N-E-W TECH™: RESOURCE RECOVERY IN A NOVEL FUNCTIONALIZED BIOCHAR, CATALYTIC OXIDATION, REACTIVE FILTRATION WATER TREATMENT FOR N/P REMOVAL/RECOVERY AND PATHOGEN/PRIORITY SUBSTANCE DESTRUCTION

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Abstract

N-E-W Tech is an innovative water treatment process at the nutrient, energy, and water nexus. N-E-W Tech integrates reactive filtration with iron-functionalized biochar and ozone for catalytic oxidation water treatment, sterilizing reclaimed water, and producing a value-added nutrient upcycled fertilizer product that addresses the need for carbon sequestration. N-E-W Tech addresses the negative aspects of several current alternative technologies to water reuse and recycling including their high energy inputs, removal but not destruction of contaminants and pathogens, high capital-maintenance-operations costs, and their poorer sustainability footprint.

In this work we report on the design-build, water treatment performance, energy efficiency and general operations of this technology built as a 15-gpm pilot process on a mobile trailer. Reactive filtration is our award-winning commercialized, high-efficiency nutrient removal process installed at 10+ MGD at wastewater treatment plants; it uses an iron oxyhydroxide adsorptive process in a moving sand bed filter. Biochar is a bioenergy byproduct made from the pyrolysis of agricultural and forestry biomass. In N-E-W Tech, we demonstrate the addition and recovery of 1 to 10 grams of micronized iron-functionalized biochar per gallon, using this substrate as a sorbent and as a sacrificial catalyst with ozone to form hydroxyl radicals. Oxidation reduction potentials (Eh) ranging from 800 to 1300+ mV are maintained in the reactor during the 10-20 minute process time, demonstrating trace organic compound oxidation capacity. Nutrients selectively adsorb to the recovered functionalized biochar demonstrating agricultural fertilizer potential in this carbon sequestering substrate. Initial N-E-W Tech effluent results from municipal secondary water demonstrate turbidity <0.1 NTU, log 4.5+ removal of E. coli and fecal coliforms, often to below assay count detection limits, effluent total P <0.020 mg/L, pharmaceutical/hormone/steroid destruction to mostly below ng/l analytical detection limits and other promising results.

Keywords

Pathogens, Phosphorus, Priority Substances, Reactive Filtration, Resource Recovery

Introduction

Intensification of resource recovery is a global prime mandate for sustainability. The trajectory of increasing population and increasing resource demand for water and food security create an innovation imperative for sustainability in the context of the Food-Energy-Water nexus. Addressing this innovation imperative requires transdisciplinary thinking, creative systems approaches, and translational research products that address the grand challenges of our shared future.

Nutrient Pollution

The impact of nutrient pollution from phosphorus and nitrogen on the Earth’s waters is significant. For example, the estimated annual cost of nutrient pollution in the United States in freshwater is greater than US$2.2 billion (USEPA 2015). The U.S. Environmental Protection Agency (USEPA) found that about 40% of stream miles in the United States had elevated phosphorus levels, and 27% had elevated nitrogen levels (USEPA 2013). The National Estuarine Eutrophication Assessment Update has estimated that nutrient pollution has had a moderate to high impact in 65% of the coastal areas observed (Bricker, Longstaff et al. 2007). The source of pollution includes point sources, non-point sources such as agriculture runoff and air deposition, storm water runoff, and sewer overflows.

Phosphorus Resources

Phosphorus is required for food security, yet mineral resources are limited with significant reserves isolated in only a few countries around the globe (USGS 2015). Increasing human population drives increasing demand for food, fiber, biofuel and other agricultural products. Phosphorus is a key soil nutrient in agriculture, sustaining plant and animal growth. Intensive agriculture requires input and replacement of nutrient phosphorus—as harvest removes soil phosphorus—and food or fiber distribution transports it from local ecosystems. Phosphorus is returned to soil as fertilizer or amendment. It is a mined from the Earth’s finite rock phosphate mineral reserves or replaced by land application of manures or treated human waste.

