A GPC Process to Reduce Total Nitrogen, BOD_5 and TSS concentrations in the Final Effluent at a Wastewater Treatment System

Michael B. McGrath[1] and Timothy M. Santos[2]

Abstract.

This report describes a process identified as the GPC process that reduces dissolved Total Nitrogen, Five Day Biochemical Oxygen Demand and Total Suspended Solids of already highly treated wastewater effluent at a small scale wastewater treatment system. This new process adds and mixes a proprietary manmade organic carbon to previously treated effluent having low concentrations of dissolved organic carbon and low concentrations of dissolved Total Nitrogen. The mixed fluid is dosed intermittently to a specially constructed, proprietary stratified slow sand filter, prior to discharge to the environment. This step removes about 53% of the dissolved Total Nitrogen applied to the proprietary filter. The final effluent has concentrations of Five Day Biochemical Oxygen Demand and Total Suspended Solids at or near Detection Level. The GPC process also reduces concentrations of some Pharmaceuticals and Personal Care Products.

Introduction

Traditional treatment of wastewater easily removes most Five Day Biochemical Oxygen Demand ($BOD_{5)}$ and most Total Suspended Solids (TSS) from the treated fluid. Nitrogen is more difficult to remove from wastewater than most other constituents. The final effluent from wastewater treatment systems usually has concentrations of BOD_5 less than 30 milligrams per liter (mg/l). The concentrations of Total Nitrogen (TN) are usually less than 10 mg/l. BOD_5 is not a true representation or measurement of dissolved organic carbon in the water since BOD_5 is a measurement of the amount of oxygen needed to treat wastewater to secondary treatment levels. When highly treated final effluent is discharged into the ground, the discharged water usually has more dissolved nitrogen than dissolved readily decomposable organic carbon on a mass basis. If water with the wrong ratio of dissolved carbon to dissolved nitrogen is discharged into the ground, then the soil bacteria and soil micro-organisms cannot use the dissolved carbon and dissolved nitrogen efficiently. The dissolved carbon is usually used before the dissolved nitrogen. Then the dissolved nitrogen will drain and move down through the vadose zone and travel for long distances in the groundwater with limited or minimal microbial attenuation.

This report describes the process of mixing a certain proprietary organic carbon, here called GPC Carbon, dissolved with the final denitrified effluent from a wastewater treatment system and periodically dosing it onto a special stratified filter, here called a GPC Filter. Before the water is mixed with the GPC Carbon and applied to the GPC Filter, the fluid has undergone advanced treatment and has already passed through a denitrification stage. The described process further reduces the low concentrations of dissolved TN in denitrified water. This technique removes a significant portion of the remaining dissolved nitrogen in the waters passing through the GPC Filter. The process uses a stratified sand filter that mimics the soil formation in coastal outwash

[1] Holmes and McGrath, Inc. and Ground Penetrating Carbon, Inc., Falmouth, MA
[2] Holmes and McGrath, Inc. and Ground Penetrating Carbon, Inc., Falmouth, MA

plains and sandy alluvial soils. The process establishes the proper microbial environment to induce denitrification by soil bacteria in the sands of the GPC Filter. This same process could be induced in natural sandy soils.

The GPC Filter removes almost all dissolved readily decomposable carbon as measured by the concentration of BOD_5 in the GPC Filter effluent. During the operation of the process, it was discovered that the GPC Filter discharged insoluble organic particulates. The insoluble particles included some portion of carbon that will eventually become available to soil bacteria in the soils in the vadose zone and the soils in the groundwater.

In limited testing, the GPC Filter was found to reduce the concentrations of Pharmaceuticals and Personal Care Products (PPCP's) in the water that passed through the process.

Methods and Materials

The GPC Filter was installed and developed at a small scale RUCK™ wastewater treatment system in Yarmouth, Massachusetts. The RUCK™ system serves sixty houses. The design capacity for the constructed RUCK™ system is 22,440 gallons per day (gpd). The wastewater from the houses is collected in gravity sewers draining to the lowest part of the site. The wastewater is then pumped to the RUCK™ treatment system. Initially, the wastewater undergoes settling in a series of anoxic tanks with a total capacity of 50,000 gallons. The settled wastewater is intermittently and alternately pressure dosed onto one of a pair of RUCK™ filters. RUCK™ filters are modified, stratified, vented sand filters. Effluent from the RUCK™ filters almost always has low concentrations of BOD5 and TSS and is also completely nitrified. In a series of denitrifying tanks with a total capacity of 15,000 gallons, MicroC™, a manmade organic carbon, is added to the nitrified RUCK™ effluent for denitrification. The denitrified fluid is then pressure dosed over a pair of GPC Filters before disinfection by ultraviolet light. After disinfection, the treated water is discharged into the ground by pressure dosing into leaching trenches.

As part of the permit to operate the wastewater treatment system, a Certified Treatment Plant operator oversees the treatment plant process. Weekly, the operator installs composite samplers to draw waters for testing of the raw influent and final effluent simultaneously. The composite sampler is an Isco GLS Portable Sampler, manufactured by Teledyne Isco. Every half hour the composite sampler draws $1/48^{th}$ of the required volume of water needed to perform the required testing. The operator occasionally gathers grab samples at various points in the treatment train to assess proper operation of the treatment system and to test the influent to the GPC Filter.

When gathering samples, the operator uses sample bottles furnished by a testing laboratory certified by the Massachusetts Department of Environmental Protection (DEP) to test water in Massachusetts. The operator keeps the samples on ice and transports the samples to the testing laboratory on the same day as the samples are drawn. The testing laboratory issues written reports to the operator. Monthly, the operator reports the results of the testing to the DEP.

In testing for PPCP's, grab samples of the influent and effluent of the GPC Filter were taken by an operator in accordance with the protocol issued by Eurofins Eaton Analytical Laboratory for a Broad Spectrum assessment of PPCP's. Samples were gathered in the provided sample containers. The samples were iced and shipped overnight to the Eurofins Eaton Analytical Laboratories.

Nitrogen in the Environment

Excessive concentrations of dissolved nitrate in surface and groundwater can cause health hazards and accelerated eutrophication of estuarine waters. The Maximum Contaminant Level (MCL) of nitrate in drinking water as established by the United States Environmental Protection Agency is 10 mg/l. Excessive concentrations of nitrate have been linked to methemoglobinemia or "blue baby syndrome." Nitrate is the limiting nutrient in salt water and estuarine systems. Dissolved nitrates in groundwater and surface waters draining to estuaries cause accelerated eutrophication of salt-water environments. The concentration of nitrate that causes eutrophication of estuarine waters is much lower than the MCL for drinking water. Chapelle (2001) estimates that nitrate concentrations in excess of 3 mg/l in the groundwater draining to estuaries will cause estuarine eutrophication.

