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Testing the Effectiveness of Pollution Control Measures at the South Dade Landfill : The Reduction of Un-ionized Ammonia in Landfill Leachate

By

Matt Mitchell

Submitted to the Faculty of Nova Southeastern University Oceanographic Center in partial fulfillment of the requirements for the degree of Master of Science with specialty in:

Marine Biology/Coastal Zone Management

Nova Southeastern University April 2006

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Nova Southeastern University 2006

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Abstract

The purpose of this research was to evaluate the overall effectiveness of the pollution control measures in place at the South Dade Landfill, located in Miami, Florida. Pollution control measures in place at the landfill include the lining and capping of landfill cells, a landfill wetland retention basin and a groundwater remediation interceptor trench (GWRIT). This study was performed over a ten (10) month span beginning in October, 2002 and ending in July, 2003. This study dealt specifically with the effectiveness of the GWRIT and landfill wetlands in reducing the amount of un-ionized ammonia (NH₃) in the landfill leachate. Through the analysis of surface water and groundwater surrounding the landfill, it was concluded that the pollution control measures reduced levels of un-ionized ammonia by 98% of the concentration of NH₃ found in the landfill's leachate.

Introduction

In coastal marine environments, the un-ionized form of ammonia (NH₃) can be an extremely harmful pollutant. Most ammonia that is produced in the United States is incorporated into fertilizers, ammonium salts and certain household products. Ammonia is also a product of the breakdown of urea and protein; therefore it is a part of most forms of domestic wastewater (Figure 1). Ammonia is present in various concentrations in many surface and groundwater supplies. Any spike in the ammonia concentration in surface or groundwater is often a chemical indicator of pollution.



Figure 1. The Nitrogen Cycle

Ammonia is an inorganic form of nitrogen. It is also the least stable form of nitrogen in water. Ammonia exists in two principal forms, ionized and un-ionized. Ionized ammonia refers to ammonium (NH_4^+) , it is also known as dissociated or dissolved ammonia. An ammonium ion (NH_4^+) has a positive charge. Conversely, Un-ionized ammonia (NH₃), has no charge. Un-ionized ammonia is the most toxic form of

ammonia. The term total ammonia, or TAN (total ammonia nitrogen), refers to the sum of ammonium and unionized ammonia.

In the water column, the equilibrium between ammonia (NH_3) , and ammonium (NH_4^+) , is controlled by temperature and pH. The dominant form of ammonia present depends on these two parameters. The reaction between ammonia and ammonium is shown by the equation below:

Equation 1. $NH_3 + H_20 \leftrightarrow NH_4^+ + OH^-$

When it comes in contact with water, ammonia (NH₃) dissociates into ammonium hydroxide. Ammonium hydroxide (NH₄OH) is a combination of NH₄⁺ (ammonium) ions and ⁻OH (hydroxyl) ions. At normal pH levels around 7, this dissociation of ammonia doesn't pose a problem. As pH levels rise, the increase in hydroxyl ion concentration pushes the "equilibrium" of the equation more to the left, and more un-ionized ammonia is formed. As pH rises above normal levels, the un-ionized ammonia can cross cell membranes more easily in which case the ammonium hydroxide becomes toxic to both plants and animals.

Un-ionized ammonia (NH₃) is the principal form of toxic ammonia. Other nitrogen compounds, such as ammonium (NH₄⁺), are not toxic to marine and/or freshwater organisms. The exact toxicity of un-ionized ammonia varies. Toxicity levels are affected by environmental factors such as dissolved oxygen, temperature and pH. The toxicity of un-ionized ammonia is, however, more dependent on pH levels than temperature. In brackish and saline waters, the toxicity of un-ionized ammonia increases as temperature and pH decrease. As salinity increases, pH increases as well. Ammonia is extremely soluble in water at low pH. Freshwater systems such as lakes and rivers usually have low pH levels. One volume of freshwater will dissolve nearly 1,300 volumes of un-ionized

ammonia (Five Mile Action Committee, 2003). Additional formation of un-ionized ammonia is also more easily accomplished at higher pH levels. There are usually higher levels of un-ionized ammonia in saline waters with higher pH levels. At lower pH levels, lower concentrations of NH₃ ammonia may be just as toxic as higher concentrations of NH₃ at higher pH levels. At lower temperatures and pH levels, such as in freshwater systems, the ammonia and freshwater combine readily to form ammonium and hydroxide ions (Five Mile Action Committee, 2003). In freshwater systems, the effect of pH on the toxicity of ammonia is usually described in terms of "joint-toxicity." This combined toxicity includes both un-ionized ammonia as well as ammonium ions. In estuarine and brackish waters, typically with higher temperatures and pH levels, the breakdown of ammonia to ammonium and hydroxide ions doesn't occur as easily. This makes high levels of NH₃ especially toxic to marine organisms. Marine and freshwater plants are more tolerant of ammonia than animals and fish. Unlike fish, invertebrates are less sensitive to ammonia levels as temperatures decrease. Excess ammonia can accumulate in the tissues of a marine organism and cause harm. Negative affects on marine organisms include a loss of equilibrium, increased heart rate and increased oxygen uptake. Most studies that have been performed on fish document that gill damage can occur at NH₃ levels as low as 0.05 mg/L. High levels of un-ionized ammonia, most often between 1.5 and 2.0 mg/L are lethal. In most fish, elevated levels of NH₃ decrease the hatching success and growth rates of juveniles. Other studies have shown similar results in invertebrates such as sea urchins and shrimp. More recent studies have demonstrated that either toxicity from the ionized form is greater than expected or that toxicity results from an interaction between other parameters (e.g. pH) and the un-ionized form (Greenstein et al. 1994).

