plasma reactors for water treatment. Rather, it was in the application of cold plasma for nanoparticle synthesis.

The development of PWCP technology has actually progressed rapidly from inception. The following is an historical summary of Pellucid Water and development of its technology:

2013 - CPAM was decommissioned.

2014 - Dr. Manolache left the University and co-founded Pellucid Water. Dr. Manolache subsequently developed an R&D program based on design of plasma discharges used a *branching* mechanism, rather than *advanced oxidation*. *Branching* is more suitable than *advanced oxidation* for application to water decontamination and disinfection. The treatment efficiencies are higher and the energy consumption is lower.

2015 - Pellucid Water designed the first research prototype continuous flow cold plasma reactor using a *branching* mechanism.

2016 - Pellucid Water substantially improved the initial prototype, creating a commercial prototype (PWCP) reactor that produces AC discharges rather than DC between stationary electrodes.

2017 - Pellucid Water seeks opportunities to conduct tests of PWCP reactors in pilot-scale facilities, either through collaborations with channels or through financial support from federal research grants.

APPENDIX 1

Resumes of Key Personnel

Dr. Sorin Manolache
Pellucid Water, LLC
Global Water Center; 247 W. Freshwater Way, Suite 240
Milwaukee, WI 53204
Phone: (608)772-4309
e-mail: s1manolache@gmail.com

A. PROFESSIONAL PREPARATION

"Gh. Asachi" Polytechnics Institute, Iasi, Romania	Chemical Eng.	BS/MS	1984
"Gh. Asachi" Polytechnical Institute, Iasi, Romania	Chemical Eng.	PhD	1996
University of Wisconsin – Madison, CPAM	Plasma Chemistry	Postdoc	2001

Special Trainings

1992 New techniques in chromatography – Hewlett-Packard Analytical (Vienna, Austria)
1996 GC1 – Hewlett-Packard Analytical (Waldbronn, Germany)
1996 GC/MS – Hewlett-Packard Analytical (Waldbronn, Germany)
1997 GC 6890 – Hewlett-Packard Analytical (Waldbronn, Germany)
1997 HPLC 1100 – Hewlett-Packard Analytical (Waldbronn, Germany)

B. APPOINTMENTS

2014	Co-founder/Manager, Pellucid Water LLC
2005 – 2014	Assistant Scientist, Center for Plasma-Aided Manufacturing, UW-Madison
2001 – 2005	Assistant Researcher, Center for Plasma-Aided Manufacturing, UW-Madison
1998 – 2001	Research Associate, Center for Plasma-Aided Manufacturing, UW-Madison
1997	Principal Scientific Investigator (CP3), "P. Poni" Institute of Macromolecular Chemistry, Iasi, Romania
1992 – 1997	Head of the Department of Electroactive Polymers and Plasma Chemistry, "P. Poni" Institute of Macromolecular Chemistry, Iasi, Romania
1986	Scientific Investigator, "P. Poni" Inst. of Macromolecular Chemistry, Iasi, Romania
1985	Chemical engineer, "Moldoplast" Plastics Company, Iasi, Romania
1984	Chemical engineer, Plastics Company, Focsani, Romania

C. PRODUCTS

Relevant Products:

1. **S. Manolache**, V. Shamamian and F. Denes, Dense Medium Plasma-Enhanced Decontamination of Water of Aromatic Compounds, *Journal of Environmental Engineering* **130(1)**, 17-25 (2004).
2. D. C. Johnson, V. A. Shamamian, J. H. Callahan, F. S. Denes, **S. O. Manolache** and D. S. Dandy, Treatment of methyl tert-butyl ether contaminated water using a Dense Medium Plasma Reactor: A Mechanistic and kinetic investigation, *Environmental Science and Technology* **37**, 4804-4810 (2003).

3. **S. Manolache**, E. B. Somers, A. C. L. Wong, V. Shamamian and F. Denes, Dense Medium Plasma Environments: A New Approach for the Disinfection of Water, *Environmental Science and Technology* **35(18)**, 3780-3785 (2001).
4. F. Denes and **S. Manolache**, Macromolecular Plasma-Chemistry: an Emerging Field of Polymer Science, *Progress in Polymer Science* **29(8)**, 815-885 (2004).
5. Method for Disinfecting a Dense Fluid Medium in a Dense Medium Plasma Reactor, F.S. Denes, **S. O. Manolache**, A.C.L. Wong, and E.B. Somers, 06/15/2004, *US 6749759 B2.*

Other Significant Products:

1. F. S. Denes, **S. Manolache** and H. Jiang, Dense Medium Plasma Environments Used for the Synthesis of Nanoparticle Systems and Structural Modification of Liquid Media, *J. Photopolymer Sci. Technol.* **26(4)**, 513 – 527 (2013).
2. Apparatus and Methods for Producing Nanoparticles in a Dense Fluid Medium, F. S. Denes, **S. O. Manolache** and H. Jiang, 01/04/2011, *US 7862782 B2.*
3. Colloidal Nanoparticles and Apparatus for Producing Colloidal Nanoparticles in a Dense Medium Plasma, F. S. Denes, **S. O. Manolache** and N. Hershkowitz, 10/05/2010, *US 7807112 B2.*
4. Plasma synthesis of micro- and macromolecular-wt. organic compounds in thick liquids or dispersions, C. I. Simionescu, F. Denes, and S. Manolache, 12/09/1991, *RO 103646 (C08F2/58).*
5. **S. Manolache** (PI), Dense Medium Plasma Water Purification Reactor (DMP WaPR), Orbital Technologies Corp. (ORBITEC Co.) $20,000 (subcontract of SBIR Phase I for NASA), 2006.

D. SYNERGISTIC ACTIVITIES

1. Reviewer for various peer-review journals.
2. Actively mentor undergraduate students for Undergraduate Research Scholars (URS).
3. Initiated plasma modification of nanotopography studies involving undergraduate and graduate students.
4. Development of novel low- and atmospheric-pressure, plasma-enhanced reaction mechanisms and related technologies for surface functionalization of natural and synthetic polymeric substrates (patents licensed by Intel).
5. Design and development of original plasma-chemistry tools (patents licensed by Intel).

