BIOBRIMSTONE™ WASTEWATER TREATMENT EFFECTS ON PHARMACEUTICALS AND OTHER CHEMICALS

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ABSTRACT

Pharmaceuticals, hormones, and other organic and chemical wastewater contaminants entering wastewater are becoming an environmental concern. The wide variety of chemicals, their ever changing composition and occurrence in minute amounts constantly entering wastewater streams, makes their removal difficult. Most traditional municipal wastewater treatment plants produce secondary treated recycled effluent, which does little to degrade, but removes some of these chemicals. Tertiary treatments have some effect on removal and degradation of these pharmaceuticals and chemical contaminants, but generally address only certain pharmaceuticals and chemical types, which are often expensive to implement and monitor. This article will outline the manner in which proprietary patented hybrid chemical/biological dewatering and disinfection wastewater treatment technology owned by Earth Renaissance Technologies, LLC (ERT)[1] may be employed for inactivating, degrading, and removing a number of pharmaceutical and chemical components. This ERT wastewater treatment technology entails an oxidation/reduction, acidification/alkalinization cycle to condition recovered wastewater to grow aquatic photo biomass to inactive, degrade, and remove those susceptible pharmaceuticals and chemicals. The Biobrimstone™ method was employed as a retrofit at the Montalvo Municipal Improvement District's wastewater treatment facility in Ventura, California to condition secondarily treated wastewater to raise duckweed in open ponds as a biofuel feedstock for burning. The Biobrimstone™ technology thus provides a wastewater treatment option to inactivate, degrade, and remove a number of

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[1] Earth Renaissance Technologies, LLC (ERT) is owned by Stewardship Water & Gas Company's (SWAGCO) and Harmon Systems International (HSI), which was formed to blend SWAGCO's wastewater treatment technology with HSI's extensive irrigation water and soil conditioning technology to recover and condition wastewater for an end user's agricultural and soil needs. ERT holds key patents on its technology and has accumulated additional related water treatment technology, all of which are the subject of pending patent applications.

different pharmaceuticals and chemicals as part of a multi-step treatment process to provide recovered wastewater suitable for land application.

INTRODUCTION

Pharmaceuticals in wastewater streams have become a cause for concern as pharmaceuticals and their metabolites have been established as nearly ubiquitous environmental pollutants in ground and surface waters. Chemicals used everyday in homes, industry and agriculture can enter the environment in wastewater. Unfortunately there are thousands of different chemicals entering a wastewater treatment system, the composition of which constantly changes. These chemicals include human and veterinary drugs (including antibiotics), hormones, detergents, disinfectants, plasticizers, fire retardants, insecticides, and antioxidants.[2] The shear number of the different types of chemicals, their low concentrations[3], and continually changing makeup makes the design of wastewater treatment systems to remove the same, impractical. For example, if a wastewater treatment system is designed for removal of a particular chemical, manufacturers may cease producing the product, or alter its composition to accelerate decomposition, rendering the design useless. Or waste disposal plans for a particular pharmaceutical may be adopted by a municipality for gathering the same for disposal preventing the pharmaceutical from entering the wastewater gathering system[4]. Further, it is very difficult to test the effectiveness of a wastewater treatment system to remove all of these chemicals and pharmaceuticals. Most small wastewater treatment facilities do

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[2] USCG Fact Sheet FS-027-092, Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, June 2002, Background.

[3] For example, steroid estrogens have the potential to exert estrogenic effects in the low ng/L (1 part/trillion) level, whereas alkylphenolic compounds are estrogenic at µg/L (1 part/billion). Natural and synthetic hormones are frequently detected in sewage treatment work effluents and receiving surface waters with concentrations ranging from pg/L (1 part/quadrillion) to ng/L (1 part/trillion); see page 4 "Municipal Wastewater Concentrations of Pharmaceutical and Zeno-Estrogens: Wildlife and Human Health Implications" by Maxine Wright Walters and Conrad Voltz; www.chec.pitt.edu?Exposure_concentration_of_Xenoestrogen_in_pharmaceutical_and_Municipal_Wastewster_Final8-28-07%5B1%5D.pdf.