For pollution control, many organizations propose different limits on ammonia concentrations for discharge into the environment. Freshwater limits are generally higher than marine limits. For freshwater organisms, ammonia toxicity has been reported anywhere from 0.53 to 22.8 mg/l during 48 and/or 96 hour exposure tests. For marine organisms, as toxicity levels are lower, the criterion for concentrations in wastewater discharge are more stringent and are set for either continuous exposure to ammonia or for maximum acceptable concentrations.

The standard for un-ionized ammonia set by the Miami-Dade County Department of Environmental Resource Management (DERM) is 0.5 mg/l. This is the desired limit set in order to protect marine organisms. This criterion is based on limits set by the US Environmental Protection Agency (EPA). The generally accepted "no-remediation" limit for ammonia ($NH_3 + NH_4^+$) in groundwater is 2.8 mg/l in Miami-Dade County. Any levels higher than 2.8 mg/l require that some form of remediation must be done in order to decrease the levels of ammonia.

The DERM standard set for ammonia in surface water is 0.02 mg/L. This limit, however, is set for freshwater, as there is no state (FDEP) or DERM numerical standard for ammonia in saline and/or brackish waters. A DERM narrative exists for a standard for "the waters of Biscayne Bay." This narrative is referred to as the "Non-Degradation" standard, but has no set numerical standard. The EPA limits from which the Miami-Dade limits (groundwater and surface water) originated from are considered reasonable. An EPA NH₃ surface water limit of 0.035 mg/L was established in 1989 for brackish and marine systems. The EPA limits, specifically the surface water limit for marine systems, are designed to protect only 95% of the species tested and a caveat is usually included which notes that some local sensitive species may not be adequately protected (Nordin

1990). This limit, however, has not been strictly adhered to, as sufficient data supporting the limit does not exist.

The proximity of the South Dade landfill and Old South Dade landfill to Biscayne Bay (Figures 2 & 2A) makes it a possible polluter of the marine environment. In the past 100 years, Biscayne Bay has been drastically affected by urban development. The channelization of sheet flow and construction of levees that impaired the health and functionality of the Everglades had negative effects on Biscayne Bay. In addition to changes in the flow and timing of freshwater discharge into Biscayne Bay, the overall quality of the freshwater input has been dramatically reduced. Agriculture, landfills and other sources have caused dramatic increases in nutrient loading into the bay. The nearshore aquatic environment has displayed symptoms of both a decrease in primary productivity and an offshore migration of desirable benthic communities (Meeder et al. 1997). This has greatly reduced the estuarine zone of Biscayne Bay (Alleman et al. 1995). Drastic measures have been made in order to prevent further pollution. Previous studies have shown that the different measures, both active and passive engineering controls, have been effective thus far. The purpose of this was to further evaluate the effectiveness of measures designed to prevent or limit significant amounts of un-ionized ammonia (and other related pollutants) from entering the environment surrounding the South Dade Landfill.









The South Dade Landfill began receiving solid waste in 1979. The first two cells were constructed with a natural marl-bottom liner for the control of leachate. This liner met compliance control standards at the time of construction and use. The original two cells were covered and closed in 1997. Each subsequent cell has been constructed using either a single or double bottom liner (Camp, Dresser & McKee, 2001). The site is currently using its fourth cell.

In the mid-1980's, studies began to show elevated levels of ammonia in the groundwater surrounding the landfill sites (Swim Plan- Basin Issues, South Florida Water Management District). Similar high levels of ammonia were also found in the wetland basin directly to the east of the landfill, along with Black Creek and Gould's canals. Black Creek and the Gould's Canal are adjacent to the landfill to the north and south, respectively. Black Creek is located between the landfill and the South District Wastewater Treatment Plant. The Gould's Canal is located between the South Dade Landfill and the Old South Dade Landfill. The canals intersect directly east of the Black Point Marina and enter directly into Biscayne Bay.

A groundwater remediation plan published in 1990 suggested the construction of an interceptor trench along the eastern edge of the landfill site (Figure 1A). This groundwater remediation interception trench (GWRIT) was then constructed in 1993 and first operated in 1996 (Camp, Dresser & McKee, 2001). The trench captures groundwater contaminated with leachate that is then pumped to the adjacent Miami-Dade Water and Sewer Authority wastewater treatment plant. Landfill leachate is formed when water from precipitation soaks into and through the landfill. The leachate picks up a variety of suspended and dissolved materials as it percolates through the waste. Once treated, the treated leachate is pumped below the Biscayne and Floridan Aquifers via

deep injection wells (McNeill, 2000). In order to assess the effectiveness of this system, 17 clusters of monitoring wells were installed around the down gradient perimeter (the east and south sides) of the South Dade Landfill site. Each cluster contains 3 separate wells measuring 15, 30 and 60 feet deep, respectively.

