No Sweetener in Your Stormwater, but What About Your Reclaimed Water?

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Nitrogen and phosphorous loading into waterways from point and non-point sources is of increasing concern throughout the United States. The rise in nutrient levels resulting in waterbody impairment from designated beneficial uses frequently occurs in tandem with escalating urbanization. With impending numeric nutrient criteria regulations being proposed throughout the U.S., one beneficial resource from wastewater treatment facilities (WWTFs) is reclaimed water, which is now a potential target as a non-point source due to possible overspray and/or runoff. Knowledge of reclaimed effluent water quality is, therefore, of importance to regulators and stormwater professionals in order to understand its potential contribution of non-point source nutrient loading to waterways. Being able to single out reclaimed water from other sources—non-point and point alike—is becoming more and more important.

Effective control measures to minimize nutrient loading from point and non-point sources requires not only the advancement of treatment technologies, but also the development and validation of markers that can serve as tools in identifying nutrient loading sources that can be used, for example, to distinguish the wastewater and/or reclaimed water from stormwater. This information can then be used to establish appropriate regulations, reuse water treatment needs, loading rates, and best management practices.

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Background

Surface waters and shallow unconfined aquifers in urbanized regions are vulnerable to pollutants that can impair their beneficial uses. Pathogens, nitrogen, and phosphorous loading into waterways from municipal discharges/sewage, unspecified non-point source discharges, and urbanized runoff/stormwater, are all of increasing concern throughout Florida and the U.S. Urban water pollution originates from wastewater point source discharge of treated effluents, wastewater non-point source intrusions from septic tanks, misapplication of recycled wastewater used for irrigation, or urban runoff from mobilization of pollutants deposited to impervious surfaces through atmospheric deposition and human activities during small rain events, erosion from pervious surfaces during large storm events, and dry weather flows (Paul and Meyer, 2001).

Chemical indicators have been proposed as alternatives to microbial indicators as a more definitive means of identifying fecal contamination from human sources (Glassmeyer et al., 2005). Nitrogen input levels and oxic conditions are the major variables correlated with higher observed nitrate concentrations in groundwaters throughout the United States (Burow et al., 2010). Quantifying waterbody pollutant mass loads back to contributing sources within an urbanized watershed is complex and frequently depends upon modeling strategies that incorporate estimates and uncertainties about each source's flow and pollutant concentration levels (Nix, 1994; Oppenheimer et al., 2011). The mass loadings are further attenuated by specific fate and transport processes that are not adequately characterized, and therefore, to effectively mitigate impaired waterbodies, all of the major contributing factors and sources must be fully understood.

The rise in nutrient levels, leading to waterbody impairment from designated beneficial uses, frequently occurs in tandem with escalating urbanization. Excessive levels of nutrients can result in an increase in biomass of phytoplankton and macrophyte vegetation, reduced carbon available to food webs, increased blooms of gelatinous zooplankton, increased incidence of fish kills, reduced diversity of habitats, increased taste and odor problems and dissolved oxygen depletion (Smith and Schindler, 2009). From a human health perspective, bloom-forming algal species can produce deleterious public health effects due to toxins produced. Furthermore, the possibility of a direct correlation between eutrophication and human disease may be an issue (Bruno et al., 2003; Townsend, 2003).

Although nutrients (i.e., nitrogen and phosphorus) are essential to survival of aquatic organisms (Freeman et al., 2009; Bricker et al., 2007), excess nutrient loading to waterbodies can impact designated uses of water (FDEP 2009). The eutrophication (excessive plant growth) arising from nutrient enrichment represents one of the most significant water quality issues in surface waterbodies today.

Since the early 1990s, Florida has undertaken numerous studies to diagnose and control nutrients in the state. However, significant nitrogen and phosphorus pollution persists, which has been the result of hydrological modifications, intensive agricultural production, population growth, and associated urban and suburban development. In Florida, there are approximately 16,000 kilometers (km) or 9.942 mi of rivers and streams, 7,800 lakes and reservoirs, more than 700 springs, and four aquifers. Based on data from the Florida Department of Environmental Protection (FDEP), approximately 3,087 km (1,918 mi) of the state's flowing waters are impaired, which consists of 27 percent of the estuaries and coastal waters and 33 percent of the streams in the state. In addition, nearly 152,971 hectares (ha) or 378,000 acres constitutes 39 percent of the lakes in Florida and are classified as impaired waterbodies, according to the narrative criteria that has been set forth by the Impaired Water Rule.

After working with the state for a number of years to develop numeric criteria to limit this nutrient pollution, the U. S. Environmental Protection Agency (USEPA) was sued by Earth Justice on behalf of five environmental groups. The lawsuit argued that the USEPA had an obligation to promulgate the standards itself until the state acted, and that USEPA had previously determined that numeric nutrient criteria were necessary under the Federal Clean Water Act. As a result of this lawsuit, USEPA in early 2009 determined that numeric limits for both nitrogen and phosphorus were necessary to protect the state's waterbodies, whether issued by the state or USEPA.

The FDEP has developed numeric nutrient criteria and rule language, which received tentative approval by USEPA on Nov. 3, 2011, was adopted by the state's Environmental Regulatory Commission (ERC) on Dec. 8, 2011, and became law on Feb. 16, 2012. The state's proposed rules were challenged, and an administrative hearing was held where the administrative law judge issued a final order affirming the proposed rules in all respects. On June 13, 2012, the FDEP submitted the changes to Florida's water quality standards to USEPA for review and approval in accordance with Section 303(c) of the Clean Water Act. While many states have adopted some version of numeric nutrient criteria to parts of their waterbodies, Florida's numeric nutrient criteria rule would be the first one in the country that is applied on a statewide basis. The effective date for USEPA's approval of Florida's "Water Quality Standards for the State of Florida's Lakes and Flowing Waters: Final Rule," was extended from July 6, 2012, to Jan. 6, 2013.