The United States Geological Survey, Mineral Commodity Summaries 2015, projects world consumption of P_2O_5 fertilizers of 42.2 Mt in 2014 would increase to 45.9 Mt in 2018. With global reserves at 300 billion tons of phosphate rock, concerns that global phosphorus demand will outstrip supplies within the next several decades have increased demand for practical and economically feasible approaches for phosphorus reuse and recycling for food security (Cordell and White 2011, Neset and Cordell 2012, USGS 2015). The European Union, with limited domestic P supplies, considers sustainable P as a major challenge in the 21st Century and has organized the European Sustainable Phosphorus Platform to promote P recycling technology; in January 2016 Switzerland became the first country to mandate P recovery (Platform 2016). Engineered precipitation of struvite ($NH_4MgPO_4 \cdot 6H_2O$) from high nutrient municipal and animal agriculture wastewater for use as fertilizer is a major thrust area in reuse and recycling of phosphorus (Westerman, Bowers et al. 2010). However, the struvite precipitation process 1) requires equimolar phosphate and ammonium with addition of expensive magnesium salts, 2) competes with Ca and only partially removes the target nutrients, and 3) typically requires additional secondary or tertiary nutrient removal treatment prior to water discharge. Phosphorus removal with iron chemistry has been noted as a preferred approach to P recovery where energy recovery from wastewater is desired: *“We believe that a process for recovering P using Fe should be developed in two steps. First, suitable FePs should be identified and characterized. Second, specific tools for mobilizing P from these compounds should be identified. Developing a biomimetic process to recover P from FePs would be an important step toward WWTPs acting as energy and nutrient factories”* (Wilfert, Kumar et al. 2015).

Climate Change and the Need for Carbon Negative Processes

In an era of climate change from human impact, The Emissions Gap Report 2013, United Nations Environment Programme, 2013 forwards the analysis that “regarding biomass, bioenergy production combined with carbon capture and storage (BioCCS) technology is a negative-emission solution that could offer a powerful means to reduce GHG emissions.” Furthermore, they state “the use of BioCCS depends on the technical and social feasibility of large-scale CCS and the technical and social feasibility of sustainable large-scale bioenergy production.” The 2015 Paris Agreement on climate change addresses the accelerating need for carbon negative human systems and processes (UN 2015). Thus there is a need to design and develop new approaches for biomass energy generation systems that co-produce clean water and enhance sustainable agriculture as a means to advance technical and social feasibility of BioCSS.

Biochar Biocarbon

Biochar (BC) is a highly variable carbonized material that derives its chemical and physical make-up from the biomass carbon source, pyrolysis or hydrothermal charring method, and any post-processing of chemical treatment to modify the surface properties of the substrate. In general, there are native or enhanced oxygen containing functional groups on the BC surface that can include carboxylic acid groups, ethoxy groups, ether groups, carbonyl groups and alcohol groups that add to the surface reactivity. The carbon structure of biochar can vary to include aromatic bonds and incorporated trace metals and metalloids, as well as P and N moieties present in the original plant biomass prior to pyrolysis. A desirable property of many BCs is the very high surface area afforded by the carbon superstructure in the original biomass that can be maintained in the charring process. The surface area of BCs can be about 200-400 m^2 per gram and thus presents a very large reactive surface area (Lehmann and Joseph 2009). This attribute has been exploited in charcoals for many applications. BC amendment to soils demonstrates positive agronomic and environmental impacts (Granatstein, Kruger et al. 2009, Lehmann and Joseph 2009, Galinato, Yoder et al. 2011, Spokas, Cantrell et al. 2012).

Binding Phosphorus Compounds on Biochar

Native biochars have been noted as a phosphorus source and as a binding agent for aqueous P (Biederman and Harpole 2013, Sarkhot, Ghezzehei et al. 2013). Metal modification of BC has demonstrated enhanced aqueous P removal and fertilizer potential (Cheng, Lehmann et al. 2006, Chen, Chen et al. 2011, Yao, Gao et al. 2013, Fang, Zhang et al. 2014, Zhou, Gao et al. 2014).