This project was undertaken in order to test the effectiveness of the South Dade Landfill pollution control measures, specifically the Groundwater Remediation Interceptor Trench (GWRIT) and the wetlands retention basin, in the reduction of unionized ammonia (NH₃). Prior to this study, based on related studies performed by the Miami-Dade County Department of Environmental Resource Management (DERM), it was believed that the pollution control measures in place at the South Dade Landfill were effective in the reduction of the amount of pollutants entering the surface and groundwaters surrounding the landfill, specifically the near-shore waters of Biscayne Bay. It was thought that the combination of the GWRIT, which collected leachate before it entered the groundwater, and the wetlands retention basin, which acts as a natural biological filter, were successful in keeping the levels of pollutants, specifically unionized ammonia) below both state and federal pollution limits. This study was designed specifically to sample and analyze water samples from the areas surrounding the landfill in order to either support the theory that the pollution control measures were effective or to identify other possible localized sources of un-ionized ammonia pollution. There were numerous possible polluters, such as Gould's Canal, Black Creek or the Black Point Park Marina (Figure 2A). Both Gould's Canal and Black Creek were identified as possible polluters, by bringing contaminated surface waters from inland Miami Dade County. Black Point Marina, with a large number of live-aboard vessels was another possible point source of ammonia pollution. The live-aboard vessels, mainly small boats and

houseboats, could act as major sources of pollution if on-board sewage tanks leaked or were pumped into the marina waters.

A significant body of data exists and additional data from the well clusters and designated surface water sample sites was collected. The data collected from the analysis of the water samples was used to show average levels of ammonia, as well as trends in ammonia levels near the site. The analyzed data documented ammonia levels over time, on a seasonal basis or in relation to specific rainfall and/or tidal events. Data collected during this study, along with archived data were used to show ammonia levels in relation to surface water levels surrounding the landfill site. Due to its unique location, the landfill's leachate (that which hasn't been retained by the trench) is affected by surface water levels, tidal stages and groundwater gradients. The flow of leachate is now believed to be hydrogically driven. Both normal and high water levels in Black Creek and Gould's Canal act as a barrier, trapping most leachate within the landfill property. Conversely, low water levels allow leachate plumes to extend out away from the landfill site. These plumes extend down-gradient (south/southeast). By comparing historical water level data with ammonia concentrations, this study shows whether or not plumes of ammonia are related to specific water level changes. The analysis of the surface and well waters surrounding the landfill may help pinpoint other potential local point sources of ammonia such as runoff from local agriculture, sewage leakage from Black Point Marina or the upward migration of deep injected treated leachate from the adjacent Miami-Dade Water and Sewer South District Plant.

Materials and Methods

Surface water and groundwater data was collected over a ten- month period from October 2002 through July 2003. All samples were collected at the pre-determined sample locations surrounding the South Dade Landfill Property. The sample locations consisted of 11 groundwater well clusters and 13 surface water sample locations within the landfill wetlands retention basin, along with an additional 5 surface water sample locations in Black Creek, Gould's Canal and Black Creek Marina.

Samples were taken monthly at each of the designated sample points. Each groundwater well cluster was sampled from both a shallow well (15 ft depth) and an intermediate well (30 ft. depth). The 11 well clusters were located to the East and South of the South Dade Landfill (Figure 3). Well clusters S4, S8, S9, S10 and S11 were located along the western edge of the landfill wetlands, directly east of the interceptor trench and the landfill itself. Clusters S12, S13 and S14 were located within the constructed landfill wetlands. The remaining clusters S5, S15 and S16 were located on the easternmost edge of the landfill property, adjacent to Black Point Marina.

The surface water sampling sites were also located to the East and South of the landfill. There were 5 surface water sample locations (SU-Series) located in the canals and channels east and south of the landfill (Figure 4) along with 10 surface and bottom water sampling locations (SDLSW-Series) within the wetlands retention basin (Figure 5). Sample sites SU1 and SU2 were located in Gould's Canal, running East-West along the southern edge of the landfill. Sample sites SU4 and SU5 were located in the landfill wetland canals between the landfill wetlands and Black Point Marina. The channels













within the wetlands retention basin are all interconnected via culverts, but not directly connected to either of the canals. Any plumes or discharges from the retention basin into Gould's Canal and Black Creek would occur only as a result of groundwater interchange, as there are no culverts or control structures to allow for a direct hydrologic connection to the canals and Biscayne Bay.

At the surface water sample points surrounding the landfill, samples were taken at 1 foot below the surface as long as the total depth exceeded 18 inches. Within the wetlands retention basin, samples were taken at 1 foot below the surface and at 1 foot above the bottom. Samples were not taken at locations with less than 1 ft. of depth. Due to water levels, however, only 4 of the 10 SDLSW sample points had surface and bottom samples taken throughout the 10-month period. Field parameters pH, salinity and temperature were collected for each sample. Each sample was then laboratory analyzed for total ammonia nitrogen concentration. Using the Total Ammonia concentration and the collected field parameters, each sample was analyzed for the concentration of unionized ammonia using the DEP calculation formula.

In addition to the monthly sampling, quarterly samples of the landfill leachate were collected from the South Dade Landfill treatment facility located at the Miami-Dade Water and Sewer South District Plant. The leachate samples were taken for comparison of levels of ammonia in the leachate collected by the GWIRT versus the groundwater and surface water samples taken in the surrounding areas.

Groundwater Sampling Procedures

The groundwater purging and sampling procedures (Appendix A) used for this project were within the guidelines set forth by the Department of Environmental

Protection SOP's (DEP-SOP Manual-001/01) revised in January 2001 and again in 2003. The monitoring wells were purged using a vacuum driven pump. This vacuum pump was attached to a 5-liter Erlynmeyer flask with 25 feet of polyethylene tubing. Using the vacuum created with the flask, water was drawn from the wells in order to measure different environmental parameters such as conductivity, pH, temperature, turbidity and dissolved oxygen. These parameters must be stable in order for a sample to be collected. Other parameters, such as salinity, color and odor, were taken depending on what the samples were being analyzed for. This project required salinity readings for the proper measurement of un-ionized ammonia only for the surface water samples. These parameters are only a portion of the elements necessary for proper purging and sampling methodology. Parameters required include, but are not limited to; well characteristics, purging and sampling procedures, time, date, analyses and type and size of sample bottles. All wells sampled and parameters taken for this project were recorded using DEP groundwater sampling log field sheets (Figure 6).