E. COLLABORATORS & OTHER AFFILIATIONS

Collaborators: Petit, Peter; Denes, Ferencz; Jiang, Hongquan; Sarmadi, Majid; Uygun, Aysegul; Oksuz, Lutfi; Hershkowitz, Noah; Turkoglu-Sasmazel, Hilal; Gulec, Ali; Kiristi, Melek; Gumusderelioglu, Menemse; Aday, Sezin; Rowell, Roger; Wang, Amy; Young, Raymond
Graduate advisor: Cristofor I. Simionescu, "Gh. Asachi" Technical University of Iasi, Romania
Postdoctoral advisor: Ferencz S. Denes, University of Wisconsin – Madison, CPAM
Graduate / Undergraduate Adviser / Co-adviser for: Li, Ying; Mansuroglu, Dogan; Totolin, Vladimir; Han, Yoosoo; Dong, Bayian; Gutierrez, Klinsmann; Hall, Charles; Turkoglu-Sasmazel, Hilal
Post-doctoral / Visiting fellows: Martinez-Gomez, Alvaro; Uygun, Aysegul; Gursoy, Songul; Simsek, Onder

F. AWARDS & HONORS

2000 Photopolymer Science and Technology Award - Japan, Chiba – 2000.

Professional Affiliation

2000-2002	American Chemical Society, Affiliate Member (Polymer Division)
2002-Present	American Chemical Society, Full Member (Polymer Division)

MARK E. RAABE

Pellucid Water, LLC
Global Water Center; 247 W. Freshwater Way, Suite 240
Milwaukee, WI 53204
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e-mail: raabe626@ymail.com

A. PROFESSIONAL PREPARATION

University of Wisconsin – Madison	Civil/Environmental Engr.	B.S.	1979
Cornell University	Biological Systems Engr.	M.S.	1990

B. PROFESSIONAL AFFILIATIONS

2014 – present	Co-founder / Manager, Pellucid Water LLC
2011 – 2013	Crockett Technologies; engineering consultant; design of energy management systems.
2008 – 2010	RRT Design & Construction; project manager; design and construction of municipal solid waste recycling systems.
2006 – 2007	Key Engineering Ltd.; project manager; subsurface soil and water investigations.
1997 – 2005	University of Wisconsin – Madison; coordinator of non-profit organization and researcher
1993-1997	Stanley Consultants, Inc.; office manager and project manager; water supply and wastewater treatment
1992 – 1993	CH2M Hill International; project coordinator; water supply and wastewater treatment
1990 – 1992	Louis Berger International, Inc.; project engineer; environmental impact assessments

C. PRODUCTS

1. Egosi, N.G.; **Raabe, M.E.**; Weidner, R.; and Freel, G.A. 2010. Plant Upgrade: Recovery of Non-ferrous Metals from a Municipal RDF Facility. Presented to the 2010 North American Waste To Energy Conference (NAWTEC), Paper No. NAWTEC18-3510, Orlando, Fl. Published by ASME, May 2010.
2. Kammel, D.W.; **Raabe, M.E.**, and Kappelman, J.J. 2002. Design of High Volume Low Speed Fan Supplemental Cooling System in Dairy Free Stall Barns, Presented as a poster session to the 2002 ASAE National Convention. Chicago, IL.
3. Reinemann, D. J.; Malison, J.A.; **Raabe, M.E.**; Byrd, V. L. and Lima, L. 2001. Demonstration of the Use of Natural Fiber Filters and Airlift Pumps in Recirculation Aquaculture Systems, ASAE. Paper No. 0181, in ASAE Meeting Proceedings, Sacramento, CA.

Raabe, M.E. and Gunkel, W. 1989. The Sanitarian – An Expert System for Design and Installation of Onsite Sewage Disposal Systems. Presented as a poster session at the ASAE National Convention in Quebec City, CANADA.

APPENDIX 2

Early Research on Cold Plasma Conducted at the University of Wisconsin

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Dr. Manolache et al. (2004) conducted research at the University of Wisconsin – Madison on the application of Dense Media Plasma (DMP), which is a fore-runner to Pellucid Water's cold plasma technology. The data shown in Table 2.1 indicates that DMP achieves a higher efficacy in removal of organic compounds in comparison with other advanced discharge techniques, including ozone treatments.

Table 2.1. Comparison of existing plasma-based Advanced Oxidation and DMP techniques.

Reference	**Joshi et. al. 1995**	**Sunka et. al. 1999**	**Goryachev et. al. 1999**	**Sun et. al. 2000**	**Hoeben et. al.1999**	**Gurol et. al. 1987**	**Manolache et al. 2004**
Method	Corona in water	Corona in water	Corona in water	Corona in water	Corona in air	Ozon-olysis	DMP
Pulse Energy/mJ	1750	800	30	880	7	-	4.38×10^{6}
Frequency (Hz)	60	50	50	48	100	-	Continuous
Half time (min)	180	260	180	7	25	8	0.2
G50*	7.3×10^{-12}	4.2×10^{-12}	3.1×10^{-10}	3.7×10^{-9}	1.4×10^{-8}	5.2×10^{-8}	7.8×10^{-7}

*G50 is defined as the ratio of the number of moles comprising 50% attenuation divided by the amount of energy expended up to that point (higher means better efficacy).

APPENDIX 3

Advanced Research on Cold Plasma Conducted by Pellucid Water

Pellucid Water investigated the potential for further improvement in the efficiency in the cold plasma using controlled pulsed discharges. This initiates processes that aggregate the molecules in solution into macro/supra structures that then separate from solution through flocculation and precipitation. Table 3.1 compares the major benefits of PWCP with other water treatment technologies.

Table 3.1. PWCP versus other water treatment techniques.

	Other Treatment Technologies	**PWCP installation**
Method	Decompose or precipitate contaminants by reaction with an added compound	Create free radicals that produce macromolecular separable compounds
Added chemicals	Yes	No
Energy for process	High: Chemical energy required to react with each contaminant molecule	Low: Chemical energy to create a few free radicals that initiate a type of polymerization
End products	CO_2 – environmental problems Waste – disposal cost	Macromolecular compounds; components may be recovered and reused
Complex contaminants mixture	Separate processes that target specific categories or chemical compounds	Chemical and biological compounds processed in the same time; the more complex, the greater potential for decontamination
Reminiscence	Some end in reaction tank. Some continue to act downstream but are associated with specific smell / taste (e.g., chlorination process)	Trapped free radicals can continue removal of contaminants outside of plasma reactor, in sedimentation tank; no smell / taste effects
Foot print	Large typically	Small

The precipitates formed by PWCP are stable (i.e., they will not re-solubilize) and nontoxic.