Once approved by USEPA, the rule will be used as a part of the state's impaired waters assessment process. Florida's numeric nutrient criteria could likely result in greater regulatory costs in terms of its design, implementation,

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Table 1. Description of Wastewater Reclamation Facilities Surveyed

ID #	2007 Reuse Flow (MGD)	Treatment Process Description	County
1	7.95	Modified Ludzack-Ettinger activated sludge	Orange
2	3.35	Biological nutrient removal complete mix activated sludge system	Indian River
3	7.26	Conventional activated sludge	Palm Beach
4	12.28	5-stage Bardenpho™ activated sludge	Hillsborough
5	0.89	Modified Ludzack-Ettinger activated sludge	Duval
6	1.65	Oxidation ditch (extended aeration activated sludge) and denitrification filters	Lee
7	4.44	Oxidation ditch (extended aeration activated sludge)	Sarasota
8	7.70	Conventional activated sludge denitIR™	Lee

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and monitoring, as well as potentially having large impacts on agencies employing water reuse as a means of water resources management. Currently, there are 482 domestic WWTFs with permitted capacities at or above 0.1 million gallons per day (mgd) that make reclaimed water available for reuse. Data from FDEP's 2010 reuse inventory documented that approximately 659 mgd of reclaimed water was reused from WWTFs for beneficial uses within the state.

A survey of 50 selected WWTFs around the state was performed as part of this study to determine the concentration of both total nitrogen (TN) and total phosphorus (TP) in the reclaimed water that is produced from these facilities. This indicated that 40 percent of the sampled WWTFs had a TN concentration less than 5 milligrams per liter (mg/L), and 70 percent had a TN concentration less than 10 mg/L. The remaining 30 percent of the WWTFs that exhibited TN levels greater than 10mg/L were primarily from facilities that were either solely concerned with the carbonaceous biochemical oxygen (CBOD) removal or provided partial or complete nitrification and, as such, they contained much higher levels of ammonia and/or nitrates in their effluents. The majority of the WWTFs had total kjeldahl nitrogen (TKN) concentrations in their reclaimed water ranging from 1 to 6 mg/L and the median values were less than 2.5 mg/L, with the exception of one facility. Regarding TP concentrations in the reclaimed water, 40 percent of the sampled facilities were below 1 mg/L and 90 percent had levels below 5 mg/L.

Of the 50 WWTFs surveyed, eight were then shortlisted to achieve a representative range for the following factors:

- Effluent nutrient concentrations
- Treatment flow and reuse capacity
- Geographical location
- Treatment process train

Summarized in Table 1 are descriptions of the various wastewater treatment processes that are operated at each of the shortlisted WWTFs. The locations of these eight WWTFs are illustrated in Figure 1. The TN and TP concentrations of the 50 surveyed WWTFs are graphically presented in Figure 2, and as noted, the reclaimed water quality from the eight shortlisted WWTFs were generally consistent with the nutrient effluent levels observed from the 50 WWTFs that were surveyed.

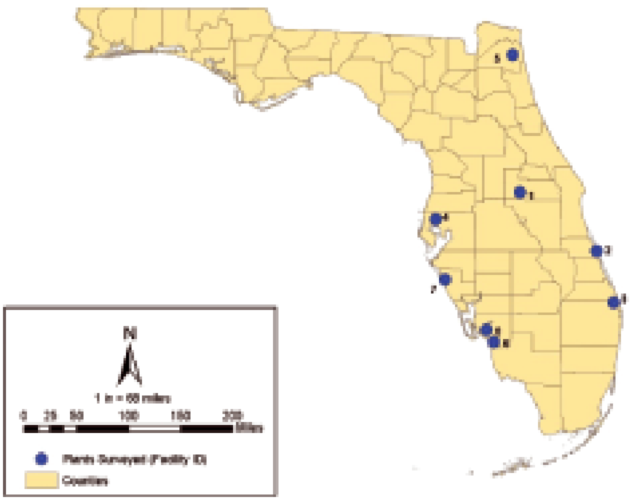

Figure 1. Location of Eight Surveyed Wastewater Treatment Facilities

Nutrient Markers and Tools Selection

Nutrient loadings to a waterbody need to be accurately traced back to application sources in order to establish best management practices that will meet established total maximum daily load (TMDL) requirements for impaired waterbodies. Establishing this relationship is complicated by several factors:

- Occurrence of multiple nutrient application sources within a watershed.
- Presence of non-point as well as point sources.
- Site-specific biogeochemical transport processes that alter nutrient concentrations from initial application concentrations.
- Poorly documented temporal variability in application rates.

In order to distinguish treated wastewater effluents from other nutrient sources (i.e., urban stormwater runoff), a wastewater specific marker must be identified. Many compounds have historically been utilized to determine sources of nutrients transported to

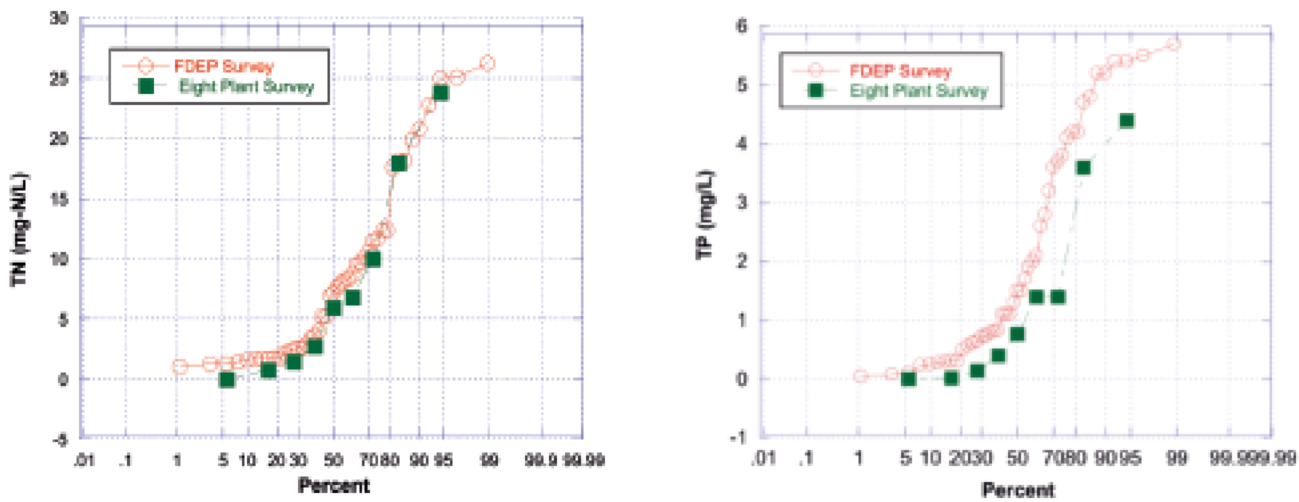

Figure 2. Comparison of Nutrient Loadings for FDEP Survey and Eight Wastewater Treatment Facilities Survey