In order to determine how much water had to be purged in order to obtain a stable sample, the well volume was measured by calculating the total well depth, the depth of the water in the well and the diameter of the well casing. The total well depth was measured using an electronic water probe. Depth to water was measured first, followed by the total well depth. Total well depth minus depth to water gives the height of water in the well.

21DEP-SOP-001/01 Form FD 9000-24 GROUNDWATER SAMPLING LOG

ITTE						SITE LOCATION:		-		•		
SAMPLE ID:					DATE:			DATE:				
		-	•		PUF	RGING DA	TA					
TUBING DIAMETER (inches): DIAMETER (inches): TWELL VOLUME = (TOTAL			WELL SO DEPTH: TAL WELL DEF	WELL SCREEN INTERVAL STATIC DEPTH DEPTH: feet to feet TO WATER (feet)			EPTH R (feet): X WELL C	PURGE PUMP TYPE OR BAILER: L CAPACITY				
in fill out if a	applicable)	RGE: 1 EQUI	= (PMENT VOL	= PUMP VOI	feet – .UME + (T	UBING CAPAC	feet) ITY X	X TUBING LE	gallons/foo NGTH) + FLOW CE	t = LL VOLU	ME	gallon
y fill out if a	applicable)			= g	allons + (gall	ons/foot X		feet) +	gai	lons =	gallor
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TIME	VOLUME PURGED (gallons)	CUMUL. VOLUME PURGED (gallons)	PURGE RATE (gpm)	DEPTH TO WATER (feet)	pH (standar units)	d TEMP. (°C)	COND. (μmhos/c m or μS/cm)	DISSOLVE OXYGEN (circle mg/L % saturatio	ED TURBIDITY or (NTUs)	CC (des	OLOR scribe)	ODOR (describe)
	T.T.	10										74
ELL CAPAC JBING INSIE	DE DIA. CAP	Per Foot): 0. ACITY (Gal./Fi	75° = 0.02; L): 1/8° = 0.	1" = 0.04; 0006; 3/16 '	1.25" = 0 = 0.0014;	1/4" = 0.002	6; 3" = 0. 26; 5/16" NTA	37; 4" = 0.6 = 0.004; 3	35; 5" = 1.02; 18" = 0.006; 1/2"	6" = 1.47 = 0.010;	7; 12" 5/8"	= 5.88 = 0.016
MPLED BY	(PRINT) / AF	FILIATION:	5	SAMPLER(S) S	IGNATUR	ES:		SAMPLING	AT:	SAMP	LING D AT:	
UMP OR TUI	BING ELL (feet):		S F	AMPLE PUMP LOW RATE (r	nL per min	per minute): TUBING MATERIAL CODE:						
ELD DECON	TAMINATIO	N: Y N	F	IELD-FILTER	ED: Y nent Type	N FILT	ER SIZE:	µm	DUPLICATE: Y N			
SAMPLE CONTAINER					SAMPLE PRESERVATION							PLING
AMPLE ID	CONTAIN	# MATERI CONTAINE AL VOLUN RS CODE		PRESER	TOTAL VO	FOTAL VOL FINAL D IN FIELD (mL) pH		ANALYSIS AND/OR METHOD		EQUIPMENT		
CODE	RS	E AL CODE	VOLUM	USI	D	ADDED IN FIEL	D (mL)	рН	METHOD			JODE
CODE	RS		VOLUM		ED	ADDED IN FIEL	, D (mL)	рН	METHOD	*		
	RS				ED	ADDED IN FIEL	, D (mL)	рН	METHOD			
	RS				ED	ADDED IN FIEL	Ď (mL)	рН	METHOD	× 1		
	RS				D	ADDED IN FIEL	2 (mL)	рН				
MARKS:	RS				Đ	ADDED IN FIEL	2 (mL)	рН				
MARKS:	ODES:	AG = Amber	Glass: CG	E USI	PE =	ADDED IN FIEL	20 (mL) 0 (mL)	pH	S = Silicone: T = T	efion:	0 = Oth	er (Specify)

2. STABILIZATION CRITERIA FOR RANGE OF VARIATION OF LAST THREE CONSECUTIVE READINGS (SEE FS 2212, SECTION 3)

pH: \pm 0.2 units Temperature: \pm 0.2 °C Specific Conductance: \pm 5% Dissolved Oxygen: all readings \leq 20% saturation (see Table FS 2200-2); optionally, \pm 0.2 mg/L or \pm 10% (whichever is greater) Turbidity: all readings \leq 20 NTU; optionally \pm 5 NTU or \pm 10% (whichever is greater)

Equation 2. Volume = [Gallons per Foot of Water] x H Where: V = volume in gallons H = height of water column (in feet)

Well Casing Diameter (inches)	Approximate Gallons per Foot of Water				
1"	0.04				
2"	0.16				
4"	0.65				

* All wells sampled had a 2" diameter.

**(DEP FS 2200, January 2001)

Table 1. Well volume calculation (GPF).

Each well was purged of at least three well volumes. Each well volume purged is analyzed for pH, temperature, specific conductance, dissolved oxygen and turbidity. The sample was collected after three consecutive measurements were within accepted limits (Table 2). As the majority of wells sampled were extremely turbid, samples were collected with readings above said limits but within the criterion that the last three measurements must be within 5 NTU's or 10 % of each other, whichever is greater.