APPENDIX 4

PWCP in Comparison with Advanced Oxidation Processes

PWCP is often mistakenly associated with other plasma technologies that incorporate advanced oxidation, and with electrocoagulation – see Appendix B10 for more information. Table 4.1 lists the major differences between PWCP plasma technology and electrocoagulation (from Kuokkanen et. al., 2013).

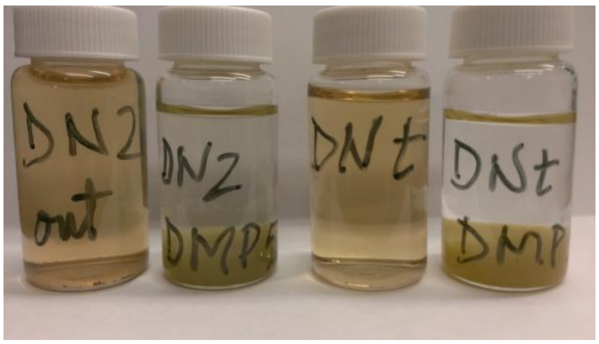
Table 4.1. Comparison of electrocoagulation technology with PWCP technology.

Criteria	Electrocoagulation Technology	PWCP Technology
Incorporates advanced oxidation	Yes	No
Requires 'sacrificial anode'	Yes	No
Methods: removal of Chemistry	Precipitation and Volatilization	Precipitation only
Chemical recovery potential	High for metals; Low for organic compounds, due to oxidation and volatilization.	High, due to minimal change in the chemistry; no metal contamination from electrodes.
Removal Efficiency dependent on pH	Yes, performs optimally at neutral pH	No, able to perform well within a wide range of pH
Process dependent on conductivity	Yes, increasing conductivity reduces energy consumption.	No, low conductivity reduces energy consumption.
Relative Energy Consumption	High, based on hydrolysis for generating oxygen free radicals.	Low, based on plasma affecting only some of the chemical bonds.
Relative Maintenance Requirements	Medium, periodic replacement of electrodes.	Low, electrodes are unaffected; flocculent produced downstream.

APPENDIX 5

Analytical Results from Bench Study: Integrated Pulp and Paper Mill

In January 2015, Pellucid Water conducted a bench study on effluent from an integrated pulp and paper mill (IPPM) located in central Wisconsin. [Note: The name of the company is withheld at the request of the company and is hereto referred to as IPPM.] The objective of the study was to show efficacy of Pellucid Water's cold plasma technology on their chemical matrix, currently being treated at their WWTF – a conventional secondary treatment system installed in 1976.



Pellucid Water received samples of effluent from the IPPM at two locations: after the primary clarifier (and before secondary treatment); and after secondary treatment. The samples treated with PWCP were returned to the IPPM for analysis. A visual comparison of the control samples and treated samples is depicted in Figure 5.1.

Figure 5.1. Treatment of effluent from pulp and paper mill. [From left to right: Final effluent after secondary treatment; Final effluent after treatment with PWCP; Initial effluent before secondary treatment; Initial effluent after treatment with PWCP.]

The water quality parameters invested in the study included BOD, COD, Total & Ortho Phosphorus, and Total Suspended Solids (TSS). The analytical results are summarized in Figure 5.2. [Note: A copy of the report is available upon request, with amendments to remove the company's identity.]

BOD, initial sample: 60.0% decrease from the IPPM untreated sample.
BOD, final sample: no residual BOD remaining from the IPPM treated sample.

COD, initial sample: 42.0% from the IPPM untreated sample.
COD, final sample: 50.2% decrease from the IPPM treated sample.

Total P, initial sample: 91.7% % decrease in residual from the IPPM untreated, filtered sample.
Total P, final sample: 94.6% decrease in residual from the IPPM treated, filtered sample.

Ortho P, initial sample: 56.7% % decrease in residual from the IPPM untreated, filtered sample. [Note: The initial IPPM concentration was very low, 0.03 PPM]
Ortho P, final sample: 93.1% decrease in residual from the IPPM treated, filtered sample.

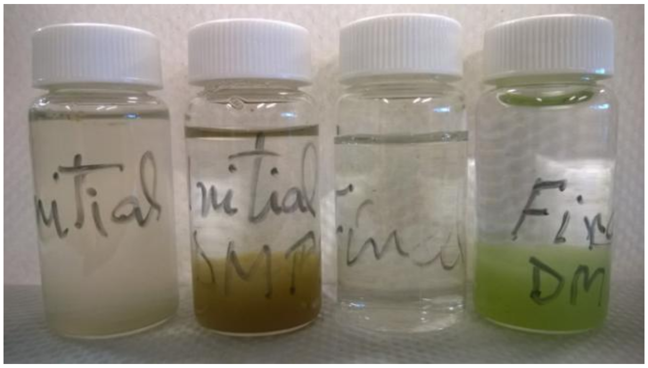
TSS, initial sample: The amount collected was 12.8x greater than the IPPM untreated sample.
TSS, final sample: The amount collected was 53.2x greater than IPPM treated sample.

Figure 5.2. Summary analytical results from bench study on IPPM effluent.

APPENDIX 6

Analytical Results from Bench Study on Phosphorus: Municipal WWTF

Pellucid Water conducted a bench study of effluent from a municipal WWTF located at Whitewater, WI. The purpose of the study was to show efficacy in the removal of Total Phosphorus from solution. [Note: At the time of the study, the municipality was evaluating various tertiary treatment technologies to comply with new state water quality effluent standards of 0.07 PPM.]



Samples of effluent were obtained at the head end of the WWTF (after primary clarification) and at the tail end (after secondary treatment). Each water sample was then treated with PWCP. Figure 6.1 depicts each sample before and after treatment with PWCP.

Figure 6.1. Treatment of effluent from a municipal WWTF. **[**From left to right: Initial effluent before secondary treatment; Initial effluent after treatment with PWCP; Final effluent after secondary treatment; Final effluent after treatment with PWCP.]

The samples treated with PWCP were analyzed by the municipality and a report prepared. A copy of the report is located in Figure 6.2.

Phosphorus test results - WHITEWATER WWTF

Test: Total Phosphorus
Method: Standard Methods 21st ed., 4500-P B 5 (Persulfate Digestion Method) & 4500-P E (Ascorbic Acid Method)
LOD: 0.015 mg/L
LOQ: 0.050 mg/L
Sample date: 12/17/14
24 hour composite

In-house samples:
Raw Influent (preserved to pH<2, 5mL analyzed): 6.253 mg/L
Final Effluent (preserved to pH<2, 25mL analyzed): 0.985 mg/L

Pellucid-altered samples:
Raw Influent (not preserved, 10mL analyzed): **0.039 mg/L**
Final Effluent (not preserved, 25mL analyzed): **0.047 mg/L**

Figure 6.2. Analytical report on phosphorus removal prepared by the City of Whitewater, WI.