receiving waters, including stable isotopes (i.e., nitrogen and oxygen) and inorganic ions (i.e., chloride and bromide). Traditional markers, such as stable isotope ratios (i.e., $\delta^{15}N$) and inorganic ions (i.e., chloride), often lack source specificity (Gasser et al., 2010; Katz et al., 2004). However, interpreting isotope ratio data in an impacted waterbody was difficult and stems from the biological fractionation that typically occurs during transport in the environment. Another factor that limited the use of isotope data included the ratio changes that occur for both isotopic and ionic compounds due to mixing of multiple sources in the receiving water. Therefore, the use of ratios needs to be supplemented with additional markers that are source specific, such that presence/absence criteria can be used to eliminate spurious conclusions regarding volumetric input from certain sources. For example, if an environmentally conservative marker specific to wastewater sources can be identified, and this marker remains analytically quantifiable for wastewater volumetric inputs of 1 percent or greater, then its absence in a receiving waterbody could likely eliminate wastewater as the primary cause of nutrient impairment. Furthermore, if the nutrient range of possible contributing wastewater sources is well characterized, then a conservative estimate of the maximum nutrient mass loading to the waterbody may possibly be derived from the volumetric loads estimated for the wastewater sources.

Moving from conservative nutrient estimates to actual nutrient estimates would then require identification of additional markers that could fulfill two purposes:

- The ability to discriminate between multiple wastewater sources (i.e., reclaimed water irrigation overspray, septic system intrusion, etc.) that could have an order-of-magnitude difference in their nutrient effluent concentrations.
- To aid in understanding the nutrient attenuation occurring during transport.

Conventional wastewater treatment methods do not remove many trace compounds that can be used as markers, which include pharmaceuticals, hormones, steroids, volatile organic compounds, and synthetics organic compounds. While a large number of these trace compounds could possibly be utilized to determine the influence of wastewater into receiving waterbodies, the transport and attenuation of these constituents in the environment can be affected by site-specific conditions; transport pathways; physical, chemical, and biological degradation during transport; and groundwater chemistry. Considering these factors, the U.S. Geological Survey (USGS) and USEPA scientists identified 35 compounds in wastewater from sewage treatment plants that had potential to be used as markers (USGS, 2009; Glassmeyer et al., 2005).

Reconnaissance surveys of surface waterbodies in the U.S. (Kumar and Xagoraraki, 2010) have suggested several anthropogenic organic compounds used as pharmaceuticals, personal care products, food products, pesticides, and hospital wastes as potential chemical markers of pollutant loading due to their behavior as persistent aqueous organic pollutants (Benotti et al., 2009; Bester, 2007; Buerge et al., 2009; Focazio et al., 2008; Glassmeyer et al., 2005; Guo and Krasner, 2009; Jjemba, 2008; Standley et al., 2008; Yamamota et al., 2009). However, recent research findings are increasingly showing that some of these compounds originating from anthropogenic activities behave nonconservatively, and therefore, cannot be considered as acceptable domestic wastewater markers since they are detected in multiple water sources.

Summarized in Table 2 are the reported detection frequencies (DF) of candidate anthropogenic organic compounds and their characteristics to serve as a wastewater marker due to occurrence in treated wastewater effluents and resistance to secondary wastewater

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Table 2. Reported Detection Frequencies of Organic Chemicals in Wastewater Effluents, Percent Removals Through an Activated Sludge Process (Oppenheimer et al., 2011; Dickenson et al., 2010; and USEPA, 2010)

Compound (Usage)	Average DF (percent)[a]	Percent Removal via Activated Sludge[b]
Acetaminophen (anti-inflammatory)	Low[a]	97 (n = 4)
Atenolol (beta blocker)	Low[a]	61 (n = 4)
Atrazine (pesticide)	Low[a]	No data
Benxophenone (fragrance)	100	84 (n = 6)
Bisphenol-A (plasticizer)	Low[a]	78 (n = 41)
Caffeine (stimulant)	81	94 (n = 7)
1,7-dimethylxanthine (caffeine metabolite)	Not on List	77 (n = 1)
Carbamazepine (mood stabilizer)	88	22 (n = 5)
Codeine (cough suppressant)	84	29 (n = 1)
Coprostanol (sterol)	Low[a]	97 (n = 1)
Cholesterol (sterol)	Low[a]	85 (n = 1)
Cotinine (nicotine metabolite)	Low[a]	No data
N,N-diethyl-meta-toluamide (DEET) (insect repellant)	89	54 (n = 7)
Diclofenac (anti-inflammatory)	75	44 (n = 23)
Dehydronifedipine (antihistamine)	91	No data
Estrone (hormone)	Low[a]	77 (n = 46)
Galaxolide (HHCB) (fragrance)	100	56 (n = 25)
Gemfibrozil (anti-cholesterol)	92	77 (n = 13)
Ibuprofen (anti-inflammatory)	78	90 (n = 32)
Meprobamate (muscle relaxant)	83	No data
Naproxen (anti-inflammatory)	92	85 (n = 18)
4-nonylpheno (detergent)	100	78 (n = 10)
Phenytoin (dilantin) (seizure control)	100	44 (n = 1)
Primidone (mood stabilizer)	100	No data
Sulfamethoxazole (antibiotic)	94	58 (n = 15)
Tonalide (AHTN) fragrance)	100	67 (n = 20)
Triclosan (anti-microbial)	98	60 (n = 10)
Trimethoprim (anti-bacterial)	86	No data
Tris(2-chloroethyl)phosphate (flame retardant)	Low[a]	27 (n = 27)
Tris(dichloropropyl)phosphate (flame retardant)	100	No data

Note: [a] <5 x limit of quantitation (LOQ)

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treatment process operations (Oppenheimer et al., 2011). Notably absent from the short list for most studies performed in the U.S. are artificial sugar substitutes (i.e., acesulfame, cyclamate, saccharin, and sucralose), which have been included in several reconnaissance surveys conducted in Europe (Scheurer et al., 2011, 2010, 2009; Buerge et al., 2009; Brorstrom-Lunden et al., 2008; Loos et al., 2009). Cyclamate and saccharin are unsuitable as markers because of high levels of reduction through biological treatment processes (>90 percent) and cyclamate has been banned for distribution in the United States since 1970. Acesulfame and sucralose degradation through WWTFs has also been demonstrated to be minimal for measurements through full-scale facilities and laboratory-scale aerobic biodegradation reactors (Torres et al., 2011; Buerge et al., 2009; Scheurer et al., 2009, 2010; and Neset et al., 2010).