Traditional Measurements of the Performance of Wastewater Treatment

The success of wastewater treatment was once considered excellent if the discharged effluent had low concentrations of BOD_5 and TSS. BOD_5 is a value that describes the amount of oxygen needed in five days to oxidize the readily decomposable organic matter and to oxidize some of the dissolved chemicals in the water. Obviously, there is some carbon that does not readily decompose or oxidize within five days. There are also some chemicals that will not oxidize in five days. The measurement of BOD_5 is a standard test that evolved decades ago. The use of BOD_5 concentration values allows for the design of suitable vessels with an added appropriate volume of air added to obtain suitable treatment of wastewater.

TSS is a measure of suspended solids in the water. The reduction of TSS normally results with sufficient aeration in the reduction of BOD_5.

Today, the increase in population and development in coastal areas has caused greater impacts of dissolved nitrogen on drinking water and estuarine water quality. Excess dissolved nitrogen discharged into the ground and into surface water has caused eutrophication of estuaries, harbors and salt ponds across the nation. The removal of dissolved nitrogen from wastewater is much more important now with strict regulatory limits being imposed in the treatment of water to reduce dissolved nitrogen to very low concentrations.

When the final effluent is discharged into the ground at a wastewater treatment facility the regulatory approval requires that the system discharge final effluent meeting certain low concentrations of BOD_5, TSS, pH, TN and other constituents. The measurement of these constituents is always of the final effluent prior to discharge. The original regulatory approach was often to discharge the most highly treated water that could be obtained. The capabilities of the soil bacteria and soil micro-organisms were ignored since the discharged water was so highly treated. Because the ability of soil micro-organisms to attenuate the pollutants downstream in the groundwater is not accepted or understood the discharge of the treated effluent often creates long plumes of dissolved nitrogen in the groundwater.

We believe that the proper approach to mitigate nitrogen pollution from the discharge of treated effluent from wastewater treatment facilities into the soils is to induce further treatment by the soil bacteria and soil micro-organisms below the soil absorption system. The soil bacteria and soil micro-organisms will further treat and denitrify the discharged fluid as it moves through the soils. In order to enlist the soil bacteria and soil micro-organisms we need to provide enough carbon for their growth and metabolic needs.

The use of BOD_5 does not allow us to identify if the proper dissolved Carbon to Nitrogen (C:N) ratio is present in the discharged water for the best microbial treatment to be induced in the soils below and downstream of the soil absorption system. What is the relationship of TOC to BOD_5? According to Crites and Tchobanoglous (1998), the ratio of TOC/BOD_5 in treated wastewater varies between 0.2 and 0.5. What is the desired C:N ratio for microbial treatment in the soils? The soil micro-organisms below the discharge surface have carbon to nitrogen ratios in the range of 3:1 to 5:1 according to Paul and Clark (1996).

The true C:N ratio cannot be assessed from the concentration of the BOD_5 of the treated effluent discharged into the soils. If the BOD_5 concentration is low, and the concentration of TN is low, then most likely there is less dissolved carbon than dissolved nitrogen in the effluent.

Before the water enters the GPC process, the water has already been denitrified. The dissolved TN is usually primarily dissolved organic nitrogen. This influent water to the GPC process has very low concentrations of TOC. If we have the proper carbon to nitrogen ratio in the water applied to the soil, we will not only have in situ treatment of the water as it passes through the vadose zone but we will most likely induce further long term denitrification in the groundwater plume.

To demonstrate this capability of the soil bacteria and soil micro-organisms to further treat highly treated water we will dose already denitrified water mixed with an appropriate C:N ratio onto a GPC Filter. The modified, stratified GPC sand filter resembles, in a general way, the natural stratified formation of sandy soils in coastal outwash plains or sandy alluvial soils. We will show how the addition of GPC Carbon to denitrified fluid and dosing the fluid onto a stratified filter removed a significant portion of the dissolved TN in the waters passing through the GPC Filter. The GPC Filter also further treats the applied water in surprising and unexpected ways.

The Removal of Dissolved Nitrogen from Water

Bacteria drive the nitrogen cycle. Various bacteria transform nitrogen into the different compounds. The efficient treatment and removal of dissolved nitrogen from water requires the arrangement of environments having the appropriate combination of carbon, oxygen and nitrogen. Organic nitrogen and ammonia dissolved in any water needing treatment must first undergo nitrification. Nitrification is the microbially driven oxidation of organic nitrogen and ammonia to nitrite and then nitrate. Nitrification is driven by two dominant species of bacteria. Initially, bacteria nitrosonomas oxidize ammonia (NH_3) into nitrite (NO_2). The bacteria nitrobacter then oxidize nitrite into nitrate (NO_3). These bacteria are slow growers and tend to take a long time to reach an effective population density to provide complete nitrification of the organic nitrogen. Limitations on microbial nitrification are pH, alkalinity, excessive carbon concentrations and certain chemicals (Oakley, 2003). The most common limitation is the lack of alkalinity. Alkalinity

is the capacity of water to neutralize strong acids. According to Crites and Tchobanoglous, (1993), the alkalinity in water helps to resist changes in pH. Alkalinity is measured as the concentration of calcium carbonate ($CaCO_3$). Since nitrification is limited by pH, there are well-understood formulas that state that for every milligram of NH_3 oxidized, 7.1 mg of $CaCO_3$ are consumed (Oakley, 2003). Alkalinity can and will be a limiting factor in nitrification.

The only significant loss of dissolved nitrogen is denitrification, where oxidized nitrogen is converted to nitrogen gas. Denitrification is the microbially driven removal of dissolved nitrate from water. Denitrification requires nitrate, sufficient time, temperature, bacteria, available carbon and anoxic conditions. Under correct conditions, dissolved nitrate will be completely denitrified with the end products being free nitrogen gas, free carbon dioxide gas, dissolved organic nitrogen and dissolved organic carbon in the water and organic nitrogen and organic carbon in biomass. Denitrification takes place in anaerobic microsites in soils and sand filters. Such microsites occur in the smaller pores in the sand, at the narrow channels at the intersection of sand particles, and at the change of textures. Since denitrification can only occur if the form of nitrogen is nitrate, any dissolved organic nitrogen or ammonia that enters a denitrification site will only undergo dilution as treatment. Dissolved organic nitrogen and ammonia pass through any denitrification site.