Improvement in clarity of the sample at the head end of the WWTP that was treated with PWCP, and the accumulated precipitate in both samples treated with cold plasma, gives evidence that additional chemistry within the matrix of the control samples was also precipitated from solution. However, the municipality did not expand the analysis to document the reduction in other water quality parameters. [Note: Based on plasma chemistry, Phosphorus is removed through chemical bonding with an organic molecule; thus, dissolved organic compounds were also removed from solution. This is confirmed by the earlier bench study on effluent samples from a pulp and paper mill.]

APPENDIX 7

Commercial Prototype, Continuous Flow, Cold Plasma Reactor

Figure 7.1 depicts a commercial prototype, continuous flow, cold plasma reactor (and commercial pump) developed by Pellucid Water. The electrical system operates at approximately 400 V and up to 2 Amp, and the reactor/pump has a maximum flow rate capacity of 7000 l/hr and typical power consumption of 150 – 250 W. The power supply is expandable to serve multiple reactors.

Figure 7.1. Commercial prototype cold plasma reactor.

APPENDIX 8

White Paper to US Environmental Protection Agency

In April 2016, Pellucid Water submitted a White Paper to the USEPA in collaboration with the University of Wisconsin – School of Freshwater Sciences. The subject of the paper is the application of PWCP for removal of pharmaceuticals and personal care products (PPCPs) from wastewater effluent and raw water supply.

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UNIVERSITY of WISCONSIN UWMILWAUKEE Water Technology Accelerator

PELLUCID WATER LLC

Cold Plasma Technology for Removal of Chemicals of Emerging Concern

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SUMMARY

In May 2012 the Office of Inspector General of the U.S. Environmental Protection Agency (EPA) in a report, entitled *EPA Inaction in Identifying Hazardous Waste Pharmaceuticals May Result in Unsafe Disposal*, expressed concern regarding the Agency's inaction in regulating pharmaceuticals found in the nation's freshwater resources. This is a subset of the larger concern regarding the presence of Chemicals of Emerging Concern (CECs), which includes not only pharmaceuticals and personal care products (PPCPs), but also alkylphenols, flame retardants, hormones steroids and pesticides. Gabriel Eckstein, a professor at Texas Wesleyan University states in a 2012 comment, entitled *Emerging EPA Regulation of Pharmaceuticals in the Environment*, that the estimated number of commercially available pharmaceuticals and PPCPs substances alone may be as high as six million worldwide.

The major inputs of CECs into the environment are from municipal wastewater treatment facilities. Their treatment processes have not been modified or optimized to remove influent CECs. EPA published a literature review database in 2010, entitled *Treating Contaminants of Emerging Concern*, which provides performance data on the most prevalent methods of wastewater treatment used and available commercially. They include activated sludge, activated carbon, chlorine, ultraviolet light, ozone and reverse osmosis. These technologies are not suitable alone or in combination to address the task of treating the enormous number and diversity of chemicals comprising CECs. *New technologies are required with enhanced capabilities.*

Considerable attention has been given to 'advanced oxidation' as an alternative technology for both decontamination and disinfection. Some processes are available commercially (e.g. UV photolysis and ozone based technologies) or are under study by the scientific community. However advanced oxidation using these methods has various constraints (e.g., high operational costs and by-product production) that preclude its wide application for removal of CECs. An area of emerging interest is the use of cold plasma that does not appear to have these constraints.

Pellucid Water LLC has developed an alternative cold plasma methodology that has potential to effectively address the problem of CECs. Pellucid Water's cold plasma (PWCP) does not breakdown molecules and ions by oxidation in solution; rather, it induces them to aggregate into macro-molecular / supramolecular structures that enable them to precipitate from solution. This same methodology can be applied for disinfection, where cold plasma not only kills organisms and removes them from solution, but also precipitates the organic compounds in solution that nourish the organisms.

Intellectual Merit: Current methods of water decontamination are based on the use of chemical agents, ion exchangers, bioreactors, catalysts, or membrane-based systems. The application of PWCP does not require any additional biological agents, materials or consumables, and therefore is a fundamental advancement in the science. PWCP uses only the internal chemistry of the water and its contaminants. An electrical discharge creates a highly reactive environment by producing positively and negatively charged particles and free radicals, that are capable of aggregating chemicals and biological compounds by producing branched molecular structures.

Broader Impact / Commercial Potential: As PWCP is effective in removing all organic compounds, it has the potential to become a standard treatment methodology for all CECs. Additional benefits include the simplicity of the technology, low energy requirements, simultaneous treatment of both chemical as well as biological agents, and potential application to organic and inorganic compounds. A single broadly based and effective treatment process could greatly reduce infrastructure while at the same time expanding its treatment capabilities. Improved treatment efficiency, together with increased options for recycling/reuse/marketing of recovered chemicals or new polymers, should result in financial, environmental and health benefits.

Proposed Study: Pellucid Water, in collaboration with the University of Wisconsin - Milwaukee, School of Freshwater Sciences, requests the opportunity to submit a proposal to EPA for investigation of the application of PWCP for removal of CECs. The scope of this initial study will focus on the following objectives: 1) validate the efficiency of PWCP for removal of the different classes of PCPPs found in water samples from wastewater treatment plants of the Milwaukee Metropolitan Sewerage District, using a prototype PWCP continuous flow reactor; and 2) validate that energy requirements for this methodology are substantially less than other treatment technologies, including conventional advanced oxidation processes. Upon confirmation of these results, consideration could be given to a broader study in treatment of other classes of CECs.

Key Words: Chemicals of Emerging Concern (CECs), cold plasma, pulsed plasma, Dense Medium Plasma, organic compound, pesticides, pharmaceuticals, pharmaceuticals and personal care products (PPCPs), petroleum hydrocarbons, PAHs, PCBs, water treatment, xenobiotic compounds.

BACKGROUND

Pellucid Water LLC has its origins at the University of Wisconsin - Madison (UW) and "Petru Poni" Institute for Macromolecular Chemistry in Romania, where Dr. Sorin Manolache was a research scientist. He conducted studies on cold plasma in both the gas and liquid phase. Dr. Manolache and Mark Raabe founded Pellucid Water LLC in 2014.