Parameter	Acceptable Range for Sample Collection			
pН	± 0.2 standard units			
Temperature	\pm 0.2 standard units			
Conductivity	5 % of reading			
Dissolved Oxygen	≤ 20 % saturation			
Turbidity	≤ 20 Nephelometric Turbidity Units (NTU's)			

Table 2. DEP SOP FS 2212 Acceptable ranges for sample collection.

Well samples were collected once the well had been purged of at least three (3) well volumes, parameters were within acceptable limits and all documentation was complete. Sampling methods are also strictly defined in order to reduce any possible contamination to the samples themselves. All ammonia samples were collected in 250 ml

Harden & Land Dalla and

polyethylene bottles and preserved with sulfuric acid (H_2SO_4). The samples were taken using a glass bailer attached to a roll of non-leachable nylon string. The bailers also had to be de-contaminated after each well was sampled. All decontamination procedures were performed in accordance to DEP SOP FC1000 (Field Decontamination), using de-ionized water and 99% isopropyl alcohol.

Surface Water Sampling Procedures

As with groundwater sampling, surface water sampling procedures were used to collect representative samples. In accordance with DEP SOP FS 2100 (Appendix A), each sampling event was performed to ensure that samples were not altered or cross-contaminated due to improper handling or sampling. All surface water samples for this project were taken manually, using a pole sampling device and an intermediate sample container. The samples were taken within the top or bottom 12 inches of the water column. The intermediate sample container was rinsed and de-contaminated after each use. The intermediate sample container was then rinsed with ample amounts of sample water prior to collecting the first sample. Surface water samples were field analyzed for ph, conductivity, temperature, dissolved oxygen, turbidity and salinity. Samples were collected in 250 ml polyethylene bottles and preserved with H₂S0₄.

Analytical Methods

For this project, all samples were analyzed for ammonia concentration, including Total ammonia-nitrogen (TAN), ionized and un-ionized ammonia. After the samples and field parameters were collected, all samples were transported for analysis at Spectrum Labs, Inc. These samples were properly recorded and logged into an electronic database, the samples were analyzed using two EPA and Florida DEP accepted methods. The first method entailed analyzing the samples for total ammonia nitrogen, followed by calculation of the ionized ammonia to determine un-ionized ammonia concentrations.

Florida DEP method for Nitrogen, Ammonia: EPA Method 350.1

Method 350.1 covers the determination of ammonia in drinking, surface and saline waters, domestic and industrial wastes in the range of 0.01 to 2.0 mg/l NH₃ as N (total nitrogen). A continuous flow analyzer (TRAACS 880) with an automated sampler and inline distillation apparatus was used. Within the flow cell of the machine, Ammonia reacts with the reagents hypochlorite and alkaline phenol to form indopheol blue that is, in turn, read through the flow cell at 660 nm. The reading of the indophenol blue at 660 nm is proportional to the amount of total ammonia (TAN) in the sample.

Florida DEP Method for calculating un-ionized ammonia (NH₃) SOP 10/03/83

In an aqueous solution, un-ionized ammonia exists in equilibrium with an ammonium ion and a hydroxide ion. The equilibrium constant for this reaction is a function of the temperature and pH of the sample. Therefore, if this constant is known for a particular temperature and pH, the fraction of un-ionized ammonia can be calculated. Then, if the total ammonium (NH_4^+) concentration is known from laboratory analysis, the concentration of un-ionized ammonia can be calculated. The concentration of un-ionized ammonia is dependent on the ionic strength of the solution. There is a slight decrease in the fraction of un-ionized ammonia as the ionic strength of a solution increases.

The Florida Department of Environmental Protection (DEP) calculation technique for un-ionized ammonia was designed for solutions/samples of zero salinity. This

technique is applicable to solutions with low salinity without serious error. This calculation was used for the analysis of un-ionized ammonia in samples for this project. If all necessary parameters are within the appropriate ranges, un-ionized ammonia can be calculated in a sample of brackish or saline water. Only field measurements of these parameters were used. The accepted range of salinity is between 5 and 35 parts per thousand (ppt). (Note: the average salinity of seawater is 34.6 ppt). The temperature range is between 5 and 35 degrees Celcius. The ideal range of pH is between 7.8 and 8.3. The average pH value for the groundwater samples of this project was 7.6, the effect on the equation was negligible.

For this project, un-ionized ammonia for surface water samples was calculated using the DEP Un-ionized Ammonia Calculator v1.2 (Figure 7). Using the MS Excel spreadsheet calculation created in v1.2, a similar MS Excel spreadsheet was created in order to obtain the values of un-ionized ammonia for the groundwater samples. The calculation was made available for download by the DEP and incorporated the necessary parameters (total ammonia-N, pH, temperature and salinity). The Un-ionized Ammonia Calculator v1.2 is acceptable for both fresh and saline waters.

Unionized Ammonia Calculator v1.2; Original by Dr. Landon Ross Florida Department of Environmental Protection

Unionized Ammonia (mg/L as NH3)

Enter values into yellow cells

4

Figure 7. DEP Un-ionized Ammonia Calculator v1.2

「日本からたんですで

Data Analysis

All water samples were analyzed at Spectrum Laboratories Inc. using standard methods, which I and other analysts at the lab were certified to perform. The data was used to assess the possible negative impacts of high ammonia levels on Biscayne Bay. Past ammonia toxicity studies from estuarine and marine environments were included for comparison of ammonia concentration limits. Relative levels of un-ionized ammonia have been studied, taking into account the varying environmental parameters of temperature, pH, salinity and dissolved oxygen. The results have been used to evaluate the degree of effectiveness of the South Dade landfill groundwater remediation interception trench. The results have also been used to assess the ability of the wetlands in the reduction or prevention of the discharge of high levels of ammonia into the marine ecosystem of Biscayne Bay and to determine if levels of ammonia in the Bay in the vicinity of the landfill are related to the landfill or other sources.

