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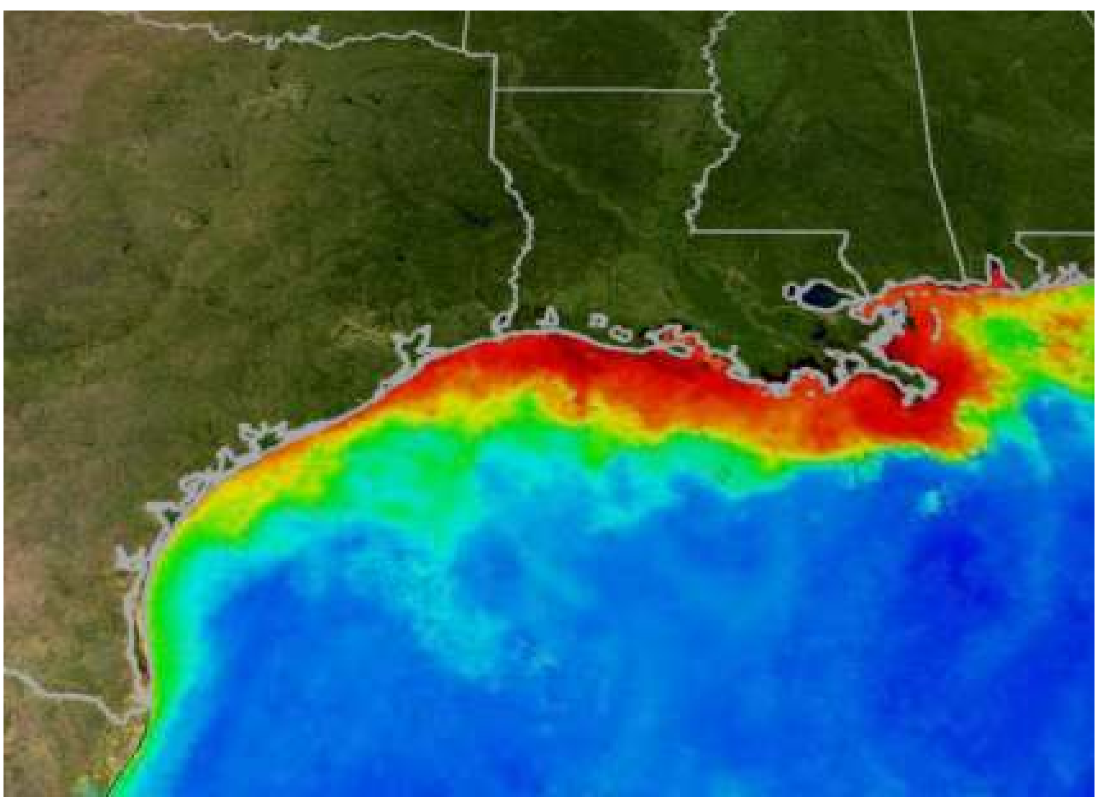
The Affect of Innovation: Killing the Dead Zone

In 2008, the industrial agriculture complex of the United States spread approximately thirteen million tons (26 billion pounds) of nitrogen onto crop fields in the form of fertilizer. It is estimated that 14% of this nitrogen, or approximately 1.8 million tons, washes away from the fields and into the country's waterways. Having migrated from the corn fields of Nebraska, the potato beds of Idaho, and the waving wheat fields of Kansas into the thousands of tiny streams and brooks that feed into hundreds of small rivers, which in turn flow into the Mighty Mississippi River, this super nitrogen-rich water reaches the warm sunny climes of the Gulf of Mexico and forms massive algae blooms near the water's surface. The result: a six- to seven-thousand square mile area in the Gulf of Mexico devoid of all marine life which is known, appropriately, as the Dead Zone.



Gulf of Mexico Dead Zone (photo courtesy of NASA)

In a natural system experiencing homeostasis, the nitrogen would be depleted in the soil, absorbed by plant life in the form of nitrates and ammonium. The nitrogen levels in soil and water would be balanced, and algae growth would remain normal. The overabundance of nitrogen created by the annual fertilization of crop fields moves the system out of homeostasis, causing an overgrowth of algae, which in turn alters the food chain and depletes the affected area of dissolved oxygen in a process known as eutrophication. In the case of the Gulf of Mexico Dead Zone, the hypoxic water causes native species of marine life to die off. The Gulf historically has provided the United States with 72% of it shrimp consumption, and 66% of its oyster consumption. The Dead Zone has greatly depleted these forms of marine life, resulting in significant negative financial impact to the Gulf's coastal economies.