While at the UW, Dr. Manolache conducted research at the Center for Plasma-Aided Manufacturing (CPAM), investigating an innovative technology called Dense Medium Plasma (DMP) for decontamination and disinfection of water. Starting with plasma chemistry experiments in organic liquids (Simionescu *et al*., 1993), DMP has been used for nanoparticle synthesis and functionalization (Denes *et al*., 1996; Denes *et al*., 1999; Denes *et al*., 2006; Denes *et al*., 2010; Denes *et al*., 2011) in organic environments. Water treatment for removal of hydrocarbons (Manolache *et al*., 2004), ether (MTBE) (Johnson *et al*., 2003) or biological contaminants (Manolache *et al*., 2001) has been possible after installation design modification (Denes *et al*., 2004).

Research studies indicate that use of DMP as a treatment process achieves a higher efficacy in removal of organic compounds (Manolache *et al*., 2004) in comparison with the best available other advanced discharge techniques including ozone treatments (Table 1).

Table 1. Comparison of existing plasma-based Advanced Oxidation and DMP techniques.

Reference	Joshi et. al. 1995	Sunka et. al. 1999	Goryachev et. al. 1999	Sun et. al. 2000	Hoeben et. al.1999	Gurol et. al. 1987	Manolache et al. 2004
Method	Corona in water	Corona in water	Corona in water	Corona in water	Corona in air	Ozon-olysis	DMP
Pulse Energy/mJ	1750	800	30	880	7	-	$4.38\ x10^{6}$
Frequency (Hz)	60	50	50	48	100	-	Continuous
Half time (min)	180	260	180	7	25	8	0.2
G50*	$7.3x10^{-12}$	$4.2x10^{-12}$	$3.1x10^{-10}$	$3.7x10^{-9}$	$1.4x10^{-8}$	$5.2x10^{-8}$	$7.8x10^{-7}$

*G50 is defined as the ratio of the number of moles comprising 50% attenuation divided by the amount of energy expended up to that point (higher means better efficacy).

DEVELOPMENT OF PWCP TECHNOLOGY

Pellucid Water investigated the potential for further improvement in the efficiency in the cold plasma using controlled pulsed discharges. This initiates processes that aggregate the molecules in solution into macro-molecular / supramolecular structures that then separate from solution through flocculation. Table 2 compares the major benefits of PWCP with other water treatment technologies.

Table 2. PWCP versus other water treatment techniques.

	Other Treatment Technologies	**PWCP installation**
Method	Decompose or precipitate contaminants by reaction with an added compound	Create free radicals that produce macromolecular separable compounds
Added chemicals	Yes	No
Energy for process	High: Chemical energy required to react with each contaminant molecule	Low: Chemical energy to create a few free radicals that initiate a type of polymerization
End products	CO_2 – environmental problems Waste – disposal cost	Macromolecular compounds; components may be recovered and reused
Complex contaminants mixture	Separate processes that target specific categories or chemical compounds	Chemical and biological compounds processed in the same time; the more complex, the greater potential for decontamination
Reminiscence	Some end in reaction tank. Some continue to act downstream but are associated with specific smell / taste (e.g., chlorination process)	Trapped free radicals can continue removal of contaminants outside of plasma reactor, in sedimentation tank; no smell / taste effects
Foot print	Large typically	Small

The precipitates formed by PWCP produces macro-molecular / supramolecular structures are stable (i.e., they will not re-solubilize).

PWCP is often mistakenly associated with other plasma technologies that incorporate advanced oxidation and with electrocoagulation. Table 3 lists the major differences between PWCP plasma technology and electrocoagulation (Kuokkanen et. al., 2013).

Table 3. Comparison of Electrocoagulation Technology with Pellucid Cold Plasma Technology

Criteria	Electrocoagulation Technology	PWCP Technology
Incorporates advanced oxidation	Yes	No
Requires ‘sacrificial anode’	Yes	No
Methods: removal of Chemistry	Precipitation and Volatilization	Precipitation only
Chemical recovery potential	High for metals; Low for organic compounds, due to oxidation and volatilization.	High, due to minimal change in the chemistry; no metal contamination from electrodes.
Removal Efficiency dependent on pH	Yes, performs optimally at neutral pH	No, able to perform well within a wide range of pH
Process dependent on conductivity	Yes, increasing conductivity reduces energy consumption.	No, low conductivity reduces energy consumption.
Relative Energy Consumption	High, based on hydrolysis for generating oxygen free radicals.	Low, based on plasma affecting only some of the chemical bonds.
Relative Maintenance Requirements	Medium, periodic replacement of electrodes.	Low, electrodes are unaffected; flocculent produced downstream.

Pellucid Water developed a commercial prototype PWCP reactor/pump (Figure 1). The electrical system operates at approximately 400 V and up to 2 Amp, and the reactor/pump has a maximum flow rate capacity of 7000 l/hr and typical power consumption of 150 – 250 W. The power supply is expandable to serve multiple reactors.