Limitations on the Removal of Dissolved Nitrogen from Water in Soils

In order to enlist the soil bacteria to address nitrogen pollution, discharged effluent should have sufficient carbon for both denitrification and microbial metabolism. As described above, if the BOD_5 concentration is low, and the concentration of TN is low, then most likely there is less dissolved carbon than dissolved nitrogen in the effluent. For instance, if a wastewater treatment facility discharges effluent with a BOD_5 concentration of 30 mg/l and a TN concentration of 10 mg/l, the Carbon to Nitrogen (C:N) ratio in the final effluent varies from 0.6 to 1.5. If the C:N ratio is less than what the soil micro-organisms can use, then this C:N factor will limit the potential for natural attenuation in the soils below the soil absorption systems. Such treated water draining down and moving through the soils reaches the water table and will create plumes of dissolved nitrogen in the groundwater. Such plumes of nitrogen tend to travel miles because there is insufficient carbon in situ and in the groundwater to promote significant denitrification.

In operating this GPC system, we attempt to match the C:N ratio in the water applied to the GPC Filter to what the soil bacteria can use. As stated above, the water applied to the GPC Filter has already undergone denitrification. We add a highly available dissolved organic carbon, GPC Carbon, to the denitrified fluid prior to being pressure dosed to the top of the GPC Filter, a modified, stratified sand filter. Additional removal of dissolved nitrogen occurs as the dosed water, with initial low concentrations of dissolved nitrogen, drains and moves down through the stratified GPC Filter. The GPC Filter is designed to create varying environments to enhance the microbial removal of dissolved nitrogen. The stratifications create anaerobic conditions suitable for denitrification. We found the average removal rate of dissolved TN was around 53% reduction in the average dissolved TN concentration in the fluid dosed to the filter. The GPC Filter was designed to mimic the stratifications in natural soils. Any microbial process that occurs in the stratified filter will occur in natural soils of a similar arrangement. The GPC Filter effluent has very low concentrations of BOD_5 and TSS.

Wastewater Treatment Facility Location

The GPC Process was developed at a wastewater treatment facility in Yarmouth, Massachusetts. Massachusetts Department of Environmental Protection (DEP) approved a RUCK™ CFT system at the facility site on Cape Cod under the Groundwater Discharge Program. The location is shown on Figure 1.

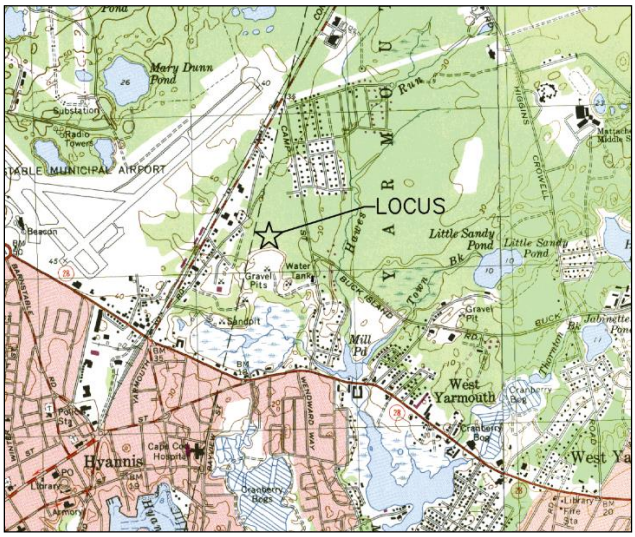

Figure 1 – Cape Cod RUCK CFT Locus

The RUCK™ system was designed to serve a 136 unit residential subdivision. The wastewater treatment system has an approved flow of 44,880 gallons per day. The RUCK CFT system can be built in phases, so approximately half of the wastewater treatment system is currently constructed. The RUCK™ system discharges treated water into land in a sandy outwash plain. There might be times when the ground water under the soil absorption system might drain towards a municipal drinking water well. MA DEP required that the treated wastewater undergo disinfection prior to discharge into the ground. The treatment train included a stratified filter to reduce TSS concentration prior to disinfection by UV light.

Figure 2 illustrates a GPC Filter.

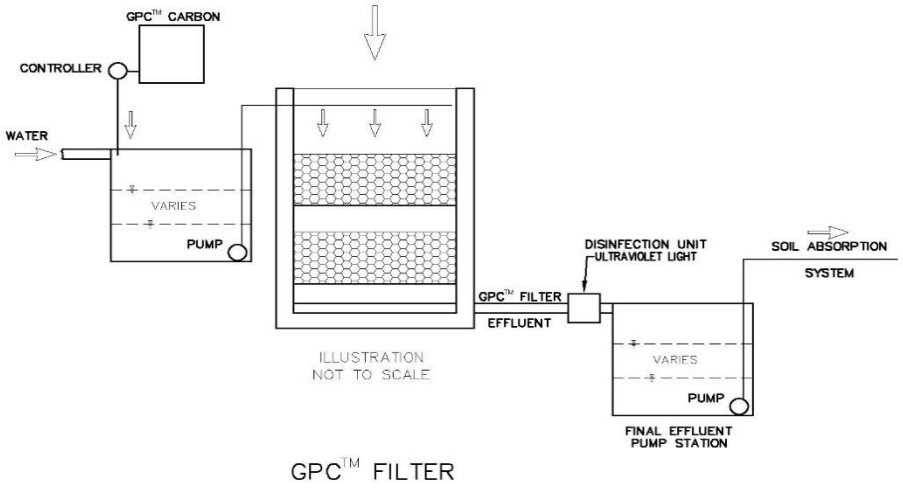

Figure 2 – GPC Filter

The GPC Filters were originally designed to remove Total Suspended Solids ("TSS") from the water to increase the efficiency of ultraviolet disinfection. The operation of the GPC Filters did achieve the anticipated reduction in TSS in the filter effluent. However, when GPC Carbon was added to the influent of the GPC Filter, there was significant removal of TN as measured by the difference in the influent TN concentration and the effluent TN concentrations to the filter. The effluent then drains and passes through an ultraviolet disinfection system and is then pressure dosed to a soil absorption system consisting of a series of leaching trenches installed about ninety degrees to the direction of groundwater flow.