Solutions to the problem abound: decreasing the amount of fertilizer used annually, and applying fertilizer at times when erosion is less likely are viable, but not complete, possibilities. Redeveloping the natural wetlands in the mouth of the Mississippi river to provide a natural filtration system is also viable, but faces strong social and political opposition. Moving away from industrial farming, wherein nutrient-depleted soil is reused by adding nutrients to it, to sustainable farming, wherein fields are allowed to go fallow and re-enrich naturally, is a more complete solution, as it would significantly reduce the amount of nitrogen-based fertilizer applied to fields. However, this approach requires that approximately one-third of all farmable acreage lie dormant each year, and thus would decrease the amount of crop yield by one-third annually. This will undoubtedly drive up food prices for those who can afford them, and cause massive worldwide starvation for those who cannot.

US food prices have already increased due to the mandate in the 2005 energy bill that requires the production of billions of gallons of biofuel annually. On its surface, this seems like a strong move toward expanding the use of biofuel and reducing dependence on fossil fuels. However, Congress buckled to pressure from agricultural giant Archer Daniels Midland and required that the majority of biofuel produced in the US be made from corn, ADM's staple product. Corn prices have already skyrocketed as a result, and adding a requirement to allow fields to regenerate their nutrient content naturally through going fallow would only exacerbate the problem. But which is the greater problem? The Gulf of Mexico is America's dumping ground, and the putrefaction of that dump is taking away the livelihood of thousands, and putting important food sources at risk. How do we continue to feed the US and the world and wean ourselves off fossil fuel while stemming the destructive tide of the Dead Zone?

HydroClean has the answer. Our patented system combines discoveries from the forefront of science with basic principles of chemistry and physics to create a solution that, once fully operational, will remove up to ninety percent of the overflow of nitrogen from the Mississippi *before* it flows into the waters of the Gulf. The HydroClean system utilizes nanotechnology to first cause the nitrogen and phosphorus, at the atomic level, to chemically bond to a nanotube, then uses simple principles of electromagnetism to collect the nutrient-laden nanotubes. HydroClean's system works in real time, without disrupting the natural flow of the river. And unlike other filtration solutions, HydroClean targets only the massive amounts of nitrogen in the water, leaving other biological agents virtually untouched. Although our technology seems elegantly simple, several difficult obstacles were overcome during the development of HydroClean.

Water: The Great Dissolver

By far the most common form of nitrogen in fertilizer is ammonium nitrate, which is made up of one nitrogen atom combined with four hydrogen atoms and one nitrogen atom combined with three oxygen atoms (NH_4NO_3). The presence of hydrogen and oxygen in the chemical makeup of ammonium nitrate make it highly soluble in water: in sixty degree water ammonium nitrate dissolves into 420g of nitrogen per 100ml of water. In eighty degree water, which is common in the Gulf coast, the pure nitrogen level increases to 576g per 100ml. Nitrogen itself is not water soluble, and remains in its atomic, elemental state in water. One of the greatest obstacles in creating a *real-time*, chemically based nitrogen filtration system for removing nitrogen from water was dealing with water itself, and its strength as a solvent.

Water treatment plants routinely remove nitrogen from water through a complex series of both mechanical and chemical filtration. Most commonly the end result is the transformation of free nitrogen atoms into nitrogen gas which diffuses harmlessly into the atmosphere. This process, however, requires several elements that are not practical in a real-time filtration system: time, control and stagnation. Water moving along a quickly flowing river such as the Mississippi does not lend itself to these conventional methods of filtration. Additionally, it is impossible to control the molecular compounds present within any given area of flowing river water, thus a real-time filtration system would need to be able to chemically target the present nitrogen while causing as little disturbance to the myriad of other molecular compounds in water. And finally, the chemical bond formed between nitrogen and the filtration element cannot be water soluble.

Chlorine: The Great Sanitizer

Chlorine has been used extensively as a cleaning and disinfecting agent for more than two hundred years. It has multiple household uses, from bathtubs to pools, and since its widespread adoption in the early 19th century as a disinfectant it has contributed greatly to extending the life expectancy of humans. Interestingly, the same attributes of chlorine that make it an ideal sanitizer also make it a prime candidate for HydroClean's needs.

Chlorine is a unique element in that it is highly reactive with other elements, both organic and inorganic. A chlorine atom has a total of seventeen electrons, two in its inner shell, eight in its intermediate shell, and seven in its outer shell; it is constantly seeking an eighth electron to complete its outer shell, making it prime for bonding. Nitrogen has a total of five electrons, two in its inner shell and three in its outer shell. These three nitrogen electrons have a weak attraction to the nitrogen nucleus, making them easily available for bonding. Thus one nitrogen atom will bond with three chlorine atoms, each of the three nitrogen electrons moving to one of the three outer shells of the chlorine atoms, thereby creating a covalently bonded molecule called nitrogen trichloride, NCl_3.