Binding Nitrogen Compounds on Biochar

Ammonium has been observed to have good adsorption on biochars and charcoals (Spokas, Cantrell et al. 2012, Sarkhot, Ghezzehei et al. 2013, Gai, Wang et al. 2014). Our preliminary bench-scale work has demonstrated 30-67% removal and recovery of total nitrogen from fortified water and lagoon filtrates on both biochar and surface modified biochar. Nitrate capture has been demonstrated although often only with very high biochar/activated charcoal carbon concentrations over longer time (Chen, Chen et al. 2011, Kammann, Schmidt et al. 2015). Ca and Mg modified biochars demonstrate both N and P removal in high nutrient concentration waters (Fang, Zhang et al. 2014, Fang, Zhang et al. 2015). In unpublished bench-scale work, we have demonstrated nitrate capture on modified biochar substrates. A recent comprehensive review of the challenges of nitrate binding for water treatment and other applications suggests that effective binding of the weakly basic nitrate anion is difficult with a synthetic receptor approach especially in polar solvents such as water (Dutta and Ghosh 2015).

Catalytic Oxidation with Ozone

In a recent comprehensive review, ozone demonstrated superior capability for the destructive removal of pathogens and trace organic contaminants of concern in water reclamation (Snyder, von Gunten et al. 2014). Catalytic ozonation with metal compounds and with charcoals offers higher efficiency and a homogeneous and heterogeneous reaction mechanism that generates hydroxyl radicals and peroxides as well as other oxidants in water treatment (Nawrocki and Fijolek 2009, Nawrocki and

Kasprzyk-Hordern 2010, Rosal, Gonzalo et al. 2011, Ikhlaq, Brown et al. 2012, Qi, Xu et al. 2012, Derrouiche, Bourdin et al. 2013, Pereira, Gonçalves et al. 2014, Bing, Hu et al. 2015).

N-E-W Tech Approach

N-E-W Tech is our innovative water treatment process at the nutrient, energy, and water nexus. N-E-W Tech, with its intellectual property foundation in eight issued or pending patents, integrates “reactive filtration” with iron-functionalized biochar and ozone for catalytic oxidation water treatment, sterilizing reclaimed water, and producing a nutrient-upcycled, enhanced efficiency fertilizer (EEF) product that addresses the need for carbon sequestration while mitigating aquatic pollution. This membrane-free approach addresses the negative aspects of several current alternative technologies to water reuse and recycling including their high energy inputs, removal but not destruction of contaminants and pathogens, high capital-maintenance-operations costs (CAPEX/OPEX), as well as their poorer sustainability footprint.

Photographs of the N-E-W Tech research trailer appear in Figure 1. N-E-W Tech takes a modern approach to common sand filtration that has been used for over 150 years. It advances basic principles of simplified, cost effective, catalytic oxidation using inexpensive sacrificial catalysts made from the iron chloride/sulfate solutions already used in water treatment. N-E-W Tech™ uses ozone—a chlorine disinfection alternative made from electricity and air—as an oxidant that is catalyzed with iron salts to initiate aggressive oxidizing chemical reactions that can destructively remove many, if not all, toxic organic compounds and pathogens into harmless carbonates, smaller non-toxic molecules, or to minute concentrations of no effect. Mineralized P and N can be captured on Fe-modified biochar and recovered as a by-product enhanced efficiency fertilizer with economic value for direct field application in agriculture and horticulture. The nutrient enhanced biochar collected in the reject cycle of the process sequesters carbon in soil when applied to agricultural fields where it enhances soil fertility and plant growth. This provides for carbon sequestration that will have market value in carbon trading markets.

Figure 1. N-E-W Tech process mobile research trailer. Reactive filters are blue, plug flow reactors are green, and the white/blue process control container contains water pumps, reagent dosing controls, air compressor, air dryer, oxygen concentrators, ozone generator, programmable logic controller, sensors, digitally controlled valves, system controls, power-process controls, lights and heat.