[4] See Page 27, Disposal programs, "Pharmaceuticals in Wastewater Streams: Disposal Practices and Policy Options in Santa Barbara", a Master's Project for the Donald Bren School of Environmental Science and Management dated May 2007 by James Kallaos, Kaleena Wheeler, Crispin Wong, and Margaret Zahller, Faculty Advisor, Matthew Kotchen.

not have the necessary laboratory testing equipment or the skilled personnel to operate the same so testing is problematic. Consequently, most wastewater treatment plants are limited to providing primary and secondary treatment.

> "Traditional [wastewater treatment plants] WWTPs treat influent by adding chemicals (alum, ferric chloride and/or synthetic polymers) to encourage coagulation (neutralizing suspended sediments) and flocculation (aggregating particles). The resulting bigger particles (flocs) are then able to be filtered out, as sewage sludge. The residual liquid is then disinfected, often with chlorine in the United States and ozonation in Europe. This system is optimized to remove pathogens, and other biological material, and dissolved organic carbon (Ellis 2006), not pharmaceuticals or other chemicals; consequently, these conventional treatment processes appear to be insufficient in removing pharmaceutical compounds (Ellis 2006; Brun et al. 2006; Snyder et al. 2003). Considering the ineffectiveness of water treatment processes, WWTPs should be considered an important and continuous source of pharmaceuticals to the environment (Brun et al. 2006)."[5]

Primary treatment allows influent to partition based on density; solids that float or settle to the bottom are filtered out[6], while liquids and smaller particles pass through. A common secondary treatment process utilizes bacteria to break down organic material in an aerated tank[7]; then, the material is allowed to settle and the water is filtered again.[8] At first blush, secondary treatment utilizing bacteria to break down organic material resulting in large carbon emissions appears to be cost effective. However, pending legislation requiring the purchase of carbon off-sets may make this alternative cost prohibitive.

Several types of tertiary treatment wastewater treatment systems have been designed to further clean secondary treated wastewaters. The following tertiary systems may also inactivate or capture pharmaceuticals: 1) reverse osmosis systems, 2) ozonation

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[5] Page 10, "Pharmaceuticals in Wastewater Streams: Disposal Practices and Policy Options in Santa Barbara", supra.

[6] Some pharmaceuticals may be removed by sorption to particles filtered out; see "Factors Affecting the Concentrations of Pharmaceuticals Released to the Aquatic Environment" by David L. Sedlak, and Karen E. Pinkston, University of California; see Page 56, Introduction, www.ucowr.siu.edu/updates/pdfn??V120_A7.pdf.

[7] Some pharmaceuticals are removed by biotransformation in this break down process; see Page 56, Introduction, supra.

[8] "Pharmaceuticals in Wastewater Streams: Disposal Practices and Policy Options in Santa Barbara", supra, page 28, Potential contamination from WWTPs, landfills, and septic tanks.

disinfection systems, and 3) light inactivation systems. Each has its advantages and disadvantages. For example, reverse osmosis systems often require the removal of suspended solids first[9] and take a lot of energy to remove a wide variety of pharmaceuticals from the wastewater streams, which are concentrated in separated brines creating brine disposal problems. Ozonation systems[10] do not inactivate those chemical species not subject to oxidation. Light inactivation systems also use a lot of energy, and are not as effective as ozone treatment of certain species[11]. Nor do they inactivate those chemical species resistant to photo degradation. Consequently, it is difficult to compare each system's effectiveness relative to one another where they operate on different chemical species in different manners.[12] This article will therefore not evaluate the effectiveness of various wastewater treatment systems to inactivate chemical and pharmaceuticals, but will address the mechanisms inherent in the Biobrimstone™

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[9] EPA 625/R-00/008 Onside Wastewater Treatment Systems Technology Fact Sheet 9, page 3, "Reverse osmosis".

[10] To reduce the release of pharmaceuticals and endocrine disruptors into the aquatic environment or to remove them from wastewater, municipal wastewater effluents may be treated with ozone; see "Oxidation of Pharmaceuticals during Ozonation of Municipal Wastewater Effluents: A Pilot Study", by Marc M. Huber, Anke Gobel, Adrino Joss, Nadine Hermann, Dirk Loffler, Christa S. McArdel, Achim Ried, Hansruedi Siegrist, Thomas A. Ternes, and Urs von Gunten, published in Environ. Sci. Technol., 2005, 39 (11), pp 4290-4299.