RESULTS

Composite samples of the final effluent were taken weekly. The testing of these samples revealed the following concentrations:

Table 1: Final Effluent Testing Results
Mill Pond Village, West Yarmouth, MA

May 13, 2011 to October 31, 2014

	BOD_5	TSS	TN	NO_3
	mg/l	mg/l	mg/l	mg/l
Average	3.1	2.3	5.1	4.5
TOTAL TESTS	181	181	181	181
NON-CONFORMITIES	0	3	13	7

Detected	6	23	n/a	n/a
Detection Level	3	3		
Total BDL	175	158		
Percent Compliant	100%	98%	92%	96%
Median	3.0	1.5	4.2	3.5
High	13.7	14.0	23.1	22.2
Low	3.0	1.5	0.8	0.4

When the testing laboratory reports that a test result is that none of the constituent was detected, the result is described as Below Detection Level ("BDL").
A non-conformity is when the final effluent has a concentration of a constituent above the limit described in a permit.

Discussion of Results of the Performance of the GPC Filter

The GPC Filter, when dosed with influent mixed with GPC Carbon, consistently reduced BOD_5 concentrations to low levels. Of 181 final effluent composite samples, 175 samples had values below the detection level of 3 mg/l. The highest measured concentration of the BOD_5 was 13.7 mg/l.

The GPC Filter also reduced TSS to low levels. Of 181 final effluent composite samples, 158 samples had values below the detection level of 1.5 mg/l. The highest concentration of TSS was 14.0 mg/l. The effluent is then clear with little measured concentrations of TSS.

The GPC Filter consistently reduced TN concentrations when dosed with influent mixed with GPC Carbon. Of 181 final effluent composite samples, 158 samples conformed to the permit level of 10 mg/l TN. The highest concentration of TN was 23.1 mg/l. In this time period, the median TN concentration was 4.2 mg/l. The non-conformities occurred when the upstream treatment system did not denitrify the water completely.

In order to measure the loss of TN in the fluid passing through the GPC Filter, we have to understand the characteristics of the water entering and leaving the GPC Filter. During the late summer and early fall of 2014, prior to the addition of the GPC Carbon, grab samples of the influent water were taken weekly by the operator, delivered to the testing laboratory and analyzed by Envirotech Laboratories, Inc. The samples had the following measured constituents:

Table 2: GPC Filter Influent Concentrations

Influent	BOD_5	TKN	NO3	NO2	TN	TSS
Sample Date	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
22-Aug-14	46.9	9.2	0.35	0.02	9.6	1.5
28-Aug-14	40.7	7.1	0.05	0.02	7.1	1.5

5-Sep-14	13.6	6.3	0.05	0.02	6.3	2
12-Sep-14	22.8	7.7	0.34	0.02	8	2
19-Sep-14	32	6.6	0.05	0.02	7	4
26-Sep-14	2	0.6	4.25	0.02	4.9	24
2-Oct-14	25.1	6.2	0.35	0.02	6.5	8
Average	26.2	6.2	0.78	0.02	7.1	6.1

During the same time period as the operation of the test filters, composite samples of the final effluent from the Mill Pond Village (MPV) wastewater treatment system were taken. This water was the final effluent of the GPC Filter described in this report. The samples of the final effluent were analyzed by Envirotech Laboratories, Inc. The samples had the following measured constituents:

Table 3 GPC Filter Effluent Concentrations

Effluent	BOD_5	TKN	NO_3	NO_2	TN	TSS
Sample Date	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
22-Aug-14	3	0.6	3	0.02	3	1.5
29-Aug-14	3	1	2.38	0.02	3.4	1.5
05-Sep-14	3	0.7	2.64	0.02	3.3	1.5
12-Sep-14	3	0.6	3	0.02	3.6	1.5
19-Sep-14	3	0.6	2.63	0.02	3.2	1.5
26-Sep-14	2	0.7	2.6	0.02	3.3	1.5
03-Oct-14	2	1.5	2.08	0.02	3.6	1.5
Average	2.7	0.8	2.62	0.02	3.3	1.5
Average Removal rate	90%				53%	
Lowest measured TN concentration of effluent				=	3	mg/l
Highest measured TN concentration of effluent				=	3.6	mg/l
Lowest TN removal				=	33%	
Highest TN removal				=	69%	

This full size GPC Filter removed virtually all detectable BOD_5 concentrations and virtually almost all detectable TSS concentrations in the water passing through the GPC Filter. The dissolved TN concentrations were reduced by an average of 53%. The final effluent TN concentration varied from 3 mg/l to 3.6 mg/l. The removal of TN was estimated using the difference between the influent concentrations compared to the effluent concentrations. This may not be a precise removal rate since it does take time for the water to drop through the filter. The difference in concentrations over time does indicate an approximate removal rate in the filter. The lowest TN removal was 33% and the highest TN removal was 69%.

The removal of dissolved TN in the water draining through the GPC Filter was accomplished by soil bacteria and soil micro-organisms. The influent to the GPC Filter primarily had organic nitrogen expressed as TKN. The effluent of the GPC filter had both organic TKN and inorganic NO_3. The reduction of TN concentrations requires that both nitrification and denitrification take place in the filter sands. Nitrification takes place near soil bacteria that reduce organic carbon and emit carbon dioxide. Since the only effective microbial removal process for dissolved nitrogen is denitrification, the results prove that denitrification occurs in the GPC Filter. Denitrification can occur in the filter due to the combination of the water being delayed and stored in the texture changes in microsites in the sands throughout the filter. There is visual evidence in the form of redoximorphic mottles in the sand that denitrification takes place at the bottom of the sand layer.

Limitation of the GPC Filter Process

The GPC Filter process does have an operating limitation. When dissolved carbon is available as an electron donor in soils and in sands, there are electron acceptors that are available in a particular order: Nitrate reducing, Manganese reducing, Iron reducing, Sulfate reducing and Methane reducing. If the filter water in the filter sands becomes highly anaerobic, and denitrification is complete, then ferric iron, FE (III) will be released from the sands or from the water. The dissolved ferric iron will travel in the filter water. When the filter water with the dissolved ferric ion reaches an aerobic zone, the ferric ion will be oxidized to ferrous iron, FE (II). Rust will result forming a relatively impermeable layer at the bottom of a sand filter at the top of the vented layers. The rust layer will have much slower permeability. To prevent this condition, the influent water has to have low concentrations of dissolved iron in the water or the GPC Filter will fail.

Testing of PPCP's

Grab samples of the influent and effluent of the GPC Filter were taken by an operator in accordance with the protocol issued by Eurofins Eaton Analytical Laboratory for a Broad Spectrum assessment of PPCP's. The GPC Filter influent was collected from the denitrification tank prior to the GPC Filter pump. The effluent was collected from the ultraviolet light (UV) trough located after the GPC Filter, but the UV lights were turned off before sampling so the UV did not provide any removal factor for the sampled compounds.