Results

The three (3) quarterly analyses of the landfill leachate yielded an average NH_4^+ and NH_3 concentrations of 427.3 mg/L and 7.35mg/L, respectively. In comparison, the average groundwater NH_3 concentration throughout the testing period was 0.2 mg/l. The average NH_3 concentrations for the surface waters were 0.14 mg/L and 0.10 mg/L for the surrounding waters and the wetlands retention basin, respectively. These averages fall well below the average NH_3 concentration found in the leachate. This shows that there is a significant reduction in the amount of NH_3 the ground and surface waters surrounding the landfill. Although a significant reduction in NH_3 concentration can be expected due in

part to dilution, these averages do however, fall below the desired 0.5 mg/l criterion set forth by Miami Dade County.

Groundwater

The eleven (11) monitoring well clusters located to the east of the landfill are aligned in three (3) sets of wells running north – south within the wetlands retention basin and Black Point Park. The three sets of well clusters run parallel to the landfill, moving progressively east towards Black Point Marina and Biscayne Bay (Figure 3). Each set of wells showed definite trends and correlation values close to the expected results of the groundwater analyses. Comparing all of the wells, both as a whole and individually, there were numerous expected results for the groundwater analyses.

The first expected result was that if the landfill was the only source of NH₃, then the concentrations found in the groundwater would decrease progressively with distance away from the landfill (Figures 8 - 11). It would be expected that the groundwater NH₃ concentrations would be highest closest to the landfill and lowest at the well clusters furthest down-gradient of the landfill. The analyses of the groundwater samples yielded results close to those to be expected (Figure 12). The line of well clusters closest to the landfill showed the highest concentrations of NH₃ throughout the testing period, specifically those well clusters southeast of the landfill. These wells often had NH₃ concentrations of ≥ 0.30 mg/l. As expected the sets further east of the landfill had averages of 0.17 mg/L and 0.05 mg/L, respectively. Individually, each well showed trends towards seasonality, along with the expected results of the highest concentrations being in those wells closest to and down-gradient of the landfill, specifically wells S 4, S10 and S 11. IL T. L.T. I & R. P. R. P. M. R.



Figure 8 - Series 1 - Wells S4, S8, S9, S10 & S11 (shallow)


Figure 9 - Series 1 - Wells S4, S8, S9, S10 & S11 (medium)

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Figure 10 - Series 2 - Wells S 12, S 13, S 14 (shallow & medium)



Figure 11 - Series 3 - Wells S 15, S 5, S 16 (shallow & medium)

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Figure 12.

A second expected result was that the concentration of NH₃ in the groundwater would fluctuate in response to pH, temperature and water levels, reflecting the seasonality of NH₃ concentrations (Figure 13). As the formation of NH₃ is easier at higher temperatures and pH levels, it would be expected that the highest concentrations of NH₃ in groundwater would occur when these levels would be highest, typically during the late summer months. For the testing period, the average NH₃ concentrations were highest in the months with elevated pH and temperature levels, specifically October 2002 and May 2003. In contrast, the NH₃ levels were typically lowest during the cooler, drier winter months of December, January and February (Figures 8-11). The largest deviation from the expected pattern occurred in May and June, when significant rainfall was recorded, causing higher than normal groundwater levels. The significant influx of freshwater resulted in lower average pH levels, which in turn impeded the formation of NH₃.

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Figure 13. Seasonality of NH₃ in groundwater

Surface Water

Expected surface water results were similar to those of the groundwater. It was expected that the NH₃ levels would follow the seasonal trends and that the concentrations would decrease with distance from the landfill. It was also expected that the retention basin would act as a biological filter, and excess NH₃ in the surface waters would be assimilated and subsequently broken down, acting as a nutrient sink.

Overall, being more influenced by external factors such as tidal influence and flushing/flow - rates, it was expected that the SU-Series sample points would have NH₃ concentrations lower than the concentrations within the groundwater. The SU Series sample locations, in general, followed the seasonal trends in a fashion similar to the groundwater wells. The highest average NH₃ readings over the 10- month sampling period took place in the beginning and end of the summer, both in May and October (Figure 14). Of the 5 sample points, locations S-2 and S-4 had the largest increases in NH₃ levels in April and into May. Sample Point S-4, in particular, had both the largest increase in NH₃ levels and the highest concentrations overall. In April and May, SU-4 had NH₃ values increase to over 1.1 mg/L, nearly double the concentrations recorded in the previous months. Sample point S-3, located within Black Point Marina, typically had both the lowest pH readings and NH₃ concentrations, especially in the winter months.