A series of samples were taken from the effluents from a number of WWTFs throughout the U.S., as well as a number of waterbodies to which these facilities discharge, in addition to a number of waterbodies with no known wastewater effluents discharges. The compounds that were detected in the wastewater effluents and two categories of source waters are presented in Table 3; only compounds that were detected in at least 35 percent of the sources with known wastewater discharges are presented in this table.

Good markers of wastewater source loading should exhibit a high ratio of mean concentration to the method reporting limit, with 100 percent detection in the wastewater effluents. Another key factor with the development of a marker is the low variability, or relative standard deviation (percent rsd), which demonstrates a compound's potential to serve as an indicator of the extent of wastewater impact (i.e., a correlation between concentration in the receiving stream and the fraction of stream flow due to upstream wastewater discharges) provided that the compound is stable in the environment during transport (Oppenheimer et al., 2011). Finally, to function as an indicator of wastewater input in the environment, a compound should also demonstrate a high detection frequency in sources with known wastewater discharges (meaning no false negatives), as well as absence from sources without known wastewater discharge influence, meaning no false positives (Gasser et al., 2010).

Of the compounds exhibiting 100 percent detection in wastewater effluents, the best performing compounds in terms of ratio of mean concentration to maximum residue limit (MRL) and lack of false positives were sucralose, meprobamate, and carbamazepine. More importantly, the low relative, low standard deviation of both sucralose and carbamazepine indicates their potential to serve as quantitative markers for wastewaters, provided their environmental stability is adequately demonstrated. Of the dataset presented in Table 3, only sucralose demonstrated no false positives or false negatives. In this case, a false positive demonstrates the lack of source specificity, and a false negative demonstrates the lack of adequate sensitivity. A number of compounds exhibited false negatives, (i.e., amoxicillin, carbamazepine, caffeine cotinine, gemfibrozil, meprobamate, primidone, and sulfamethoxazole), whereas, diuron, simazine, diethyl-meta-toluamide (DEET), iohexal, and atenolol exhibited false positives as well as false negatives.

The efficacy of sucralose as a marker of conventional biologically treated wastewater is further documented in Figure 3, which illustrates the stable sustained presence of sucralose in wastewater effluents from the eight

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Table 3. Compounds Detected in Wastewater Effluents and Source Waters With and Without Wastewater Discharges (Oppenheimer et al., 2011)

Compound (MRL, ng/L)	Wastewater (WW) Effluent				Sources with WW Discharges			Sources without WW Discharges		
	Mean (ng/L)	rsd (percent)	Detects (percent)	n	Detects (percent)	n	Detects Range (ng/L)	Detects (percent)	n	Detects Range (ng/L)
Sucralose (100)	27,000	30	100	16	100	11	120 – 10,000	100	15	
Diuron (5)	99	78	100	12	82	11	7.5 – 940	80	15	5.3 – 6.7
Simazine (5)	21	100	100	12	73	11	24 – 160	20	15	7.1 – 61
DEET (5)	269	135	100	12	73	11	2.5 – 67	13	15	2.2 – 7.1
Meprobamate (5)	323	197	100	12	70	10	5.5 – 160	100	15	
Caffeine (10)	1127	159	75	12	64	11	13 – 300	100	15	
Diamiinochlorotriazine (5)	36	209	87	12	64	11	13 – 300	40	15	10 – 100
TCEP (5)	547	66	92	12	60	10	7.9 – 66	47	15	13 – 67
Bromacil (5)	95	100	50	12	55	11	6 – 270	93	15	290
Sulfamethoxazole (10)	907	116	80	10	55	11	17 – 990	100	15	
Pprimidone (5)	159	49	100	12	50	8	20 – 54	100	15	
2,4-D (5)	248	262	83	12	45	9	11 – 23	60	15	7.4 – 21
Amoxicillin (20)	1,230	92	71	7	45	11	25 – 2,200	100	14	
Iohexal (10)	4,780	120	100	16	45	11	73 – 960	87	15	16 – 39
Atenolol (5)	1,310	1,070	100	16	45	7	6.1 – 200	92	13	19
Carisoprodol (5)	119	156	92	12	40	10	5.4 – 43	100	15	
Gemfibrozil (5)	360	131	83	12	40	10	13 – 130	100	15	
Carbamezapine (5)	416	21	100	16	36	11	31 – 190	100	15	
1,7-dimethylxanthine (5)	98	160	75	12	36	11	8.9 – 23	100	13	
Cotinine (10)	29	86	100	8	36	11	13 – 27	100	15	
Dehydronifedipine (5)	119	94	92	12	36	11	12 – 270	87	15	7.7 – 70
Lopressor (20)	3,900	149	67	12	36	11	22 - 270	100	13	
Theobromine (5)	151	158	42	12	36	11	6.4 - 41	67	15	7.8 – 25

Figure 3. Sucralose Concentration in Wastewater Effluents from WWTFs with Varying Levels of Nitrification and Denitrification

(A) = oxidation ditch with methanol feed to denitrification filter;

(B) Bardenpho™ with dual media deep bed filters;

(C) conventional activated sludge with carousel aeration and denitrification basin;