October 2014 PPCP's Analyses

The first round of samples were taken on October 10, 2014. Eurofins Eaton Analytical Laboratory reported the following results:

Table 4:

GPC Filter PPCP's Tests
Samples Received on 10/10/2014

Pharmaceuticals

	Analyte	*Influent (ng/L)*	*Effluent (ng/L)*	*Delta (ng/L)*	*MRL (ng/L)*	*Low Removal Rate*	*High Removal Rate*
1	Acetaminophen	140	ND		5	93%	>99%
2	Amoxicillin (semi-quantitative)	4000	ND		20	99%	>99%
3	Atenolol	130	9.6	120.4	5	89%	96%
4	Azithromycin	ND	49		20	increase	
5	Butalbital	6.7	11	+ 4.3	5	increase	
6	Carbamazepine	12	6.8	5.2	5	2%	85%
7	Diltiazem	11	ND		5	9%	>99%
8	Ibuprofen	90	ND		10	78%	>99%
9	Naproxen	120	ND		10	83%	>99%
10	Lidocaine	220	150	70	5	30%	34%
11	Lopressor	260	31	229	20	80%	96%
12	Pentoxifylline	40	ND		5	75%	>99%
13	Theophylline	81	ND		20	51%	>99%
14	Trimethoprim	52	ND		5	81%	>99%
15	Warfarin	9.1	ND		5	-10%	>99%

Household Chemicals

	Analyte	*Influent (ng/L)*	*Effluent (ng/L)*	*Delta (ng/L)*	*MRL (ng/L)*	*Low Removal Rate*	*High Removal Rate*
16	1.7-Dimethylxanthine	40	ND		10	50%	>99%
17	Acesulfame-K	24000	750	23250	200	96%	98%
18	Caffeine	230	25	205	5	87%	91%
19	Cotinine	19	ND		10	-5%	>99%
20	DEET	130	25	105	10	73%	88%
21	Diuron	16	ND		5	38%	>99%
22	Propylparaben	5.2	ND		5	-92%	>99%
23	Sucralose	37000	28000	9000	1000	22%	27%
24	TCEP	170	110	60	10	29%	41%
25	TCPP	1100	290	810	100	65%	83%
26	TDCPP	630	320	310	100	33%	65%
27	Theobromine	97	69	28	10	19%	39%

The Highest Removal Rate is calculated using the influent concentration plus the value of the MRL minus the effluent concentration minus the MRL.
The Lowest Removal Rate is the influent concentration minus the value of the minimum reporting level minus the effluent concentration plus the minimum reporting level.
ND denotes No Detect.
MRL denotes Minimum Reporting Level.

Discussion of October PPCP's Analyses

As a result of the PPCP's testing of the samples gathered October 10, 2014, the influent water contained fourteen detected pharmaceutical chemicals. The effluent fluid had fifteen detected pharmaceutical chemicals. The estimated removal rate varies with the minimum reporting level (MRL). If the test of the effluent had No Detect (ND), the effluent concentration was assumed to be the MRL.

The GPC Filter removed nine pharmaceutical chemicals to levels below detection, two chemicals, Atenolol and Lopressor, were reduced substantially (over 80% removal), two chemicals, Carbamazepine and Lidocaine, were reduced and one chemical, Butalbital, increased. Azithromycin was found in the effluent but not found in the influent.

Of twelve household chemicals detected in the influent, the GPC Filter removed four chemicals to levels below detection, two chemicals, Acesulfame-K and Caffeine, were reduced substantially, (over 80% removal), and six chemicals, DEET, Sucralose, TCEP, TCPP, TDCPP and Theobromine, were reduced. DEET is a chemical in insect repellants and it was reduced from 73% to 88%. TCEP, TCPP and TDCPP are fire retardants and are normally considered resistant to decomposition.

November 2014 PPCP's Analyses

The second round of samples were taken on November 24, 2014. Eurofins Eaton Analytical Laboratory reported the following results.

Table 5:

GPC FILTER PPCP's
Tests
Samples Received on 11/24/2014

Pharmaceuticals

	Analyte	*Influent (ng/L)*	*Effluent (ng/L)*	*Delta (ng/L)*	*MRL (ng/L)*	*Low Removal Rate*	*High Removal Rate*
1	Amoxicillin (semi-quanititative)	1200	ND		20	97%	>99%
2	Atenolol	120	17	103	5	82%	90%
3	Butalbital	18	15	3	5	-11%	44%
4	Dilantin	23	ND		20	-74%	>99%

5	Dilitazem	11	ND		5	9%	>99%
6	Gemfibrozil	240	ND		5	98%	99%
7	Ibuprofen	25	ND		10	20%	>99%
8	Iohexal	11	ND		10	9%	99%
9	Lidocaine	94	97		5	INCREASED'	
10	Lopressor	150	21	129	20	73%	99%
11	Meprobamate	31	42		5	INCREASED'	
12	Naproxen	11	ND		10	9%	99%
13	4-nonylphenol – semi quantitative	ND	300		100	INCREASED'	
14	4-tert-Octylphenol	ND	140		50	INCREASED'	

Household Chemicals

	Analyte	*Influent (ng/L)*	*Effluent (ng/L)*	*Delta (ng/L)*	*MRL (ng/L)*	*Low Removal Rate*	*High Removal Rate*
15	Acesulfame-K	14000	350	13650	200	96%	99%
16	Caffeine	58	9.6	48.4	5	75%	92%
17	Cyanazine	11	5.9	5.1	5	1%	92%
18	DEET	33	ND		10	39%	>99%
19	Isobutylparaben	5.6	ND		5	11%	99%
20	Sucralose	11000	16000		100	INCREASED'	
21	TCEP	54	41	13	10	6%	43%
22	TCPP	290	ND		100	66%	>99%
23	TDCPP	220	ND		100	55%	>99%
24	Triclocarban	18	ND		5	72%	99%

The Highest Removal Rate is calculated using the influent concentration plus the value of the MRL minus the effluent concentration minus the MRL.
The Lowest Removal Rate is the influent concentration minus the value of the MRL minus the effluent concentration plus the MRL.
ND denotes No Detect.
MRL denotes Minimum Reporting Level.

Discussion of November PPCP's Tests

As a result of the PPCP's testing of the samples gathered November 24, 2014, the influent water contained twelve detected pharmaceutical chemicals. The effluent fluid had fourteen detected pharmaceutical chemicals. The estimated removal rate varies and is calculated as described above.