[11] See article entitled "Degradation of Selected Acidic and Neutral Pharmaceutical Products in Primary-Treated Wastewater by Disinfection Processes" by Christian Gagnon, Andre Lajeunesse, Patrick Cezka, Francous Gagne, and Robert Hausler, Ozone: Science & Engineering, Volume 30, Issue 5 September 2008, pages 387-391 where ozone treatment was compared with UV-radiation disinfection processes carried out at the Montreal wastewater treatment plant to determine their effects on pharmaceutical products like salicylic acid, clofibric acid, ibuprofen, naproxen, triclosan, carbamezepine, diclofenac, and 2-hydroxy-ibuprofen. For ozone doses of 20 mg/L were used removal rates as high as 70% were observed. Conversely, the removal rates for UV radiation were often below 10% among the substances studied. Irradiation used for bacterial treatment (25 mJ/cm^2) was too low to cause significant breakdown of many of these pharmaceutical substances.

[12] Testing costs are also burdensome where the nature of these chemicals and pharmaceuticals and their extremely low concentration levels in wastewater makes sampling analysis difficult, and often requires sophisticated laboratory techniques, such as reversed-phase high-performance liquid chromatography–electro spray tandem mass spectrometry following solid phase extraction to determine the presence of targeted pharmaceuticals selected from a priority list.

wastewater treatment process developed by Earth Renaissance Technologies, LLC to inactivate, degrade, and remove some pharmaceuticals and chemicals.

The Biobrimstone™ hybrid chemical/biological dewatering and disinfection wastewater treatment technology was employed at the Montalvo Municipal Improvement District's wastewater treatment facility in Ventura, California where aeration is employed providing oxidation degradation of some protein pharmaceuticals.[13] Montalvo Municipal Improvement District owns the Montalvo Water Pollution Control Plant (Plant), located at 3555 Ventura Road, Montalvo, California. Treated domestic and commercial wastewaters are discharged under Waste Discharge Requirements contained in Order No. 87-092, adopted by the Regional Board on June 22, 1987.

The Montalvo wastewater treatment system consists of bar screening, comminuting, influent holding tank, two independent sequencing aerobic and denitrification batch reactors, with discharge into a final lined polishing pond. No off-site transfer or usage of treated wastewater is presently employed. The waste activated wastewater liquids between the floating and settling solids is extracted and discharged to the subsurface through two evaporation/percolation ponds with a combined capacity of two million gallons. The aerobic and denitrification treated solids and liquids have polymers added to aid in separation and are sent to woven polypropylene bags on drying beds to collect the solids. The liquids from the woven polypropylene bags in the drying beds are collected and recirculated through the aerobic digesters and denitrification batch reactors building up its bicarbonate and salt composition. As there is no off-site disposal of the treated liquids, effluent limitations are not exceeded.

In case of emergency, the Montalvo facility has an emergency power station and a one-million gallon concrete-lined pond to store untreated and/or treated wastewater