Materials and Methods

Figure 2 shows the process flow diagram for N-E-W Tech. Test waters include secondary water from the city of Moscow, Idaho USA municipal water treatment plant (advanced biological nutrient removal, very low turbidity), the city of Troy, Idaho USA (serial aerobic lagoons, high turbidity), and the dairy waste lagoons on the University of Idaho research dairy (very high turbidity). In the process research trailer, water is pumped at 0.6 to 1 l/s into the process control trailer, where ferric or ferrous chloride is added at rates of about 4-25 mg/l depending on influent water quality and research goals. The Troy process water trials required doses of HCl to adjust alkalinity in the process influent that sometimes exceeded 40 to 60 NTU turbidity and >170 mg/l total alkalinity. Bulk micronized biochar biocarbon from Cool Planet, Inc. is mixed with water to form a concentrated slurry. The 0.5 to 1% iron chloride (w/w) surface modified biochar slurry is pumped via positive displacement pump into the flowing process water at a rate of 0.25 to 2 g/l depending on influent water quality and research goals. Ozone, generated by a Pacific Ozone model SGA 11 generator, is added to the process flow at a rate of 9 mg/l using a venturi. An inline static mixer mixes the flowing process water in a 10 cm pipe before entering a 20 cm or 30 cm plug flow pipe reactor that allows for reaction time. The process water flow is then directed into an up-flow moving sand bed reactive filter (Nexom, Inc./Blue Water Technologies, Inc., model CF-3) operated with compressed air lift assembly and washbox, and a reject rate of approximately 5-10% of flow depending on influent water quality and research goals. As shown in Figure 2, the process is repeated in a second pass in filter 2 without biochar addition. The reject process water from filter 1 is routed to a 1 µm bag filter for nutrient upcycled biochar recovery.

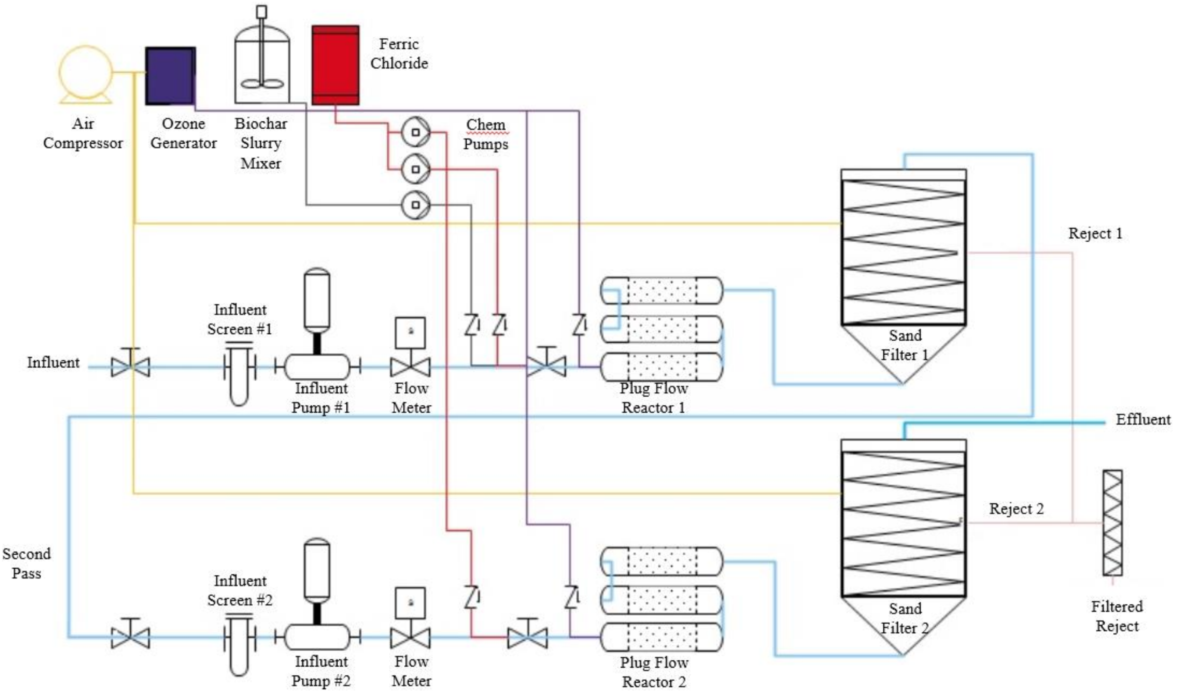

Figure 2. N-E-W Tech process flow diagram.