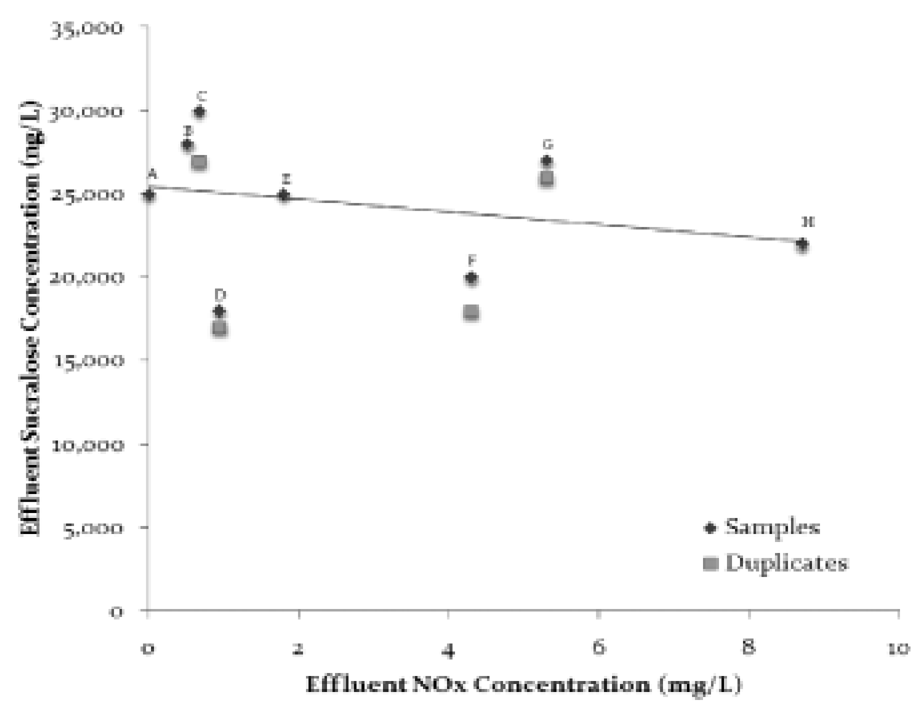
(D) complete mix activated sludge with biological nutrient removal;

(E) activated sludge with fine bubble diffused air and filtration;

(F) modified Ludzack-Ettinger activated sludge;

(G) complete mix activated sludge with anoxic basin; and

(H) oxidation ditch. Duplicates are a second sample bottle collected from the same site.



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shortlisted WWTFs. The treatment methods used at these facilities ranged from conventional to advanced treatment (biological nutrient removal with deep bed filters), and were previously described in Table 1. Although none of these facilities incorporated membranes (i.e., ultrafiltration, microfiltration), a pilot study reported to the New Mexico Environment Department showed higher average sucralose concentrations of 42,400 ng/L in MBR effluent (Lee et al., 2010). This report also showed sucralose removal of approximately 40 percent if treated with ozone and a biologically active filter, and approximately 99 percent for reverse osmosis (RO) with trace levels detectable in the RO effluent. This indicates that sucralose is probably not appropriate as an indicator of wastewater that has gone through more advanced treatment processes.

Using the datasets that were collected and reviewed, a list of potential markers was developed, and through a parsing process, a short list was established. Some of the more salient markers included as part of this study were:

- Atenolol (a beta blocker)
- Carbamazepine (a mood stabilizer)
- Dalapon (an organochlorine herbicide and plant growth regulator)
- Gadolinium anomaly (a contrast media used in magnetic resonance imaging)
- Galaxolide and Tonalide (a polycyclic musk fragrance)
- Iohexol (a contrast media used in hospital diagnostics)
- Sucralose (an artificial sweetener)

While a number of other compounds were suggested as possible markers for use in this study, the above compounds were selected based on the findings from the study's initial literature review, the existing database, and analytical logistics. These seven compounds, in addition to stable isotope ratios of nitrogen, oxygen, and carbon, and additional inorganic compounds such as boron, strontium, and uranium, were sampled and analyzed from the following sources:

- Reuse effluents
- Septic tank effluents
- Retention pond stormwater
- Rainfall
- Regional fertilizer
- Reuse water augmented with fertilizer (fertigation)
- Groundwater used for irrigation.

Presented in Table 4 are the mean and relative standard deviations for each marker in each matrix. Of these samples, the results demonstrated high levels of sucralose in the wastewater sources and its absence in the four sources without wastewater. Sucralose concentrations were much more consistent in reuse water than septic systems, which is likely due to the difference in population size utilizing these treatment systems (WateReuse, 2012). Carbamazepine, atenolol, iohexol, and gadolinium anomaly were significantly higher in reuse water, with concentrations in septic systems only slightly elevated above quantifiable levels observed in the sources without wastewater. While the results were promising, the sample sizes were limited and it is recommended that further study is needed to validate the observations and conclusions made.

Table 4. Mean and Relative Standard Deviation of Markers from Various Sources

Compound	Concentration (ng/L)						
	Reuse Water	Septic Tanks	Stormwater (no reuse)	Rainfall	Regional Fertilizer	Reuse (Fertigation)	Groundwater
Sucralose	29,000 ± 6,000	40,000 ± 23,100	<120	<100	<100	14,000	<100
Carbamazepine	230 ± 8	11.8	<5	<5	<5	160	<5
Atenolol	1,270 ± 882	4.3	<6.2	<5	36	290	<5
Iohexol	5,440 ± 3,540	5.4	<10	<10	<10	<10	<10
Galaxolide	1,020 ± 288	2,691 ± 2,710	<50	<50	<50	3,800	<50
Gadolinium Anomaly	30 ± 4	1.5 ± 1.3	1.2 ± 0.6	1.1	6	68	2

Bench-Scale Tests

The environmental stability of these markers, with the exception of galaxolide, was also evaluated through bench-scale studies designed to mimic biodegradation, adsorption, and photolysis reactions in the environment. Bench-scale experiments were performed in order to simulate the fate and transport properties of the short-listed markers via adsorption, biodegradation, and photolysis. Illustrated in Figure 4 are the bench-scale apparatuses used in this study, and Table 5 summarizes the relative susceptibility of these markers to environmental transformation from biodegradation, adsorption, and photolysis under the conditions studied.