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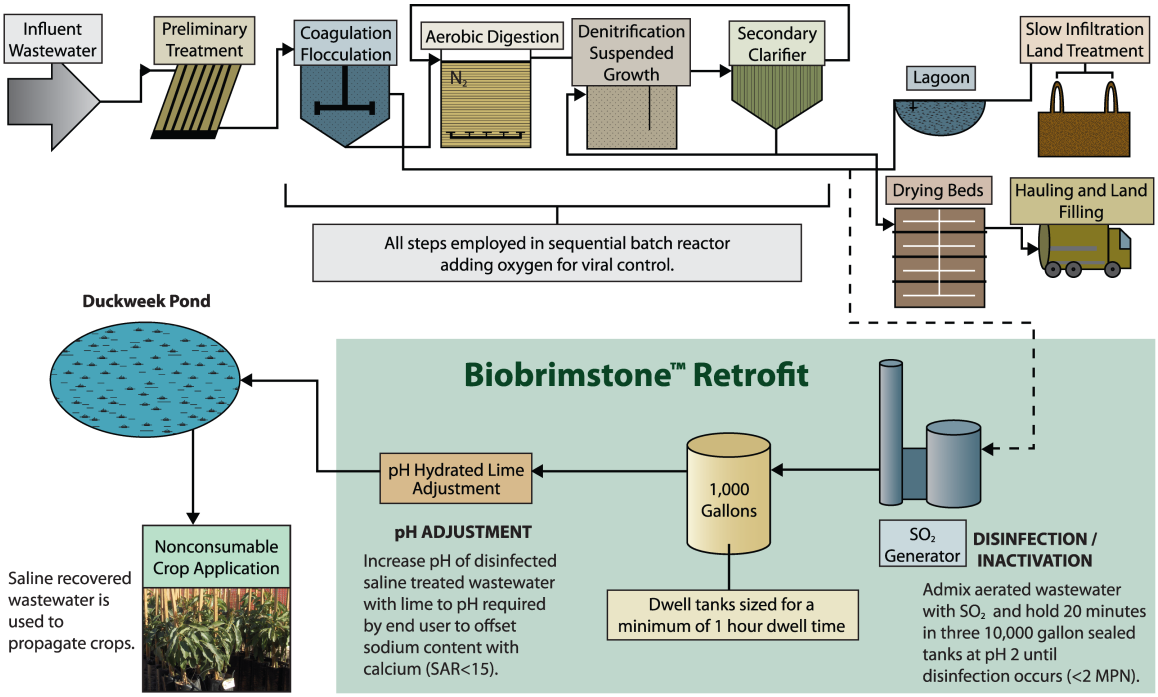
[13] Abstract, "Chemical instability of protein pharmaceuticals: mechanism of oxidation and strategies for stabilization" Biotechnology and bioengineering Journal, 1995 vol. 48, note 5 (129 p.) by Shihong Li; Schoneich C.; Borchardt, R.T.; University of Kansas Department Pharmaceutical Chemistry, Lawrence, KS 66045, 1994, Wiley, New York, New York discussing oxidation chemical degradation of methionine, cysteine, histidine, tryptophan, and tyrosine, which are most susceptible to oxidation due to their high reactivity with various reactive oxygen species

which can then be returned to the head works of the plant for treatment as needed. The drawing below outlines a processing sequence retrofitted with the Biobrimstone™ wastewater treatment technology.



The plant has a wet weather design capacity of 750,000 gallons per day (gpd). An average daily dry weather flow of up to 322,000 gpd was discharged during 1995. Waste sludge is treated onsite by aerobic digestion, and then discharged into lined sludge drying beds. Treated sludge is hauled offsite and disposed of at a legal disposal facility.

The plant and evaporation/percolation ponds are located in Section 20, Township 2N, Range 22W, San Bernardino Base & Meridian. The Plant's latitude is 34°14'17"; its longitude 119°11'34".

After aeration of the wastewater for viral control and oxidation degradation of some protein pharmaceuticals, a 50,000 gpd side stream is directed for Biobrimstone™ multi-step treatment. The first step acidifies the aerated wastewater with sulfurous acid at a concentration between a pH of 2 and 3.5. This acidified wastewater is held for sufficient time to disinfect coliforms <10 mpn in conformance with Title 22 gray water standards.[14] This acidification step can cause acid catalysis of certain pharmaceuticals susceptible to hydrolysis, which remain after oxidation.

> "…pH is perhaps the most important and widely examined parameter that affects hydrolysis of drugs based on this moiety, for example, an ester, amide, lactane, imide, or carbonate, then that drug is liable to undergo hydrolytic degradation. Hydrolysis is frequently catalyzed by hydrogen ions (*specific acid catalysis*) or hydroxyl ions (*specific base catalysis*); the reaction tends to go faster in acidic (low pH) and basic (high pH) medium, respectively than they would otherwise in a neutral system. If the drug solution is buffered, the decomposition may not be accompanies by an appreciable change in the concentration of acid or base; however, it may be catalyzed by other acidic and basic species that are commonly encountered as components or buffers. This type of catalysis is referred to as *general acid-base catalysis.*
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> Acid-base catalysis is the most important type of catalysis when drug stability is considered. Solutions of many drugs undergo accelerated decomposition upon the addition of acids and bases…"[15]

In addition, the SO_2 in the sulfurous acid wastewater acts as a strong reducing agent, which reduces chlorine and its compounds[16], and other pharmaceuticals susceptible to its strong reducing properties. Where chlorates, such as Hypochlorite, Chlorite, Chlorate, and Perchlorates are present from the manufacture of fireworks, explosives, flares, and rocket fuels[17], these strong oxidizing agents are particularly susceptible to sulfurous acid reduction.