In abundant amounts, NCl_3 is a highly explosive compound that is sensitive to light, heat, and organic compounds. It is also an eye and skin irritant. These aspects are outweighed, however, by its most important property: it is insoluble in water, and will form in water. With the full knowledge that its potentially explosive nature and potential harm to humans would need to be addressed in the design of the system, HydroClean found its filtration element.

Finding the Proverbial Needle: Filtration Element Delivery

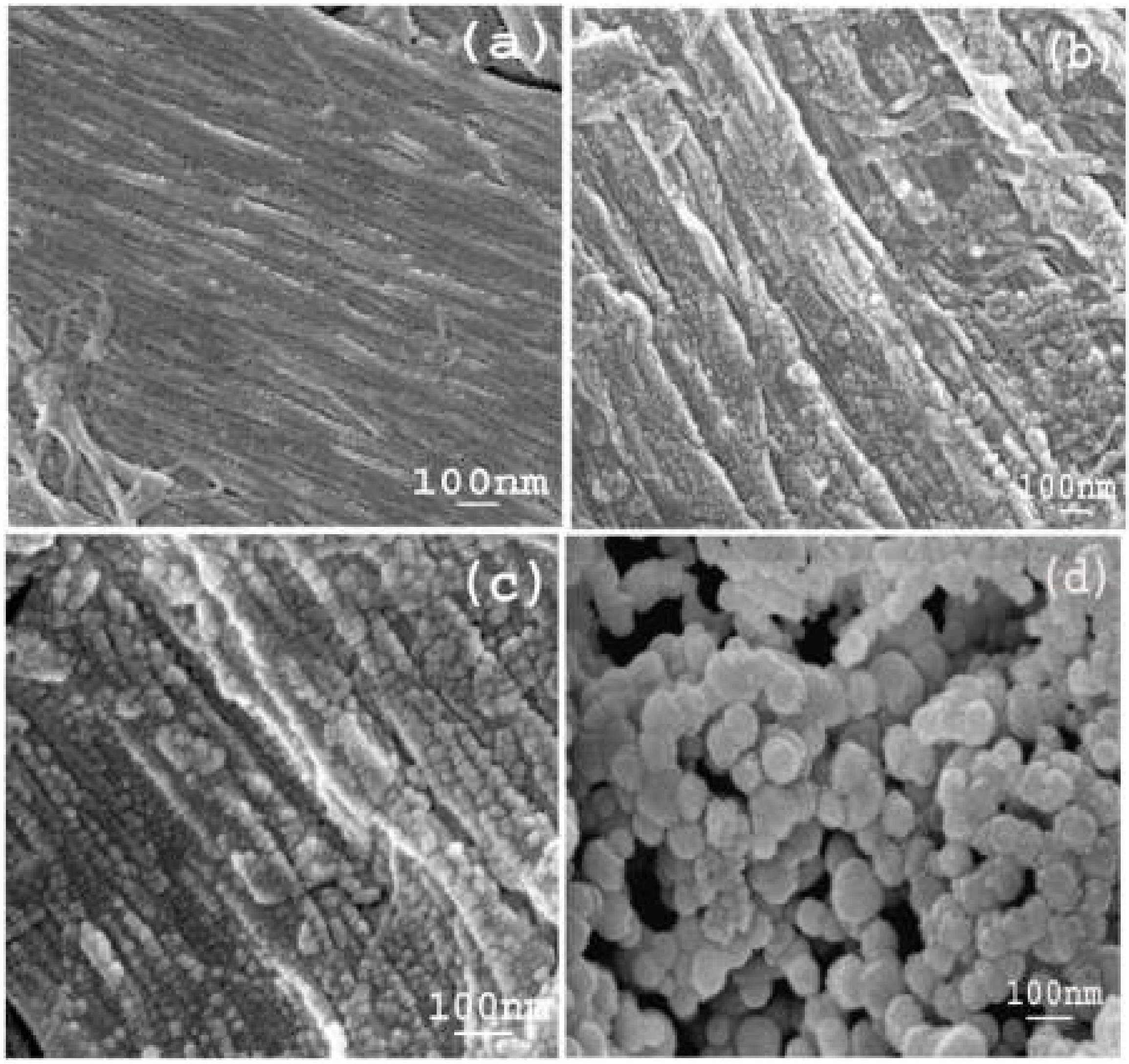
Having determined that chlorine would serve the purpose of a filtration element that would chemically bond to nitrogen in water, a means of delivering the chlorine, and subsequently removing the nitrogen trichloride, had to be devised. Pouring chlorine directly into the river water is ill-advised for several reasons: first, exposure to the chlorine for more than a very short period would cause destruction of vital organic compounds in the water. Second, removing the chlorine, and other chlorine compounds such as NCl_3, would be impossible without a traditional filtration system, which has already been identified as impractical. Thus a means of *controlled* delivery and extraction is required. This concept seems contraindicative: how to make atoms of chlorine available to bond with atoms of nitrogen in river water flowing at a rate of approximately 600,000 cubic feet per second. The elements are two needles trying to find each other in a swirling, flowing, muddy haystack. Mere decades ago this challenge would seem impossible, as it requires control at the atomic level. With the introduction of nanotechnology, however, the control and manipulation of atomic particles has become a reality.