The results from the bench-scale studies demonstrated:

- The recalcitrance of sucralose in the environment and its suitability as a conservative

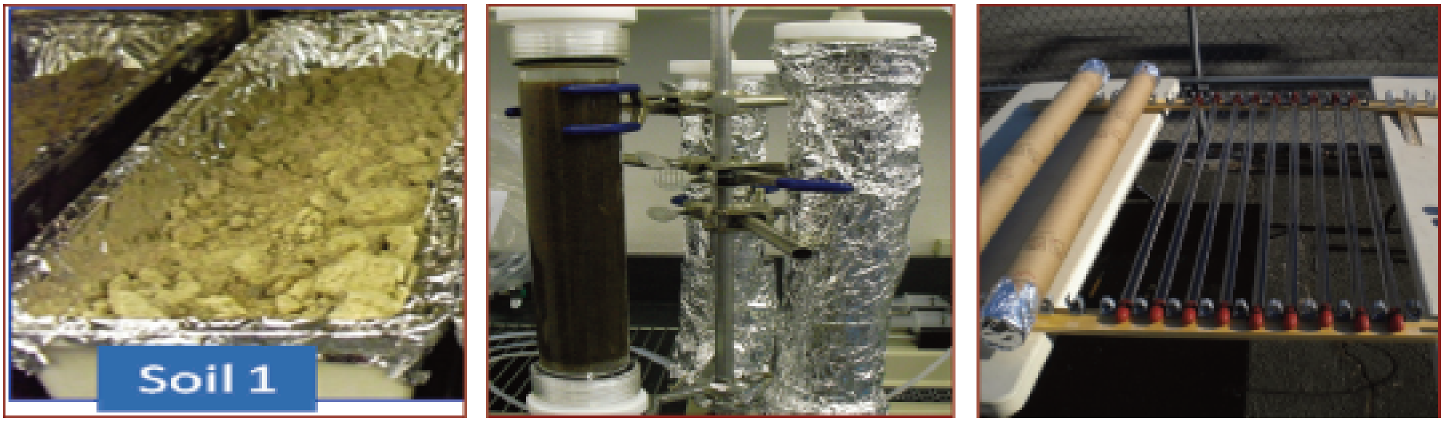

Figure 4. Bench-Scale Test Apparatuses for Adsorption, Biodegradation, and Photodegradation

marker of wastewater effluents and reclaimed water.

- Iohexol appeared to be too susceptible to photolysis and atenolol was too susceptible to biodegradation to be adequate markers, especially considering the high variability of their concentrations in reclaimed water.
- Gadolinium anomaly appeared to be fairly stable in the environment, although its lower concentrations in reclaimed water and wastewater effluents can potentially restrict the level of dilution that can be tolerated before this marker falls below background levels.
- Carbamazepine was another good marker of an influence from wastewater effluent and reclaimed water and, for the most part, it occurred in a fairly consistent ratio to sucralose. However, its susceptibility to photolysis could obscure this ratio in receiving waters that are shallow.
- The decrease in nitrate levels appeared to occur only through biodegradation, while phosphorous was impacted primarily from adsorption to soils, and to an extent, from biodegradation.

Field Studies

The eight WWTFs that were representative of the nutrient effluent levels observed for the 50 WWTFs in the FDEP survey were sampled for the shortlisted group of markers, and the results indicated that:

- The levels of sucralose consistently ranged from 17,000 to 30,000 nanograms per liter (ng/L). This is approximately two to 30 times higher than the levels reported in European studies where consumption rates and historical product availability are lower than the U.S. (Scheurer et al., 2009; Buerge et al., 2009; Minten et al., 2011), but approximately 20 percent of the levels were reported in a wastewater effluent in North Carolina.
- Coprostonol, galaxolide, and dalapon were also detected, but at lower levels (300 to 5,400 ng/L). Coprostonol was eliminated from subsequent samples, due to analytical difficulties, and dalapon was eliminated due to frequent nondetects in the wastewater effluent samples. Galaxolide levels were in the ballpark of previously reported values (Dickenson et al., 2009).
- The gadolinium anamolies were 20 to 100 times higher than naturally occurring rare earth elements in all samples, and the normalized concentrations ranged from 27 to 139 ng/L. This is similar to the levels of 68 to 140 reported in wastewater effluents in Colorado communities, with one or more magnetic resonance imaging (MRI) facilities (Verplanck et al., 2005).
- Uranium and strontium were included to determine background levels in Florida reclaimed water effluents because these compounds might serve as possible markers of fertilizer. Boron may have value as a marker based on its stable isotope ratios. For this study, the decision was made to focus stable isotope analysis on nitrogen, oxygen, and carbon, and to only gather total boron values from the different sources.

The concentrations of the markers relative to nutrient levels were compared as part of this study to determine if there was a correlation between the markers studied and nutrients in the wastewater effluents. The comparison suggests that there was no apparent visual association between the nutrient levels in the plant effluents and the marker levels. In other words, levels of markers were present in most of the plants surveyed and concentrations were not dependent on the level of biological nutrient removal observed in a WWTF. This lack of association is expected, since wastewater treatment processes do not specifically target removal of trace organic compounds. While there is little literature directly correlating wastewater effluent concentrations of nutrients and trace organics, several published studies have looked at the standard deviation of discrete trace organic compounds for a set of samples collected from different WWTFs (Dickenson, 2009), as well as diurnal variability at a single facility (Nelson et al., 2010).

Positive and negative control studies were performed to evaluate the presence of markers in the waterways at four different locations in the state in order to understand the bound-

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Table 5. Relative Susceptibility of Selected Markers to Adsorption, Biodegradation, and Photolysis

Compound	Adsorption Loss	Biodegradation	Photolysis Degradation
Sucralose	<10 percent	<10 percent	<10 percent
Carbamazepine	<10 percent	<10 percent	50 percent
Atenolol	0 – 25 percent	80 – 90 percent	35 percent
Iohexol	<10 percent	30 percent	90 percent
Gadolinium Anomaly	0 – 30 percent	<30 percent	5 percent
T-P	25 – 75 percent	30 percent	0 percent
NO_3	5 percent	100 percent	0 percent

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ary conditions under which a marker could assist in discerning the volumetric load contribution from wastewater sources. The four sites that were studied are illustrated in Figure 5. The overreaching goal of these field studies were to:

- Assess marker and nutrient differences at sites irrigating with only reclaimed water, compared to sites irrigating with groundwater.
- Assess capability to distinguish reuse from stormwater and septic.