The GPC Filter removed seven pharmaceutical chemicals to levels below detection, one chemical, Atenolol was reduced substantially (over 80% removal), one chemical, Butalbital, may have

increased but also may have decreased since the influent and effluent concentrations were close to the same value. Two chemicals, Meprobromate and Lidocaine, increased. Two chemicals 4-nonylphenol - semi quantitative and 4-tert-Octylphenol, were found in the effluent but not found in the influent.

Of ten household chemicals detected in the effluent, the GPC Filter removed four chemicals to levels below detection, while one chemical, Acesulfame-K was reduced substantially (over 80% removal). Four chemicals, Caffeine, Cyanazine, TCEP, and Triclocarban, were reduced, but Sucralose increased. DEET is a chemical in insect repellants and it was not detected in the final effluent. TCEP is a fire retardant and was reduced between 6% and 43%. TCPP and TDCPP are fire retardants and these chemicals were not found in the final effluent. TCEP, TCPP and TDCPP are normally considered resistant to decomposition.

Discussion of PPCP's Analyses

The tests report values in nanograms per liter (ng/L) or one part in one trillion (10^{12}). Some test samples were diluted during the testing process in order to accommodate the calibration range of the testing system, but both the influent and effluent values received the same dilution and MRL were adjusted accordingly. The entire round of tests on the GPC Filter influent and effluent should be repeated several times before the range of removal rates can be confirmed.

The GPC Filter does store water in the pores of the sand layers. The filter water stacks in the pores above the texture changes. That is, the pore size in the filter cloth is smaller than the average pore size in the sand. Since the water passing through the pore size drains much slower than the water draining through the pores in the sand, the pores in the sand above the filter cloth store water and these pores are saturated. The retention time in the filter is not known but most likely the GPC Filter stores water for days. The estimated removal rate in comparing the influent concentrations of a particular chemical to the effluent concentrations of the same chemical necessarily assumes that the applied concentration is the same value during the draining of water through the GPC Filter. The removal rates then are approximate and require repetitive tests to establish the true removal capacity. But, in any case, the removal rates are impressive.

The reduction of the organic carbon chemical concentrations appears to be the result of the soil micro-organisms being so numerous that there is selection in the existing soil micro-organism population for some micro-organisms to attack and use these resistant organic compounds for metabolism. The reduction of several chemicals to No Detect is an unexpected result.

Vona et al. (2014) compared different removal techniques for six selected pharmaceuticals, Ibuprofen, Acetaminophen, Diclofenac, Sulfamethoxazole, Clonazepam, and Diazepam at a concentration of 1000 ng/l in differing types of wastewater. Vona et al. tested five different removal methods by dosing the water through the following treatment techniques: ultrafiltration, nano-filtration, activated carbon absorption, biological removal through a sequencing batch reactor and oxidation with ClO_2. Of the six pharmaceuticals, Vona et al. analyzed, there are only two chemicals, Ibuprofen and Acetaminophen, in common with the testing of the GPC Filter process.

Vona et al. reported that when water with Ibuprofen passed through both Ultrafiltration and Nano filtration, the reduction rate was excellent or over 95%. The reduction of Ibuprofen was also excellent or over 95% when the water was passed through Activated Carbon filtration and during the operation of a Sequencing Batch Reactor. The GPC Filter influent had measurable concentrations of Ibuprofen in the influent in both the October and November tests. Both showed No Detect in the GPC Filter effluent. The removal rate for Ibuprofen in the GPC Filter varied from 22% to over 99%. However, the GPC Filter effluent had no detectable concentrations of Ibuprofen.

Vona et al. reported that the reduction rate of water with Acetaminophen was ineffective in both Ultrafiltration and Nano filtration. The reduction rate of water with Acetaminophen varied from 13% to 58% when the water passed through Activated Carbon filtration. The reduction rate of water with Acetaminophen was excellent when the water passed through a Sequencing Batch Reactor treatment system. The GPC Filter influent had measurable concentrations of Acetaminophen in the influent of the October test and No detect in the effluent. The removal rate varied between 93% and over 99%. No detectable concentrations of Acetaminophen were found in the November tests. However, in October, the GPC Filter effluent had no detectable concentrations of Acetaminophen.

The operation of the GPC Filter is intuitively more efficient than the operation of either Ultrafiltration or Nano filtration of treated water. Both Ultrafiltration and Nano filtration filter out or trap these chemicals on the upstream side of the filters. There is an upstream brine of trapped material of these filter processes. In contrast, the GPC Filter seemingly effectively destroys the removed chemicals. With the GPC process, there is no upstream material filtered out of the water. With the GPC Process, there is no upstream brine to be treated.

At the RUCK^{TM} full scale wastewater treatment system, after the water passes through the GPC Filter, the final effluent undergoes ultraviolet light disinfection before discharge to the ground. The final effluent will likely have less contaminants since ultraviolet light has been demonstrated to remove or reduce certain PPCP's.

Insoluble Organic Particulates

The effluent water from the GPC Filter is clear. After the GPC Filter, the effluent undergoes exposure to an ultraviolet light. After a significant rainfall event, the wastewater treatment operator found that a material coagulated in the channels leading to and exiting the ultraviolet trough. The material was unlike any other material in the experience of the operator. Samples of the coagulated material were gathered. Figure 3 is a photograph of a sample of the coagulated material in the original water.