Nanotechnology: Dancing on the Head of a Pin

In December 1959, Nobel Prize winning physicist Richard Feynman posed the question, "Why cannot we write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin?" His challenge has sparked fifty years of experimentation and innovation in a field of physical science that has come to be known as nanotechnology. And though it was not the Encyclopedia Britannica, Stanford University graduate student Tom Newman did inscribe the first page of Dickens' *A Tale of Two Cities* onto the head of a pin using a beam of electrons, at a scale that would allow the entirety of the Britannica to fit, in 1985. Today the world of nanotechnology is filled with new and exciting applications and materials, and provides HydroClean with the atomic scale mechanism to achieve its goal.

Some size perspective may be in order here: the head of a pin can fit about five million million hydrogen atoms on it. One nanoparticle with a size of one nanometer across could fit approximately fifty atoms on it. Thus a single nanoparticle is tiny indeed. HydroClean's purposes required a nanostructure that could be manipulated to contain chlorine atoms to be delivered into the river water for nitrogen bonding, as well as a layer of iron by which the nanostructures could be efficiently removed from the water utilizing magnetism. And perhaps most importantly, the nanostructures must maintain their integrity in water.

This last requirement moved into first place on the priority list, as all of the other attributes were dependent on the nanostructures being water insoluble. After many failures, HydroClean found the answer in Zinc Oxide (ZnO). Researchers at the Indian Association for the Cultivation of Science's Department of Solid State Physics in Jadavpur, India created a low cost method of manufacturing beaded chains of ZnO nanoparticles. Their method utilizes a template made of Whatman (40) filter paper upon which the ZnO is seeded. The filter paper is then incinerated at 700 degrees centigrade, leaving behind the chains of ZnO nanoparticles.[1]



FESEM images of the (a) filter paper, (b) and (c) template-grown ZnO nanostructure and (d) ZnO nanostructure grown without the template.

The most important aspect of the ZnO chains of nanoparticles is that ZnO does not dissolve in water. Once the nanoparticle chains are manufactured, they are coated on one side with a water and chlorine insoluble polymer resin, and then they are exposed to a chamber filled with chlorine gas. Chlorine atoms attach to the ZnO nanoparticle chains via the polymer resin. The layer of polymer resin is thin enough to prevent the chlorine atoms from becoming embedded in the resin, and thus they

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[1] Dutta, Mrinal, and Durga Basak. *A novel and simple method to grow beaded nanochains of ZnO with superior photocatalytic activity*. Nanotechnology. Vol. 20. 2009.

remain chemically active while being anchored to the ZnO nanoparticle chains. The opposite side of the nanoparticle chain is coated with a layer of iron, which serves two purposes. First, the iron adds density to the nanoparticle chains, causing them to sink through the flowing river water. Second, the iron causes the chains to “stick” to a magnetized filtration unit for extraction purposes.

Impossibility: A Design Construct

Many considerations must be taken into account when designing a project the magnitude of HydroClean’s filtration system. Most would consider the obstacles these considerations present to be markings of an impossible task. HydroClean considers them opportunities for innovation. The sheer volume of zinc oxide nanoparticle chains required is daunting, as is the method of delivering the completed chains to the river water. When considering the amount of water requiring filtration, the magnetized filtration device must exist on a very large scale, which in itself causes a major design hurdle: the Mississippi in lower Louisiana is a major traffic lane for worldwide oceanic shipping, and therefore any design must allow the free flow of river traffic.