Results and Discussion

Numerous system checks and operational variables were trialed over several weeks of field testing at municipal wastewater plants. During the process, typical redox Eh potentials at the beginning of the plug flow reactor were 800 to 1100 mV in the first pass and 800 to 1300 mV in the second pass, with a 10 to 20-minute process contact time suitable for sterilization. An example of fecal coliform bacteria count from a trial at the city of Moscow plant is shown in Figure 3. With lab assay maximum count of 2419 (later estimated by dilution at over 45,000 counts) process effluent counts of samples ranged from 1 to 21. E. coli counts at the maximum assay value of 2419 for process influent were reduced to 1 after treatment.

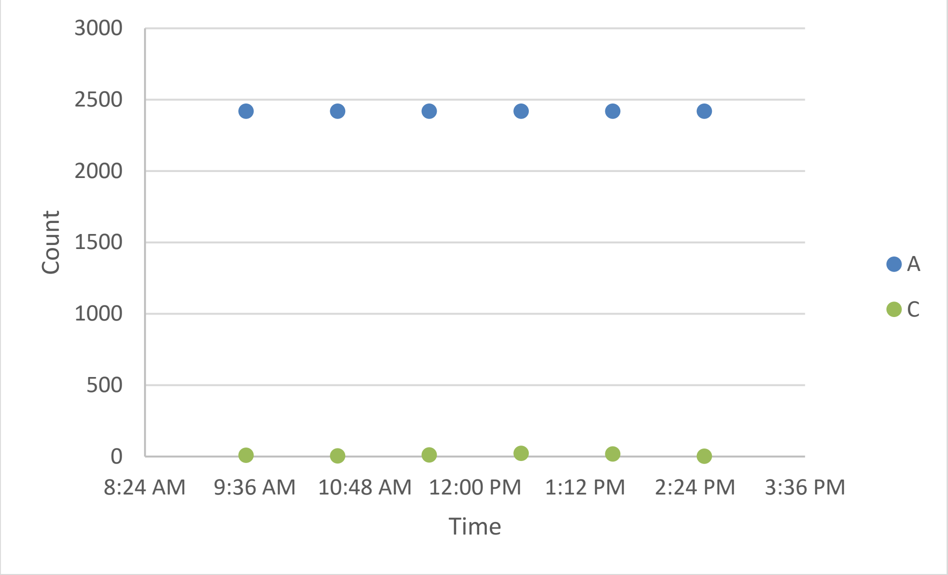

Figure 3. Fecal coliform counts for city of Moscow N-E-W Tech water influent (A) and final process effluent (C).

Total phosphorus (TP) and ortho-phosphorus (OP) for the city of Moscow secondary effluent are very low, in the range of 0.1 to 0.2 mg/l due to advanced biological nutrient removal. As shown in trials of Figures 4 and 5, N-E-W Tech removed 84% of TP and 98% of OP during this operation.