The SDLSW-Series sample locations, located within the landfill retention basin, were expected to display NH₃ concentrations between those of the groundwater wells and the SU-Series surface water sample locations. It was assumed that the landfill retention basin would act as a sink for nutrients, specifically un-ionized ammonia, and that the concentrations would be lower than the groundwater wells to the west and higher than the



surface waters to the east. As with the groundwater and SU-series surface waters, the SDLSW Series did follow the seasonal trends, with the highest average NH₃ concentrations being recorded during the early and late summer months of April-May and September-October. The overall averages, however, were lower than the SU-series sample points located east and south of the retention basin. Lower averages within the wetlands basin suggest that external sources may have a greater impact on the surface waters surrounding the landfill. Of the SDLSW Sample points with sufficient data, sample location SDLSW 10 had the highest average concentration of NH₃ (Figure 15). The average NH₃ concentration of 0.341 mg/L at SDLSW 10 was 10X the average of the remaining sample points.



NH3	(mg/L)	Surface
	(mg/L)	Bottom



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Discussion & Conclusion

For this study, the overall mean NH₃ concentration for all surface and groundwater samples taken was 0.15mg/L. When compared to the average NH₃ concentration of 7.35mg/l found within the pre-treatment landfill leachate, there was a 98% reduction in the concentration of un-ionized ammonia. This reduction highlights the overall effectiveness in the pollution control measures in place at the South Dade Landfill, specifically the landfill lining of later cells, the capping of closed cells one and two and the Groundwater Remediation Interceptor Trench. Due to the nature of the landfill, along with its proximity to Biscayne Bay, a 98% reduction is significant in terms of limiting anthropogenic effects on the Biscayne Bay ecosystem. Although there has been a well-documented increase of nutrient loading into the bay since the 1970's, the South Dade Landfill itself cannot be viewed as the major point source of nutrients and subsequent water pollution within the central portion of Biscayne Bay.

Based on previous studies and additional data collected prior to this study, it was expected that the pollution control measures would be effective and that any elevated levels of NH₃ would be a result of additional sources of ammonia coupled with the landfill leachate, as opposed to the landfill being viewed as the largest point-source of NH₃ pollution. Earlier studies, such as the Camp, Dresser & Mckee, Inc. studies of the GWRIT, conducted between 1991 and 2001, showed significant reductions in ammonia concentrations following the interceptor trench being constructed. These studies, published in 1999 and 2001, respectively, focused solely on ionized ammonia concentrations within the groundwater well clusters surrounding the landfill.

It was also assumed that due to natural dynamic factors, such as the local hydrology and hydrogeology and of the area, any plumes, or "hotspots" of elevated NH₃

concentrations would be located southeast of the landfill. This assumption held true, with the highest average NH_3 concentrations being recorded in both the wells and in the surface water sample points directly east and southeast of the landfill property (Figures 8, 9, 14 & 15).

Although the average NH_3 concentration of 0.12 mg/L found in the surface waters (SU and SDLSW Series) surrounding the landfill is 6X higher than the 0.02mg/L limit set forth by both the FDEP and Miami-Dade DERM, there is no numerical standard set for ammonia in saline surface waters. The groundwater average of 0.2 mg/L does, however, fall below the 0.5 mg/L groundwater limit. Overall, not enough data has been collected to classify the South Dade Landfill as a major polluter. Recent studies, such as McNeill's review of the upward migration of effluent from the Miami-Dade Water and Sewer South District Plant (McNeill, 2001), have documented that elevated levels of NH4⁺ and NH3 may be traced to the deep-injection of treated landfill leachate. The South District Plant contains 17 deep injection wells used for the injection of treated wastewater and landfill leachate. This study documents that the deep injection wells may not have been constructed deep enough, and that the injected effluent has migrated upward through the ground both around the wells themselves and through more permeable layers downgradient of the Plant, specifically in locations in Biscayne Bay. The results of that study document that additional sources of ammonia exist and that the South Dade Landfill may not be a major point source of nutrient loading into Biscavne Bay.

Local agriculture may be another potential source of nutrient loading and run-off driven pollution. Historically, the areas surrounding the South Dade Landfill have been used for agricultural purposes. Un-sound agricultural practices with fertilizers may lead to excessive amounts of mineral nutrients entering aquatic systems through run-off. An oversupply of in-organic nitrogen and phosphorus compounds may cause an increase in nitrification, oxygen demand, and an intensification of primary productivity, which can lead to excessive growths of macro-algae and the formation of toxic un-ionized ammonia (Kremser, 2002). An increase in primary productivity may also be a cause of red-tides.

The agricultural area(s) to the West of the landfill, including Homestead and Florida City are connected to Biscayne Bay through a complex series of canals. Gould's Canal and Black Creek Canal are two of the largest canals connecting the agricultural areas surrounding Homestead, Florida City and the remaining areas west of the landfill to Biscayne Bay. The proximity of these canals to the agricultural and urbanized areas may lead to elevated levels of both ionized and un-ionized ammonia should the source(s) of pollution be located far West of the landfill property.

Overall, there is a significant set of data from numerous studies and monitoring programs that has been collected since the construction of the South Dade Landfill that highlights the effectiveness of the pollution control measures. There is also, however, enough data to conclude that there have been, and continue to be sources of ammonia pollution within the areas adjacent to Biscayne Bay. A larger set of data, taken over a longer period of time, may be needed in order to identify point-sources of ammonia pollution. This study, conducted over a 10 month period, can only conclude that the South Dade Landfill's pollution control measures, both passive and active, have been successful thus far in the reduction of un-ionized ammonia input into the ground and surface waters surrounding the landfill. Unfortunately, due to past dumping practices, agricultural run-off and the amount of ammonia found in everyday products, NH₃ pollution in Biscayne Bay may not be a point-source problem.