HydroClean chose as its filtration site Governor Nicholls Street Wharf in New Orleans. At this major bend in the Mississippi the river’s depth reaches 200 feet, allowing the magnetized filtration device to work far below the depth required for river traffic. In addition, the width of the river is approximately 750 feet, which is relatively small compared to the river’s widest span of one mile. The filtration unit in total is twice this length, with each bank of the river housing a 400 foot long cleaning chamber. The filtration unit is anchored to the bottom of the river and rises through the water the equivalent of an eight story building. Imagine a carnival midway shooting game, wherein the targets continuously move around the shooting range on a conveyor system; the filtration unit works on the same principle. The unit in its entirety is 3,100 feet in length and 80 feet tall, moving along a massive chain driven conveyor that is approximately 1,500 feet in length. In the river, at any given point in time, two “walls” of magnetized filtration panels are moving in opposite directions.

The filtration panels are able to move, from a forty-five degree angle in relation to the river’s flow while moving through the water, to flat against the river’s flow. The filtration panels move to this flat position just before entering the cleaning chambers at either river’s edge, allowing them to slide into the chambers without allowing in the river water. In the cleaning chambers the panels are blasted with high pressure distilled water steam, which causes the nitrogen-chlorine bonds to break. The panels are then “washed” with distilled water, which flows from the cleaning chamber into a traditional water treatment plant, wherein the nitrogen is collected for reuse. The panels are once again "washed" with a solvent which dissolves the polymer resin, removing the chlorine as well. In the final stage of the cleaning process, the panel's magnetization is turned off and the spent nanoparticle chains are removed and collected. They then move through a process which separates the ZnO from the iron and collects each for reuse.

Approximately 1.5 miles upriver from Governor Nicholls Street Wharf is the Crescent City Connection, a dual bridge spanning the river. The chlorine delivery system is built between these structures, which have approximately 400 feet between them. This delivery system is simply a glorified sprinkler system, which continuously rains chlorine-laden zinc oxide nanoparticle chains via distilled water into the river water. The system runs along and between the underside of the bridges so as not to interfere with river traffic, with a sprinkler head every ten square feet, resulting in thirty thousand sprinklers. With a water pressure of 100 pounds per square inch, the system delivers almost one hundred thousand gallons of distilled water per minute. An additional bank to bank, 50 foot wide system is built on the downriver side of the structure. This set of sprinklers dispenses purified water for the purposes of "washing" river traffic which moves under the chlorine dispensing structure.

Crescent City Connection Bridge, New Orleans

Continuously feeding this dispensing structure is the chlorine-laden ZnO nanoparticle chain manufacturing facility. This facility is capable of producing enough nanoparticle chains to supply one chain per million molecules of water. Since there are about $1.266*10^{26}$ molecules of water per gallon, this represents $1.266*10^{13}$ chains per gallon of water. Before deeming this level of manufacture impossible, consider that a square meter of nanoparticle material yields 10^{16} chains measuring 10nm by 10nm. Imagine a high speed newspaper printing press, the speed of which is comparable to the speed of HydroClean's manufacturing facility. The facility contains 100,000 high speed machines which handle one square meter of nanoparticle chain "sheets" per second.

Much like a printing press, each machine is fed from a roll of Whatman (40) filter paper. The paper is first sprayed with zinc oxide, then incinerated at 700 degrees centigrade, resulting in a continuous sheet of ZnO nanoparticle chains. The sheets are coated with the polymer resin, run through the chlorine gas chamber, then coated on the opposite side with iron. In the final step the sheets are cut into 100 nanometer squares with first a horizontal, then a vertical array of lasers. In order to achieve a proper mixture, the completed nanoparticle chains are mixed with distilled water at the rate of 50 gallons per second, which is then stored in a one million gallon holding tank. The rate of manufacture compared to the rate of flow requires that the system run on a schedule of six minutes and forty seconds on, three minutes twenty seconds off. Thus the rate of manufacture will equal the rate of distribution, and the million gallon holding tank will allow for a one hour run in the event of a malfunction.

As the chlorine-laden distilled water is delivered into the river, the iron coating on the nanoparticle chains causes each chain to sink through the water, with nitrogen bonding to the chlorine atoms on the way down. The rate of sinking coupled with the rate of the river's flow allows for a drop to the level of the magnetized filtration system in the time it takes for the river to flow from the Crescent City Connection delivery structure to the filtration structure at Governor Nicholls Street Wharf.

Innovation: The Great Balancing Act

A constant balance must be struck in the natural world, and humans function best in that balance, or state of homeostasis, as well. But human lives are complicated, and therefore the means to achieve societal homeostasis are invariably complicated. In the case of preventing the negative economic and environmental effects of the Gulf Dead Zone, most suggested solutions would require negative economic and environmental effects elsewhere. Innovation is the weight that balances the scales of our societal needs. HydroClean embraces innovation. HydroClean. You may not have heard of us, but we're saving the world.