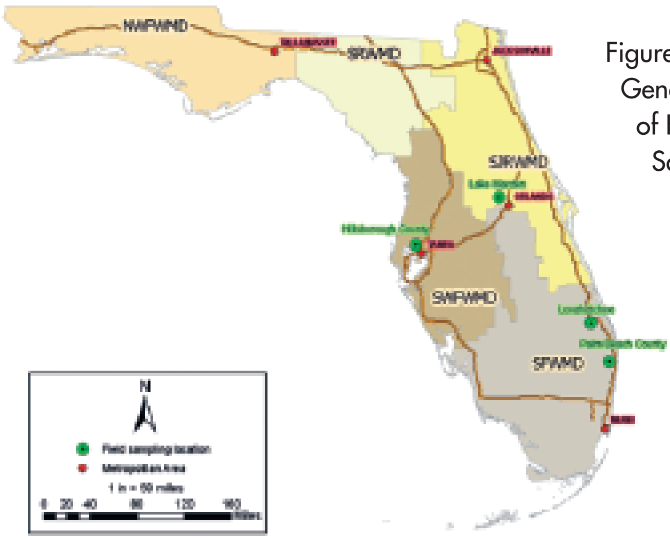

Figure 5. General Location of Field Sampling Events

Table 6. Lake Marden Field Sampling Results

Compound	Sample Location		
	Center of Lake Surface	Center of Lake Mid-depth	Opposite Outfall
Atenolol, ng/L	<PQL	<PQL	<PQL
Carbamazepine, ng/L	140	170	<PQL
Iohexal, ng/L	1,800	1,500	1,700
Sucralose, ng/L	13,000	14,000	14,000
Galaxolide, ng/L	<PQL	<PQL	<PQL
Gadolinium Anomaly, ng/L	14	14	14

Table 7. Palm Beach County Field Sampling Results

Compound	Sampling Location and Concentration (ng/L)				
	Rainwater	Golf Course A		Golf Course B	
		Irrigation Water (from pond)	Stormwater Runoff	Reuse Water and Fertigation	Stormwater Runoff
Atenolol	<PQL	<PQL	<PQL	290	<PQL
Carbamazepine	<PQL	<PQL	<PQL	160	33
Iohexal	<PQL	<PQL	<PQL	<PQL	<PQL
Sucralose	<PQL	<PQL	<PQL	14,000	1,100
Galaxolide	<PQL	<PQL	<PQL	3,800	<PQL
Gadolinium Anomaly	1.1	2	3.5	68	29

The four sites that were studied are:

- *Lake Marden* – The objective of this sampling event was to determine if selected markers could be detected in a waterbody that received only reclaimed water. The site receives reclaimed water from the Orange County Northwest Water Reclamation Facility (NWRF) previously treated through a constructed wetland treatment system. Lake Marden is used by NWRF to increase recharge to the underlying aquifer system and has no known influence from septic discharge and stormwater.
- *Palm Beach County* – The runoff from two Palm Beach County golf courses was sampled. One golf course is irrigated with groundwater (course A) and the other (course B) with reclaimed water amended with liquid fertilizer (i.e., fertigation). The purpose of this sampling event was to provide a comparison on the levels of markers and nutrients in stormwater runoff in areas irrigated in a fairly controlled matter with (i) groundwater and (ii) reclaimed water.
- *Hillsborough County* – The purpose of this sampling event was to evaluate the level of markers and nutrients in ponds receiving reclaimed irrigation water containing low levels of nutrients applied in a less controlled manner. The samples were taken before the start of the wet season when reclaimed water usage was expected to be at its highest. The sampled ponds are never directly filled with reclaimed water and only receive water from rainfall and stormwater runoff.
- *Loxahatchee River District* – Field sampling was performed in North Palm Beach County within the Loxahatchee River District to assess the effects of septic systems and presence of markers in surface waterways.

At the Lake Marden site, concentrations of carbamazepine, iohexol, gadolinium anomaly, and sucralose were detected during the sampling event, as presented in Table 6. The data from this sampling event clearly shows that these markers could be detected in a water environment where a known input of reuse water is ascertained. In comparison, atenolol and galaxolide were below their practical quantification limits (PQLs), suggesting their limited applicability as conservative reuse water markers. These results are consistent with those from the bench-scale work that was conducted.

For the two golf courses that were studied in Palm Beach County, course A utilized groundwater solely for irrigation purposes. The concentrations of the selected markers in the irrigation water and stormwater runoff were below the PQL, which was expected since reclaimed water was not used for irrigating the golf course and there are no septic systems in the vicinity. The data show that these markers are not present when there is no influence from reclaimed water or septic systems.

Sucralose, carbamazepine, and the gadolinium anomaly were measured at course B in the stormwater runoff at 1.1 ng/L, 29 ng/L, and 33 ng/L, respectively. The levels of atenolol and galaxolide were nondetectable in the stormwater runoff, suggesting their limited applicability as conservative markers. This observation is consistent with the results from Lake Marden. Iohexol was also below detectable limits in the reclaimed water used for irrigation and stormwater runoff. These results provide additional evidence that sucralose, carbamazepine, and gadolinium anomaly could be employed as conservative markers for wastewater, including reclaimed water. The results of the sampling at the two golf courses are presented in Table 7.

Table 8 presents the results from the Hillsborough County sampling. Sucralose, carbamazepine, gadolinium anomaly, and atenolol were detected at all the sampling sites. However, sucralose had the highest concentration to PQL ratio, ranging from 33 to 55. In comparison, the ratios for the other potential markers ranged from 2 to 6. These results emphasize the utility of sucralose as a conservative marker for waterbodies impacted by reclaimed water, even when nutrient concentrations may be very low.