After acidification, the next step neutralizes the acidified wastewater with lime to the pH required to precipitate out heavy metals (if a problem) or provide specific base

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[14] Sulfur dioxide treatment of wastewater also has some effect on viruses; see "Sulfur Dioxide treatment of secondary sewage—Effect on viruses" by V. Dean Adams, ScienceDirect-Environment International published 8 December 1999; htt;://www.sciencedirect.com/science?ob=ArticleURL&_udi=B6V7… wherein Reovirus (PIV or IV) was inactivated with SO2 treatment by 90% and Poliovirus in wastewater was inactivated by 907% with a 500 mg/L SO2 treatment.

[15] Chapter 8, Chemical Kinetics and Stability, V. Factors Affecting the Rate of Chemical Reactions (Drug Stability), subsection B. pH and Hydrolosis, page 238, Theory and Practice of Contemporary Pharmaceutics, by Ghosh and Jaste, Boca Ratan: CRC Press, 2006.

[16] Section 12-15, page 1261, Wastewater Engineering: Treatment and Reuse, Fourth Edition by Metcaff & Eddy, McGraw-Hill, New York, New York, 2003.

[17] Perchlorate has been found in just over 4% of public water systems nationally; see Perchlorate, Drinking Water Contaminants; http://www.epa.gov/OGWDW/contaminants/unregulated/perchlorate.html.

catalysis where problem pharmaceuticals, which can be reduced by alkalinization, are present. Typically, the types of pharmaceuticals susceptible to base catalysis are not present in sufficient concentration to merit employment of extremely high pH conditions, so the wastewater is generally pH adjusted only to that required to encourage aquatic plant growth as the final polishing step to remove nitrogen and phosphorous from the treated wastewater to prevent eutrophication when the recovered wastewater is discharged into open streams.

One preferred aquatic plant employed for this biological removal step is duckweed.

> "**Lemnaceae** is a family of flowering plants, also known as the **duckweed family**, as it contains the duckweeds or water lentils. …
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> These plants are very simple, lacking an obvious stem or leaves. They consist of a small 'thalloid' or plate-like structure that floats on or just under the water surface, with or without simple rootlets. The plants have become highly reduced from their relatives in Araceae. Reproduction is mostly by budding, but occasionally a flower consisting of two stamens and a pistil is produced (some view the 'flower' as a pseudanthium, or reduced inflorescence, with three unisexual flowers, derived from the spadix in Araceae). The fruit is a *utricle*, a sac containing air and a seed designed to float. The flower of the *Wolffia* is the smallest flower in the world; measuring in at a size of 0.3 mm long.[1]
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> Duckweed is an important food source for waterfowl and are eaten by humans in some parts of Southeast Asia (as *khai-nam*). Some duckweeds are used in freshwater aquariums and ponds where they may spread rapidly and, in a large pond, may be difficult to eradicate once established. The plants can provide nitrate removal (if cropped) and cover for fry. The plants are used as shelter by pond water species, such as bullfrogs and bluegills. The duckweeds are important in the process of bioremediation because they grow rapidly, absorbing excess mineral nutrients, particularly nitrogen and phosphates."[18]

Duckweed not only absorbs heavy metals from the wastewater, but alters and uptakes certain pharmaceuticals.[19] It is very prolific. Duckweeds are one of the fastest

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[18] Lemnaoideae-Wikepedia; http://en.wikipedia.org/wiki/Lemnaoideae

[19] Environmental engineers at the Georgia Institute of Technology have found that various chlorinated, fluorinated, and mixed chloro-fluoro compounds are taken up and sequestered in the plant tissue of duckweed (Lemna minor); see "Fixed Assets: Aquatic

growing angiosperms and can double their biomass within 2 days under optimal conditions. They have high protein content (10 to 40% protein on a dry weight basis) although the moisture content (95%) of fresh duckweed biomass is quite high as well. Potentially members of the *Lemnaceae* (of the genera *Lemna, Spirodela*, *Landoltia* and *Wolffia*) can produce edible protein six to ten times as fast as an equivalent area planted with soybeans. Species of *Lemnaceae* may have a great value in agriculture and wastewater treatment[20].