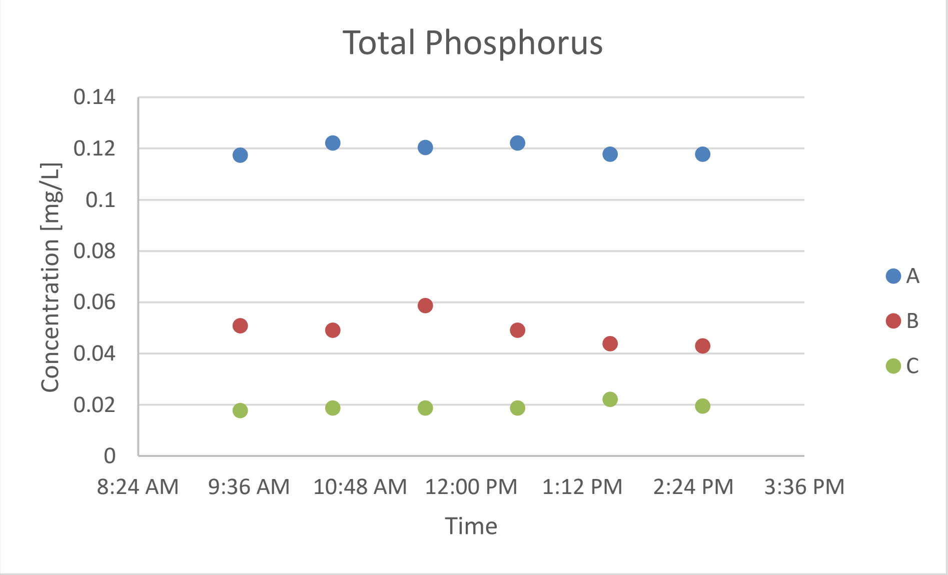

Figure 4. Total phosphorus, mg/l, for city of Moscow N-E-W Tech water influent (A), first pass effluent (B) and process effluent (C).

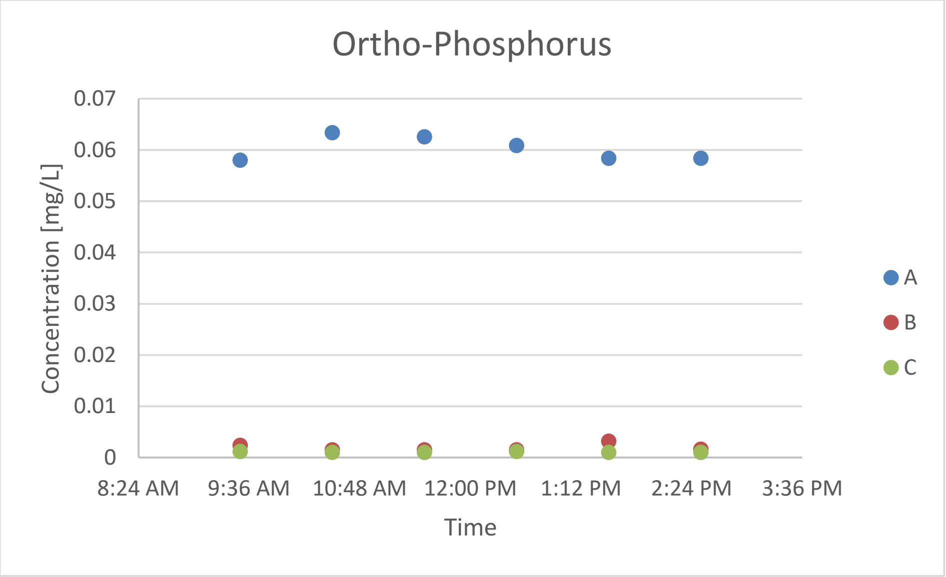

Figure 5. Ortho-phosphorus, mg/l, for city of Moscow N-E-W Tech water influent (A), first pass effluent (B) and process effluent (C).

For similar secondary wastewater trials conducted at the city of Troy, the N-E-W Tech process influent total phosphorus had an average value of 6.4 mg/l. This was reduced to an average 0.034 mg/l demonstrating a 99.5% TP removal and recovery onto the biochar substrate. OP was reduced to 0.002 mg/l. The high efficiency TP reduction is remarkable for the fact that the addition of gram levels of micronized biochar to the influent process water can add over 350 mg/l of biochar TP to the process water, some of this soluble in the native material before iron modification.

Process influent total nitrogen levels were typically about 30 mg/l at Troy and 5 mg/l at Moscow. Nitrogen removals, in both field test sites as measured by TKN, ammonia, or nitrate-nitrite were uniformly low but ranged as high as 25%. Our bench scale work is demonstrating 30 to 67% N removal and recovery on novel chemically modified biochars, and this development work is continuing.

Nutrient upcycling onto the biochar substrate was observed in both trials. For the Troy trials, the biochar TP increased 13X to 1.7% and TN increased 3X to 0.8%, dry mass values. Preliminary greenhouse plant trials with the recovered nutrient upcycled biochar showed positive results.