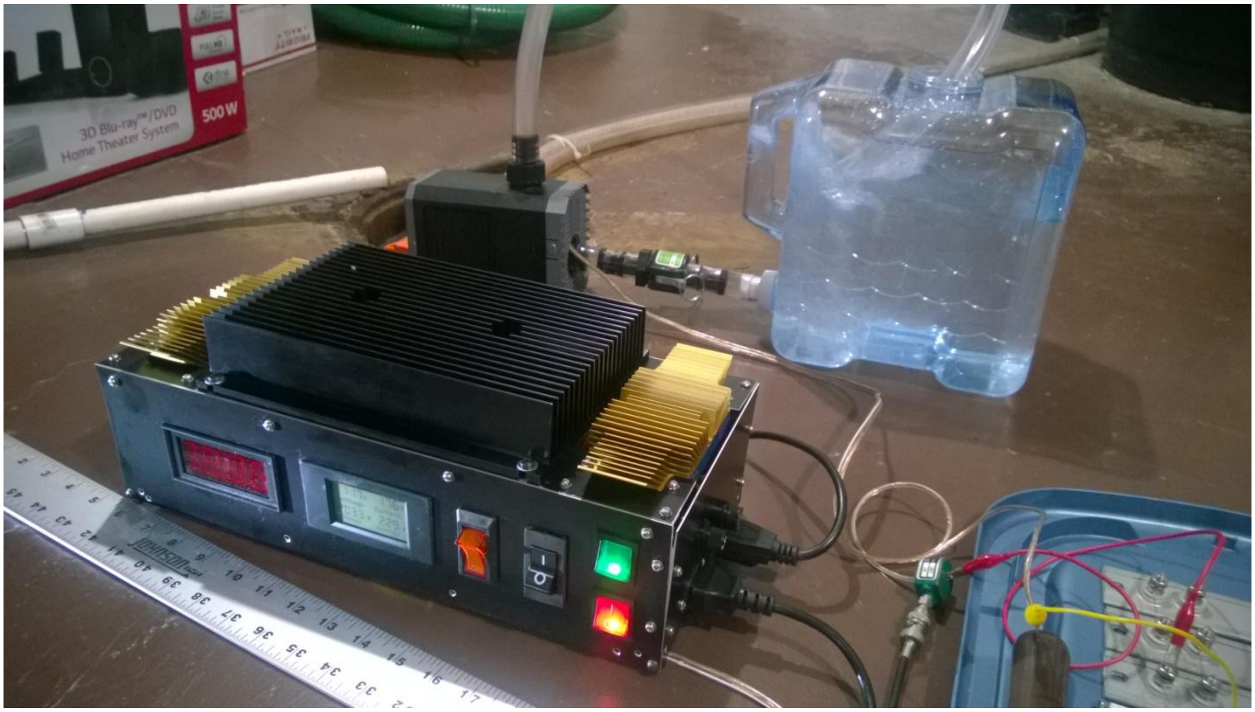

Figure 1. Pellucid Water prototype power supply and reactor/pump.

RATIONALE FOR USE OF PWCP

PWCP is a departure from conventional water treatment systems because it does not require the use of chemical agents, ion exchangers, bioreactors, catalysts, or membrane-based systems. PWCP uses only the internal chemistry of the water activated by discharges: the highly reactive environment creates charged particles and free radicals that are capable of targeting chemical as well as biological contaminants. By contrast with other technologies using plasma for advanced oxidation processes, PWCP uses plasma-produced free radicals to initiate macromolecular processes that agglomerate the contaminants and separate them as particles. Plasma produces branched, crosslinked and complex 3D molecular structures that self-assemble.

The use of plasma allows for application to a broad range of chemical and biological constituents. This is especially important with respect to the removal of CECs, which include various classes of organic chemicals. Treatment systems based on classical chemistry necessitates different treatment systems for each class, whereas plasma-based systems are effective for treatment of all classes of organic chemicals.

PWCP can be used as a tertiary treatment process together with existing secondary treatment systems associated with most municipal wastewater treatment facilities. However, because PWCP acts on the whole chemistry in solution, it can also be used in place of secondary treatment systems for removal of BOD, COD, nutrient removal and disinfection. This is an important consideration given that many municipal treatment facilities have reached their useful life and will require replacement. Application of PWCP could potentially decrease the capital cost and footprint, while at the same time improve treatment efficiency, lower recurrent costs for operation, and potentially create value-added products from recovery of valuable resources.

PWCP APPLICATIONS TO VARIOUS WASTEWATER STREAMS

Pellucid Water conducted a series of field/bench studies using PWCP for treatment of complex water samples obtained from commercial and municipal wastewater treatment facilities (Figure 2). Analytical test results indicate that treatment efficiency for removal of inorganic, organic and biological contaminants exceeds other processes. Furthermore, PWCP can be used for advanced (tertiary) treatment, where high quality water supply or residual wastewater effluent is required. For example, dissolved phosphorus concentrations in both municipal and paper mill effluent were reduced to 0.04 ppm.

Figure 2. Vials containing field samples before (left vial) and after plasma treatment (right vial). Samples from left to right: municipal WWTP, paper mill, food processing, and anaerobic digester effluent from dairy operations.

PROPOSE RESEARCH STUDY

Pellucid Water proposes a research study on the application of PWPC as a potential technology for use in removal of CECs from municipal wastewater effluent. This proposed study follows research on identification and quantification of PPCPs previously conducted by Dr. Rebecca Klaper of University of Wisconsin – Milwaukee, School of Freshwater Sciences. Dr. Klaper *et al*. published a technical paper in 2013, entitled *Pharmaceuticals and Personal Care Products Found in the Great Lakes Above Concentrations of Environmental Concern*. The concentrations of fifty-four PPCPs and hormones were assessed in surface water and sediment samples obtained at locations up to 3.2 km from wastewater treatment facilities of the Milwaukee Metropolitan Sewerage District (MMSD).

The objectives of the proposed study include the following:

- assessment of the efficiency of PWCP as a treatment technology for removal of a PPCPs, based on a limited study sample of the PPCPs identified in the Klaper study; and
- assessment of the efficiency of PWCP in electrical power consumption per unit volume of water treated using Pellucid Water's continuous flow reactor. The efficiency will be compared with published data of the efficiencies for other water treatment technologies.

Establishment of the validity of these objectives will serve as a basis for consideration by EPA for support of further research to: 1) establish the broader application of PWCP to all classes of CECs; and 2) design and construct a pilot-scale treatment system for municipal wastewater treatment.

KEY PERSONNEL

Pellucid Water:

- **Sorin Manolache**, PhD, co-founder of Pellucid Water, was formerly an Assistant Scientist at the University of Wisconsin, Madison. He is a key investigator for plasma treatments, including non-equilibrium atmospheric pressure plasmas and nanostructured layers, as well as chemical diagnostic of complex systems. The scientific efforts of Dr. Manolache has resulted in more than 74 original scientific papers and chapters in books, 30 papers in proceedings, 22 patents (14 US patents, most of them licensed by Intel) and more than 110 presentations at international conferences. Dr. Manolache has served as PI or co-PI in more than 14 projects at UW-Madison's Center for Plasma-Aided Manufacturing (CPAM).
- **Mark Raabe**, co-founder of Pellucid Water, has a B.S degree in Civil and Environmental Engineering and a M.S degree in Biological Systems Engineering. He provides a diverse background professionally to the research team in the field of water quality. Mr. Raabe has previously worked as a regulator for the Wisconsin Department of Natural Resources; as an engineering consultant in fields such as water resources, water supply and wastewater.