Where pharmaceutical and chemical duckweed absorption is too high for animal and human consumption, the duckweed is removed and used as biofuel feedstock for burning, which destroys the pharmaceuticals and unwanted chemicals. In addition, duckweed has been found to absorb pathogens and viruses where sewage water has not been previously disinfected.[21] In these cases, it is also recommended that the harvested duckweed be burned as biofuel. For example, Environmental Bio-Fuels, Inc. has developed a biofuel using duckweed as a feedstock having BTU content comparable to low grade coal. It thus is used to create a renewable fuel with a carbon neutral footprint, while disposing of absorbed pathogens, pharmaceuticals and chemicals.

The Biobrimstone™ wastewater multi-step treatment method can be adjusted to meet different pharmaceutical and chemical cleanup objectives and regulatory

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Plants Sequester Toxic Compounds in Cell Tissue, Removing Contaminants from Wetlands" dated august 23, 2004; http://gtresearchnews.gatech.edu/newsrelease/wetlands.htm. Also see "Floating Aquatic Macrophytes as a Decontamination Tool for Antimicrobial Drugs" by Cinzia Forni, Caterina Patrizi, and Luciana Miglore, Dipartimento di Biologia, Universita "Tor Vergata", Via della Ricerca Scientifica, 1-00133, Roma, Italy; Soil and Water Pollution Monitoring, Protection and Remediation, 3-23, 2006 Springer where it was found that these plants were capable of lowering antimicrobial drug concentration such as sulfonamide (Sulfadimethoxine) and quinolone (Flumequine).

[20] "Modeling duckweed growth in wastewater treatment systems" by Louis Landesman, Nick C. Parker, Clifford B. Fedler, and Mark Konikoff; http://www.Irrd.org/Irrd17/6/land17061.html

[21] See "Persistence, Transmission, and Virulence Characteristics of Aeromonas Strains in a Duckweed Aquaculture-Based Hospital Sewage Water Recycling Plant in Bangledesh" by Mokhlasur Rahman, Geert Huys, Motiur Rahman, M. John Albert, Inger Kuhn, and Roland Mollby; Applied and Environmental Microbiology, March 2007,p. 1444-1451, Vol. 73, No. 5, where a significantly high number of Aeromonas bacteria was found in duckweed, which indicates that duckweed may serve as a reservoir for these bacteria.

requirements. For example, the amount of aeration to oxygenate incoming wastewater may be adjusted by increasing exposure time if required to inactivate by oxidation certain susceptible chemicals and pharmaceuticals. In addition, the acidification/alkalinization pH ranges and dwell time may be adjusted where required to inactivate different pharmaceuticals and chemicals. Similarly, the amount of SO_2 required for reduction inactivation of certain chemicals and pharmaceuticals may be adjusted. Lastly, the type of photo biomass used for biological removal of pharmaceuticals and chemicals may be selected to better target and absorb certain pharmaceuticals and chemicals.[22] The Biobrimstone™ wastewater multi-step treatment method thus can be adjusted to meet regulatory requirements to reduce and inactivate certain designated pharmaceuticals and chemicals.

CONCLUSION

The Biobrimstone™ method may be employed as a wastewater treatment facility retrofit to treat process streams to recover wastewater to raise photo biomass in open ponds to produce a biofuel feedstock for burning. This Biobrimstone™ technology may be adapted to provide a treatment option to selectively target and inactivate, degrade, and remove a number of different susceptible pharmaceuticals and chemicals to provide treated recovered wastewater suitable for land application.

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[22] See for example page 18 of the practicum “A Comparison of Duckweed and Standard Algal Phytotoxicity Tests as Indicators of Aquatic Toxicology” by Maria Mae Gausman submitted to the Faculty of Miami University where she discusses differing accumulation of metals in the aquatic environment for duckweed and algae as well as their toxicity sensitivities.