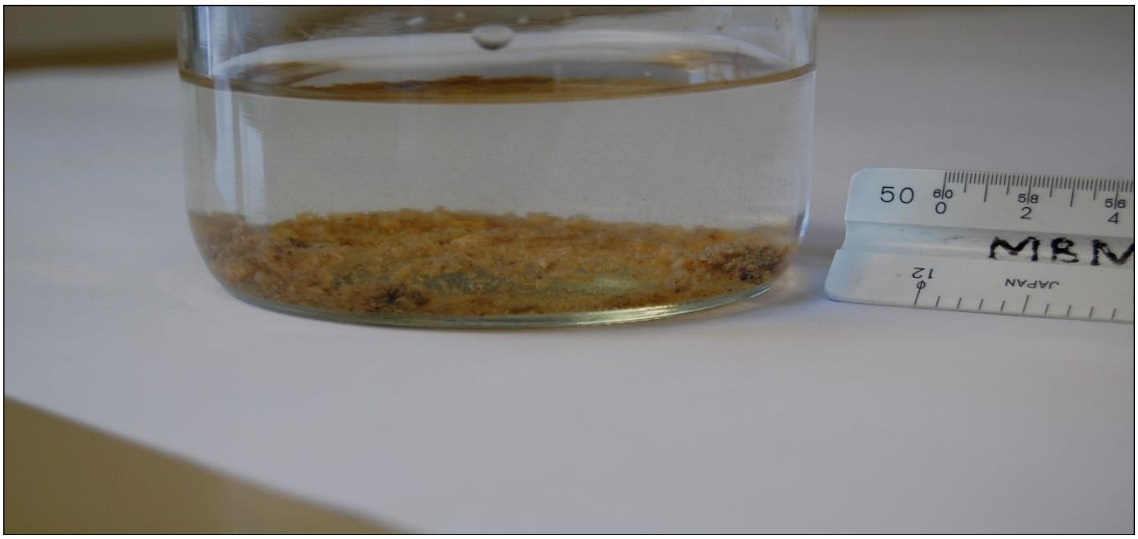

Figure 3 Photograph of Coagulated Material

It is apparent that the material is insoluble. The first sample of the material was delivered to Groundwater Analytical, Inc., a testing laboratory. An ash test showed about 22% of the sample was organic, including obviously some carbon resistant to decomposition. A second sample was stored in water in a quiet still area. The stored second sample was periodically visually examined, with the clarity of the water never changing. About forty days after collection, a green biomat appeared in the coagulated material. Clearly, the carbon in the coagulated material became available for metabolism after a time period. Since the water in the GPC Filter is stored for days, the carbon in the gathered insoluble material seems to be available in the range of forty-five to fifty days. This insoluble carbon material is extremely small in diameter since it passed through a stratified filter. The smallest expected pore sizes in the GPC Filter are 0.21 millimeters in the textile filter cloth or 0.1 millimeters in the sand.

This insoluble carbon will not show up on a standard BOD_5 laboratory test and may not show up in a TSS test. The final effluent at the wastewater treatment system is pressure dosed by pumps to the soil absorption system. The insoluble particles will flow through the ultraviolet trough and into the final effluent pump station. The pumping of the fluid will cause settled material to be eventually dosed to the soil absorption system. There is little or no sump in this portion of the system that might trap these insoluble carbon particles.

In gathering a sample of the final effluent, the operator mounts the composite sampler inside the superstructure of the pump station. The sampling tube is suspended into the water stored in the pump station with a strainer attached to the inlet to avoid collecting the settled material at the bottom of the pump station. When the composite sampler collects a sample of the final effluent it may not gather this settled solid insoluble material. If the sampler did gather some of this insoluble carbon, it would probably be reported as TSS. This insoluble carbon may exist as the Solids constituent in wastewater. This insoluble carbon may be extracellular polymeric substances. If this material is extracellular polymeric substances, then it is the cell mass and enzymes from dying motile bacteria and micro-organisms in the water and from dying soil bacteria and soil micro-organisms. According to Vandevivere and Baveye (1992), the dosing of a sand column with water

with a dissolved highly available carbon led to the discharge of extracellular polymeric substances from the bottom of a sand column. Given that the similarities of the operation of the GPC Filters to the operation of those sand columns, the insoluble carbon may indeed be composed of extracellular polymeric substances.

Providing that the effluent discharge technique at any future installation incorporates no sumps or other settling removal means, these microscopic insoluble carbon substances will pass through the soils, enter the groundwater and slowly degrade over time. This carbon is more resistant to decomposition and may become slowly available over time and may eventually provide a carbon source for in situ denitrification by soil bacteria in the soils in the vadose zone and in the soils downstream in the plume of the discharge.

Discussion of the Process

The treatment of the effluent passing through the GPC Filter is by exposure of the water to the soil bacteria and micro-organisms attached to the sand particles and by exposure of the water to the motile bacteria and micro-organisms in the water. We believe the soil bacteria and soil micro-organisms predominate because of the change in apparent soil texture of the sands in the mature GPC Filter. We assert that the soil bacteria and soil micro-organisms in natural sands will act similar to the actions of soil bacteria and soil micro-organisms in the sands of sand filters.

The soil bacteria are affixed or adhered to soil particles by either fibrillae or by slime and do not wash out of the soils. (Paul and Clark, 1989). The bacteria occupy a small portion of the voids in the soil pores. In the vadose zone, the soil biomass is usually 0.2% to 0.4% of the pore space. (Paul and Clark, 1989). It appears that the population of the soil micro-organisms in the sands in the GPC Filter must be extremely high due to the excellent removal of BOD_5 and TSS.

The removal of BOD_5 and TSS are a combination of physical straining and the microbial action. The reduction of BOD_5 to near detection levels is most likely by metabolism. A surprising observation is that there is no biomat on the top surface of the sand in the active GPC Filters. We actually dug down through an active GPC Filter and found no evidence of biomat nor of any staining except on top of the texture change at the bottom of the upper sand layer. This proves that the soil bacteria are populating the sands below the surface.

The reduction of TN concentrations requires that both nitrification and denitrification take place in the filter sands. Nitrification takes place near soil bacteria that reduce organic carbon and emit carbon dioxide. Denitrification can occur in the filter due to the combination of the water being delayed and stored in the texture changes throughout the filter and the presence of dissolved organic carbon and anaerobic bacteria throughout the filter sand particles. There is visual evidence that denitrification takes place at the bottom of the sand layer. The sands above the texture change were stained gray with light mottles. The staining and mottles are indications of redox processes.

The filter sands were moist and were very moist at the bottom of the sand layer above the texture change. When we dug down through the upper sand layer in an active GPC Filter, the side surfaces of the excavation in the moist sands down though the entire sand layer was almost vertical. The same sands, when dry, would slump. Moist sands would exhibit some greater slope stability, but

these sands stacked with vertical sides. The population of the soil micro-organisms was so great that the behavior of the moist sands in the GPC Filter was similar to that of a sand texture with significant portion of fines.

The sands in the GPC Filter have variations in the sand particle size. This variation results in a multitude of pore sizes through the filters. Water traveling through the filter has complicated travel paths because of the varying pore size and the random arrangement of the soil particles. The pathways for the water through the sand layers are tortuous and even discontinuous. The movement of water through a sand filter will be similar to how water moves through natural sandy soils of the same texture in coastal outwash plains. The GPC Filter is designed to mimic natural sandy soils in coastal outwash plains, which are almost always arranged in horizontal layers. The dosing of raw wastewater onto natural sandy soils in a coastal outwash plain will always result in complete nitrification in four vertical feet. Nitrification is complete when raw wastewater is dosed onto a RUCK^{TM} stratified filter of the same depth. The same microbial processes that occurs in the GPC Filter will occur in stratified sandy soils.