University of Wisconsin – Milwaukee, School of Freshwater Sciences:

- **David Garman**, Associate Vice Chancellor Water Technology Research and Development, University of Wisconsin Milwaukee, has a Ph.D. in Inorganic Chemistry and has been one of directing researchers, working on technology transfer to industry and implementing and developing policy for water resource management. He has widespread national and international contacts with a successful operation of 2 major research centers for 16 years in this field of research and technology transfer (water and waste management and environmental biotechnology). He worked with 6 Universities and over 40 industry partners during this time with 2 IPOs, 20 patents and applications and numerous spinoff companies. He has 6 patents and patent applications as an inventor. Recently (2011), he joined UWM as Founding Dean of the School of Freshwater Sciences to expand the role of the newly established School and to promote industry interactions and technology development. His personal research interest is in in-situ remediation and use of advanced materials as sensors and their deployment.
- **Marcia Silva,** Research Associate, has a Ph.D. in Environmental Engineering and has more than 20 years of industrial and academic experience. Since 2013, Dr. Silva has been a Research Associate with the UWM Water Technology Accelerator (WaTA) located at the Global Water Center (GWC) where she develops state-of-the-art research in materials and sensors in her laboratory, resulting in several Invention Disclosures including one that is being licensed for commercialization. Dr. Silva manages the 7000 ft^2 WaTA research facility, trains researchers on the use of shared equipment, facilitates connections to startup companies, water industries and the Water Council, and develops and collaborates on large-scale multidisciplinary research projects. Dr. Silva's most recent research lies on the interface of Environmental Engineering and Materials Science, focusing on the research, development, fabrication, and testing of novel filtration media for water purification by utilizing nanotechnology and biotechnology.

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APPENDIX 9

Planned Pilot-scale Treatment Systems using PWCP

Pilot-scale systems are in the planning stage or under consideration for the following applications:

- **Manufacture of New Wood Fiber Composites:** A pilot-scale processing system using PWCP is planned for construction at the USDA Forest Service Forest Products Laboratory (FPL), under a CRADA with a private company engaged is development of a wood fiber composite with hydrophobic properties. Pellucid Water developed a PWCP reactor for their research activities. A second, larger PWCP reactor, will be designed for the pilot system. The results of initial bench studies indicate that PWCP is highly effective for removal of dissolved organics (lost wood fiber) and chemicals in wastewater generated from a wet process system using a silicon-based chemistry to create the hydrophobicity. Chemical bonding is initiated through functionalization of the fiber surface using PWCP. This creates reactive sites and also preserves the fiber from biological decay – see **Appendix 10**. Functionalization using PWCP provides certain advantages over classical chemical methods used in processing of the fiber. It is anticipated that the pilot system will use water in a closed-loop, employing PWCP concurrently for waste recovery and reuse, and in processing of the fiber.

- **Manufacture of Existing Paper Composites:** Pellucid Water and FPL are collaborating with a small paper mill in northeastern Wisconsin in a bench study to determine the efficacy in functionalization of pulp using PWCP in the manufacture of existing paper composites. The value proposition is three-fold:

  1. reduction in the cost of energy in production;
  2. increase in production through more efficient use of materials (fiber and chemicals); and,
  3. reduction in the cost of effluent treatment through lower losses of fiber and chemicals.

  Successful completion of the bench study may lead to retrofitting of the smaller of two paper machines at this facility, in part, with funds available through Wisconsin Focus on Energy.

- **Mobile Industrial Water Treatment:** A private company in Wisconsin, providing industrial vacuum and cleaning services, is interested in expanding their business model to provide on-site treatment of industrial waste effluents. PWCP is ideally suited to this application because:

  1. the footprint of the apparatus is small;
  2. the apparatus is capable of treating the entire chemical matrix: and
  3. the flow rates are small.

The pilot-scale system will consist of integrating PWCP into their existing mobile service equipment.

APPENDIX 10

Plasma Functionalization of Organic Compounds in Water

Classical chemical methods for Siloxane grafting on cellulosic materials provide hydrophobic properties; however, the application of PWCP reduces the interaction between the fiber and water, resulting in the fiber floating to the surface (see Figure 10.1 and 10.2).

Figure 10.1. Siloxane grafting without PWCP.

Figure 10.2. Siloxane grafting with PWCP.

Figure 10.3. PWCP disinfection of cellulose.

Functionalization of organic compounds using PWCP provides disinfection over an extended time period. This is depicted in Figure 10.3. A sample of cellulose treated with PWCP was placed in the container at the top, and a sample of untreated (control) cellulose was placed in the larger container at the bottom. The containers were stored at room temperature for a period of three months. The treated cellulose remains unaltered from its initial state, while the untreated cellulose discolored due to microbial decay.

APPENDIX 11

Plasma Chemistry Mechanisms

Plasma can initiate various mechanisms as depicted in Figure 11.1. These include advanced oxidation, macromolecular / supramolecular branched structures, and crosslinking. PWCP targets macro/supra molecular branched structures. This mechanism is the most efficient for water treatment with respect to energy consumption. Furthermore, the molecule is preserved for possible recycling/reuse. Branched structures are also useful in functionalization of organic molecules as described in **Appendix 10**. [Note: Symbios Technologies *Dynamic Plasma Activation* uses advanced oxidation.]

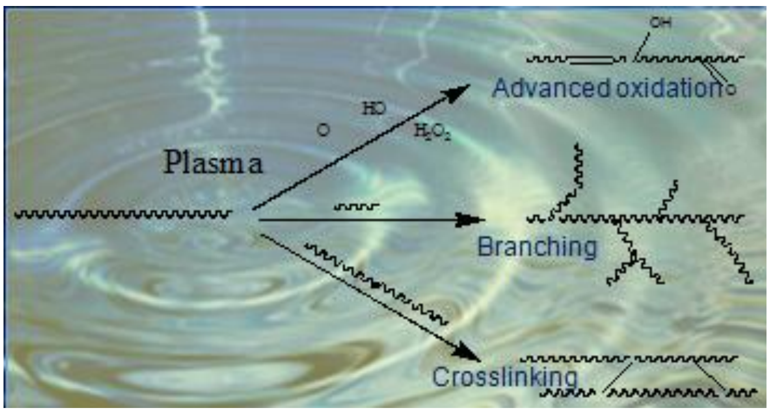

Figure 11.1. Plasma chemistry mechanisms

APPENDIX 12

Electric Discharge Regimes

Electric discharges occur within regimes depicted in Figure 12.1. Cold plasma is an arc discharge that occurs at low voltage and current. Parameters that define the plasma discharge include the following:

- Mean free path
- Debye length
- Plasma sheath
- Plasma density
- Plasma temperature
- Electron energy distribution function