At Moscow, the process influent total organic carbon and dissolved organic carbon, both typically at about 5 mg/l, only showed small decreases. Total ion analyses of before and after Moscow N-E-W Tech process water by time of flight mass spectrometry demonstrated a significant average molecular mass reduction, greater than 50% in the treated water. A survey of trace organic compounds, such as hormones and pharmaceuticals, in the Moscow trials demonstrated 90 to 99+% removals at the ng/l levels. Table 1 shows a sample listing of these results. Salicylic acid, a natural phenolic component of plant material was observed at 150 ng/l in the process effluent, presumably created by the oxidative destruction of plant macro-molecules.

Table 1. Sample listing of some of the trace organic compounds detected in the city of Moscow municipal secondary treatment water (Influent) and after the N-E-W Tech process (Effluent). Below MDL results were calculated at one half of the MDL for % removal.

Fe(II) + O_3 + Biochar	Influent, ng/l	Effluent, ng/l	MDL	% Removal
Bisphenol A	44	ND	4	95.5%
Caffeine	40	1.4	1	96.5%
Carbamazepine	380	ND	0.4	99.9%
DEET	39	0.73	0.7	98.1%
Dilantin	55	ND	0.2	99.8%
Diclofenac	47	ND	0.9	99.0%
Fluoxetine	47	ND	0.8	99.1%
Gemfibrozil	210	ND	0.5	99.9%
Hydrocodone	56	ND	0.5	99.6%

To explore the greenhouse gas emissions and energy efficiency of the N-E-W Tech research process trailer, a comprehensive audit was conducted of process inputs and outputs during a trial at the Moscow wastewater plant (Dunkel 2016). It is important to note that use of a blower rather than a compressor and water pumps with variable frequency control were not used for system development on this research platform. Table 2 shows the calculated net total global warming potential (GWP) considering electricity consumption, production of biochar, production of iron chloride, and the captured phosphorus. On the day of the audit, biochar was being dosed at a rate of 0.068 kg/min, ferric chloride (40% w/v) was being dosed at 2.71 mL/min, and water total phosphorus was being reduced from 0.117 to 0.006 mg/l. Without considering agricultural soil amendment use of the nutrient upcycled biochar substrate produced from the N-E-W Tech process, the CO_2 mass equivalent GWP is 3.32 kg CO_2 per 1000 gallons (3785 liters) of water treated. The CO_2 equivalent of the biochar dose used in this trial is 11.8 kg per 1000 gallons (3785 liters) of water treated. If the carbon negative component associated with the agricultural soil application of the biochar product is included into the overall process boundary, then the resulting system global warming potential would be a value of -8.02 kilograms of CO_2. In this scenario, the NEW Tech system could potentially be considered to be a carbon negative process from a greenhouse gas emissions standpoint, and would essentially be promoting the sequestration of more atmospheric carbon than the advanced water treatment process operations are contributing. Cool Planet, the manufacturer of the biochar used in this research, calculates a 200-year carbon sequestration for this biocarbon in agricultural applications.

Table 2. Net total global warming potential (GWP) for N-E-W Tech system operations to process 1000 gallons (3785 liters).

System Input/Output	GWP (mass CO_2 equivalent)
Electrical Consumption (kg)	2.12
Production of Biochar (kg)	0.395
Production of Ferric Chloride (kg)	0.808
Captured Phosphorus (kg)	-1.60×10^{-4}
TOTAL (kg)	3.32

Conclusions

In this work, we demonstrate the wastewater treatment potential and resource recovery opportunities with a novel functionalized biochar, catalytic oxidation, reactive filtration process. The process demonstrates N/P removal and recovery, as well as pathogen and priority substance destructive removal. Although N removal efficiency was below desired levels, new work is underway to target specific biochar surface modification and process enhancement to increase that dynamic of the process. At 99.5% TP removal and recovery from secondary water, to very low concentrations, the process exhibits state-of-the-art performance. The very high removal rates observed for all of the detected trace organic compounds suggest capacity to address the increasing concern for release of toxic priority substances into environmental waters. As well, the indication of near sterilization of process waters provide a hopeful outlook for addressing the potential public health crisis of antibiotic resistant microorganisms and disease vectors. This includes the capability for the destructive removal of antibiotic resistance genes and viruses in treated wastewater discharge.

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