The reduction of the concentrations of PPCP's was surprising. As described by Heufelder (2010), the application of wastewater onto flat soil absorption systems such as leaching fields and shallow leaching structures has demonstrated some removal capability with similar reductions of the concentrations of PPCP's. It appears that the population of the soil micro-organisms in the sands in the GPC Filter must be very high due to the excellent reduction of these PPCP's. Since some of these chemicals are considered to be resistant to microbial attack the observed reduction in those chemicals suggests that the population of soil micro-organisms must be very high in the GPC Filter sands. Perhaps there is some other reduction mechanism occurring but the GPC Filter process had been on line for over three years when the test were completed. Further periodic testing will reveal if this removal of PPCP's by the GPC Process is consistent. This PPCP's reduction capability could be a useful tool in the treatment of water.

The GPC Filter system is a slow sand filter and its use is restricted because of filter size to flows below 100,000 gallons per day. However, this RUCK^{TM} wastewater treatment facility with the GPC Process discharged treated effluent with few permit non-conformities of critical constituents above permit limitations. With the additional capabilities of the GPC Process to remove or reduce certain PPCP's' concentrations this process can make small scale wastewater treatment systems operate at very high levels similar to large scale wastewater treatment facilities.

Conclusions

Adding a highly available dissolved organic carbon called GPC Carbon to denitrified final wastewater effluent at a wastewater treatment facility and then periodically dosing the mixed water to a stratified sand filter, here called the GPC Filter, resulted in denitrification and the removal of slightly over one half of the dissolved Total Nitrogen in the water that passed through the GPC Filter.

This particular method of treating final effluent of a wastewater treatment system through the GPC Process resulted in a final effluent with low concentrations of BOD_5 and TSS. The studied GPC

Filter had no discernible biomat on the upper surface of the GPC Filter, even after the GPC filter had been dosed for over 181 months of operation.

In the event that a wastewater treatment facility discharges treated effluent into soils, we assert that the use of the constituent BOD_5 should be replaced with a measurement of Total Organic Carbon (TOC). The discharge of treated effluent should have a proper C:N ratio to induce treatment in the vadose zone and to help induce in-situ denitrification in the groundwater downstream in sandy coastal outwash plains and alluvial sandy soils. In some instances, regulatory agencies are specifying that the final effluent from wastewater treatment plants have very low concentrations of TOC in an effort to minimize the discharge of PPCP's. Since the GPC Filter reduces the concentrations of PPCP's the use of TOC concentration is inappropriate as a permit limit for final effluent when a GPC Filter is operated in the treatment train.

The GPC Filter effluent includes microscopic insoluble material of which a portion is organic carbon, resistant to decomposition. Providing that the effluent discharge technique at any future installation incorporates no sumps or other removal means, this microscopic insoluble carbon will pass through the soils, enter the groundwater and degrade over time. This carbon is more resistant to decomposition and may become slowly available over time and may provide a carbon source for in situ denitrification by soil bacteria in the vadose zone and downstream in the groundwater.

Further research should be performed by assessing and establishing if any in situ denitrification occurs in the groundwater downstream from the discharge point.

References

Barber, L. B., and Keefe, S. H., "Evolution of a Ground-Water Plume after Removal of the 60-Year-Long Source, Cape Cod, Massachusetts: Changes in the Distribution of Dissolved Oxygen, Boron, and Organic Carbon" United States Geological Survey
Available at: www://toxics.usgs.gov/pubs/wri99-4018/Volume3/SectionC/3402_Barber/index.html

Bedinger, M. S., Fleming, J. S., and M. I. Johnson. *Site Characterization and Design of On-Site Septic System.* West Conshohocken, PA: American Society for Testing and Materials, 1997.

Bettez, N. D., et al., "Nitrogen in Runoff from Residential Roads in a Coastal Area" Water, Air, & Soil Pollution, Vol. 210, numbers 1-4, October 6, 2009: 11 pages
http://www.springerlink.com/content/n703846324875m6x/

Brawley, J., Collins, et al., "Nitrogen Loading From Coastal Watersheds To Receiving Estuaries: New Method and Applications" Ecol.Appl. 1997 7/2: 358-380
Available at: http://bibapp.mbl.edu/works/21502

Chapelle, F. H. *Ground-Water Microbiology and Geochemistry. Second Edition.* New York: John Wiley & sons, Inc., 2001.

Clark, F.E., Paul E. A. *Soil Microbiology and Biochemistry. Second Edition.* San Diego: Academic Press, 1996

Crites, R. and Tchobanoglous, G., *Small and Decentralized Wastewater Management Systems.* San Francisco: 1998.

Heufelder, G R., M.S., R.S. "Effectiveness of Selected Onsite Wastewater-Treatment System in Removing Pharmaceutical and Personal Care Products". Project Number 05-04/319 2010

Hillell, D. *Fundamentals of Soil Physics.* San Diego: Academic Press, Inc. 1980.

Laak, R. *Wastewater Engineering Design for Unsewered Areas.* Lancaster, PA: Technomic Publishing Company, 1986

LeBlanc, D. R., et al., "Natural Restoration of a Sewage Plume in a Sand and Gravel Aquifer, Cape Cod, Massachusetts", United States Geological Survey

LeBlanc, D. R., et al., "Sewage Plume in a Sand and Gravel Aquifer, Cape Cod, Massachusetts" United States Geological Survey

Mancl, K., Verma, A., "Emperical Model of Effectiveness of a Single Pass Sand Filter For Wastewater Treatment", American Society of Agricultural and Biological Engineers 2001: 281-287

Salvato, J. A. *Environmental Engineering and Sanitation. Fourth Edition*. New York: Wiley-Interscience, 1992.

Vandevivere, P and Baveye, P, "Effect of bacterial extracellular polymers on the saturated hydraulic conductivity of sand columns". *Appl. Environ. Microbiol.* 1992, 58(5):1690.

Vona, A, di Martino, F, Garcia-Ivars J., Pico, Y, Mendoza-Roca, J., Iborra_Clar, M, "Comparison of Different Removal Techniques for Selected Pharmaceuticals" Journal of Water Process Engineering 5(2015) 48-57

Westgate, E. J., et al., "Fate of Anthropogenic Nitrogen in a Nearshore Cape Cod Aquifer" Biol. Bull. 2000 199: 221-223