For the Loxahatchee River District field studies, samples were collected from 29 sampling locations to assess the concentration for sucralose and gadolinium anomaly in the dry and wet weather seasons, respectively. In addition, two reference points, located in nonurbanized areas, were also taken as a background. The sampling results indicate the potential of sucralose to serve as a reliable marker of septic tank effluents during both dry and wet seasons. The quantifiable levels of sucralose found in the waterbodies ranged from 0.120 to 0.750 ng/L. It is also important to note that detectable levels of sucralose

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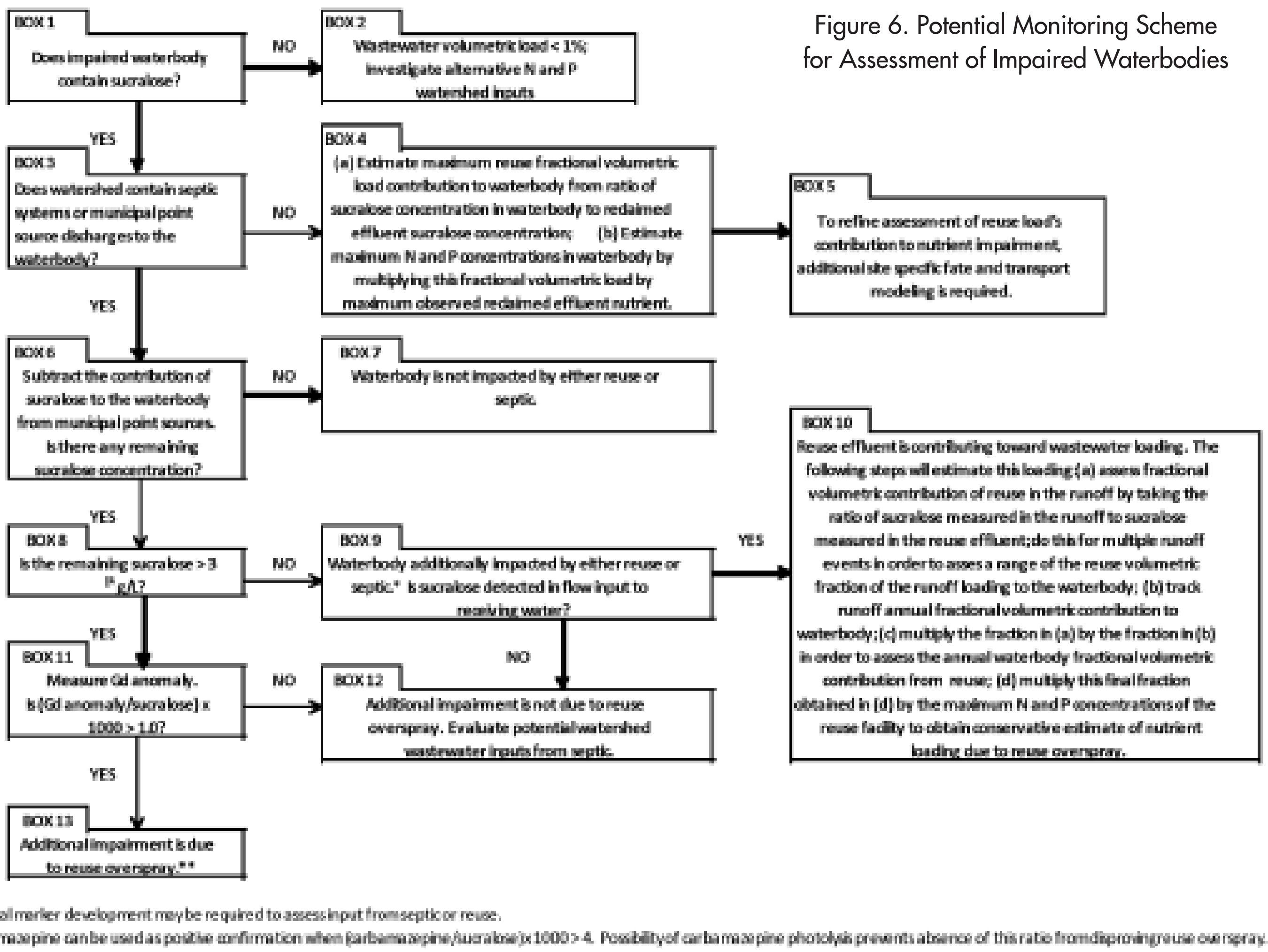
Table 8. Hillsborough County Field Sampling Results

Compound	Sample Location		
	Woodberry System	Calusa System	VanDyke System
Atenolol, ng/L	29	21	14
Carbamazepine, ng/L	5.3	7.8	5,3
Iohexal, ng/L	<PQL	28	<PQL
Sucralose, ng/L	3,300	4,400	5,500
Galaxolide, ng/L	<PQL	<PQL	<PQL
Gadolinium Anomaly, ng/L	2	4	3

Figure 6. Potential Monitoring Scheme for Assessment of Impaired Waterbodies



*Additional marker development may be required to assess input from septic or reuse.

** Carbamazepine can be used as positive confirmation when (carbamazepine/sucralose) x 1000 > 4. Possibility of carbamazepine photolysis prevents absence of this ratio from disproving reuse overspray.

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(levels below the PQL, but still above the MDL) occurred in every sample location, except for the two reference locations. Although there were two sites that showed higher levels of nitrogen concentrations above the reference concentration of 1.5 mg/L with no levels of sucralose above the PQL (false negatives), and one site showed TN concentrations below the reference concentration with detectable sucralose (false positives), there were 25 sites that support the hypothesis that sucralose detection indicates nitrogen levels above reference concentrations.

The findings of the study demonstrated that the percentage of wastewater in a nutrient impaired waterbody can be determined by measuring the sucralose concentration of that waterbody. Knowledge of the reuse water quality and incorporation of regional evapotranspiration and rainfall data can be used to translate this percentage to a conservative volumetric loading rate. The schematic presented in Figure 6 provides the logic for assessing whether an impaired waterbody is impacted by wastewater and/or reclaimed water, or septic system effluents. If in fact the waterbody is impacted, it provides a monitoring approach to determine the relative contributions of point source discharges, applied reuse water runoff, or septic system intrusion. Further information regarding how this schematic can be used is described in the final report titled, "Evaluation of Potential Nutrient Impacts Related to Florida's Water Reuse Program," from the WateReuse Research Foundation (November 2012). The areas that still need to be addressed are the ability to relate the wastewater volumetric load to a corresponding nutrient load based on environmental fate and transport assessment, and further marker development to differentiate the reclaimed water from septic tank effluent and/or failing systems.

Summary

This study provides an alternative methodology for distinguishing between sources of nutrients found in waterbodies through the use of selected organic and inorganic microconstituents. While the development of the proposed tool described herein was performed in Florida, the final product is useful to other parts of the country due to the ubiquitous presence of the markers incorporated within the assessment and data analysis scheme. Although it is recommended that a greater data set needs to be developed to refine the ratios and marker concentration decision point levels employed in the tool further, a full validation study of the final tool is also still required.

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