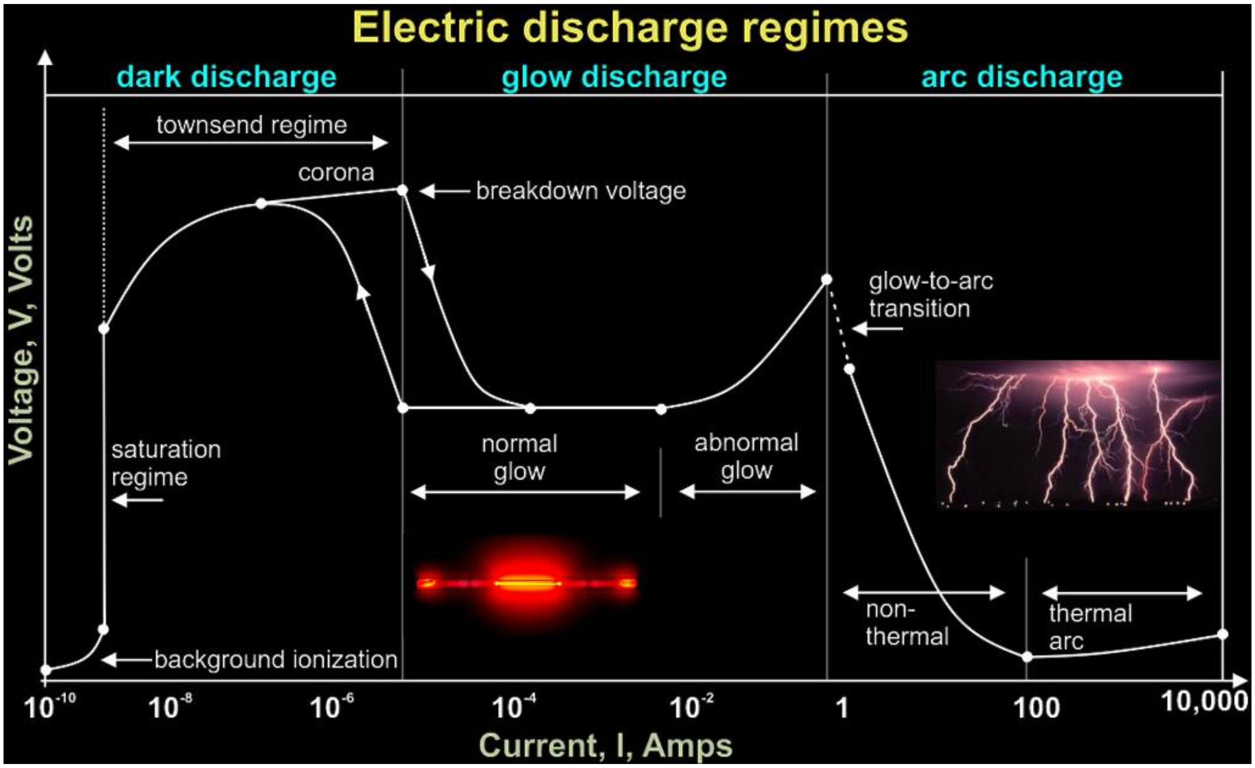

Figure 12.1. Electric discharge regimes*.

* This figure is found in Wikimedia Commons (see URL https://commons.wikimedia.org/wiki/File:Electric-discharge-regimes-illustrated.jpg) and is authorized under the Creative Commons Attribution 3.0 Unported license.

APPENDIX 13

Abstracts of Selected Technical Papers

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1. Dense Medium Plasma Environments: A New Approach for the Disinfection of Water

S. Manolache*, E. B. Somers, A.C.L. Wong, V.Shamanian, and F. Denes*

Abstract: The levels to which microbial colony forming units are permitted in various waters fit for human contact are carefully regulated. Conventional chemical and physical approaches usually are complex processes with significant limitations due to the generation of toxic side-products. In this contribution a novel plasma reactors dense medium plasma reactors is described, and its efficiency for the disinfection of contaminated water is discussed. It has been shown that owing to the intense stirring of the reaction medium (e.g. contaminated water), as a result of the specially designed spinning electrode and gas-flow system, a volume character discharge is created, which can efficiently kill bacteria. It has been demonstrated that treatment times as low as 20 seconds are enough for the total inactivation of microorganisms for 200 mL of 105 bacteria/mL contaminated water.

2. Dense Medium Plasma-Plasma-Enhanced Decontamination of Water of Aromatic Compounds

S. Manolache*; V. Shamamian; and F. Denes*

Abstract: Artificially contaminated water with aromatic compounds, including benzene, ethylbenzene, and xylenes, was exposed to dense medium plasma (DMP) environments in the presence of oxygen. This original plasma technique allows the volume exposure of liquid media to nascent plasma species under atmospheric pressure conditions. Analytical data resulting from gas chromatographic/mass spectroscopic evaluations of contaminated and plasma-exposed water, indicated that prior to any optimization the DMP technology can reduce contamination levels of 600–1,000 ppm to ppb values in treatment times as low as 1 min. It is suggested that hydroperoxide molecules generated as a result of the interaction of plasma-activated oxygen and water molecules, might play an essential role through the interaction of nascent OH free radicals with the contaminant molecules in the decontamination process. The reaction products (hydrocarbons and oxidized derivatives) have a significantly lower concentration relative to the starting contaminants ~at least two to three orders of magnitude lower concentrations!. This original plasma technology opens up new highways for efficient decontamination of water both under batch-type and continuous-flow system modes.

3. Treatment of Methyl *tert*-Butyl Ether Contaminated Water Using a Dense Medium Plasma Reactor: A Mechanistic and Kinetic Investigation

D. C. Johnson, V. A. Shamanian, J. H. Callahan, F. S. Denes, ***S. O. Manolache****, and D. S. Dandy*

Abstract: Plasma treatment of contaminated water appears to be a promising alternative for the oxidation of aqueous organic pollutants. This study examines the kinetic and oxidation mechanisms of methyl tert-butyl ether (MTBE) in a dense medium plasma (DMP) reactor utilizing gas chromatography-mass spectrometry and gas chromatography-thermal conductivity techniques. A rate law is developed for the removal of MTBE from an aqueous solution in the DMP reactor. Rate constants are also derived for three reactor configurations and two pin array spin rates. The oxidation products from the treatment of MTBE-contaminated water in the DMP reactor were found to be predominately carbon dioxide, with smaller amounts of acetone, tertbutylformate, and formaldehyde. The lack of stable intermediate products suggests that the MTBE is, to some extent, oxidized directly to carbon dioxide, making the DMP reactor a promising tool in the future remediation of water.

Chemical and physical mechanisms together with carbon balances are used to describe the formation of the oxidation products and the important aspects of the plasma discharge.