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Funding & Budget

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Tables

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Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S4 (S)	0.45981	21.3	7.44	27.1
11/26/2002	S4 (S)	0.42297	18.6	7.46	27.2
12/10/2002	S4 (S)	0.35307	20.7	7.33	27.3
1/10/2003	S4 (S)	0.00242	0.08	7.62	26.12
2/17/2003	S4 (S)	0.31793	15.7	7.44	26.17
3/5/2003	S4 (S)	0.37168	19.9	7.38	26.97
4/10/2003	S4 (S)	0.64133	35.6	7.28	29.77
5/13/2003	S4 (S)	1.12543	33.8	7.5	31.54
6/19/2003	S4 (S)	0.20163	25.7	6.99	27.28
7/22/2003	S4 (S)	0.25817	20.7	7.18	27.71
					1.5
Average	S4 (S)	0.42	21.21	7.36	27.72

Date	Location	NH ₃	NH4 ⁺	pН	Temp
10/30/2002	S4 (M)	0.4965	23	7.44	27.1
11/26/2002	S4 (M)	0.25348	14.8	7.35	26.7
12/10/2002	S4 (M)	0.33774	23.7	7.26	27
1/10/2003	S4 (M)	0.00348	0.17	7.44	26.31
2/17/2003	S4 (M)	0.36642	24.3	7.29	26.83
3/5/2003	S4 (M)	0.41857	27.4	7.27	27.68
4/10/2003	S4 (M)	0.63943	38.2	7.3	28.02
5/13/2003	S4 (M)	0.88387	36.3	7.42	29.54
6/19/2003	S4 (M)	0.26258	29.3	7.05	27.22
7/22/2003	S4 (M)	0.35243	26.5	7.21	27.65
Average	S4 (M)	0.40	24.37	7.30	27.41

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S5 (S)	0.01448	0.27	7.82	28
11/26/2002	S5 (S)	0.01614	1.21	7.24	26.7
12/10/2002	S5 (S)	0.02103	1.09	7.43	25.8
1/10/2003	S5 (S)	0.02638	1.35	7.46	25
2/17/2003	S5 (S)	0.06949	1.29	7.87	26.41
3/5/2003	S5 (S)	0.04019	0.62	7.95	26.56
4/10/2003	S5 (S)	0.01228	0.75	7.37	25.4
5/13/2003	S5 (S)	0.02017	1.05	7.44	25.41
6/19/2003	S5 (S)	0.0074	1.13	6.92	26.99
7/22/2003	S5 (S)	0.0097	0.97	7.15	25.51
Average	S5 (S)	0.02	0.97	7.47	26.18

Date	Location	NH ₃	lon	рН	Temp
10/30/2002	S5 (M)	0.07725	1.44	7.82	28
11/26/2002	S5 (M)	0.0107	0.23	7.81	26.2
12/10/2002	S5 (M)	0.00426	0.37	7.2	25.9
1/10/2003	S5 (M)	0.11563	2.41	7.86	25.02
2/17/2003	S5 (M)	0.04202	2.78	7.35	24.9
3/5/2003	S5 (M)	0.01734	0.99	~ 7.34	27.36
4/10/2003	S5 (M)	0.03387	0.76	7.8	25.89
5/13/2003	S5 (M)	0.02089	1.13	7.39	26.49
6/19/2003	S5 (M)	0.00341	0.13	7.52	27.3
7/22/2003	S5 (M)	0.01403	0.29	7.83	26.12
Average	S5 (M)	0.03	1.05	7.59	26.32

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S8 (S)	0.05546	2.37	7.5	26.3
11/26/2002	S8 (S)	0.04571	2.07	7.45	27.1
12/10/2002	S8 (S)	0.03827	2.23	7.36	26.4
1/10/2003	S8 (S)	0.00095	0.05	7.47	24.33
2/17/2003	S8 (S)	0.07468	2.11	7.71	25.45
3/5/2003	S8 (S)	0.02006	1.08	7.43	25.25
4/10/2003	S8 (S)	0.02121	1.36	7.36	25.02
5/13/2003	S8 (S)	0.05252	1.27	7.67	29.08
6/19/2003	S8 (S)	0.00415	1.85	6.46	26.75
7/22/2003	S8 (S)	0.02838	2.1	7.25	26.56
Average	S8 (S)	0.03	1.65	7.37	26.22

Date	Location	NH ₃	${\sf NH_4}^+$	pН	Temp
10/30/2002	S8 (M)	0.01662	0.71	7.5	26.3
11/26/2002	S8 (M)	0.01499	0.87	7.38	25.8
12/10/2002	S8 (M)	0.01952	0.96	7.45	25.9
1/10/2003	S8 (M)	0.00076	0.03	7.57	25.13
2/17/2003	S8 (M)	0.03784	1.23	7.66	25.04
3/5/2003	S8 (M)	0.00854	0.5	7.38	25.68
4/10/2003	S8 (M)	0.0221	0.71	7.66	25.21
5/13/2003	S8 (M)	0.02749	0.88	7.56	28.56
6/19/2003	S8 (M)	0.00558	0.86	6.92	26.85
7/22/2003	S8 (M)	0.01023	0.65	7.32	26.46
Average	S8 (M)	0.02	0.74	7.44	26.09

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S9 (S)	0.03471	1.35	7.56	25.7
11/26/2002	S9 (S)	0.03166	1.91	7.36	25.9
12/10/2002	S9 (S)	0.03463	1.77	7.43	26
1/10/2003	S9 (S)	0.00078	0.03	7.59	24.79
2/17/2003	S9 (S)	0.0762	3.48	7.51	25.01
3/5/2003	S9 (S)	0.05415	2.07	7.51	27.6
4/10/2003	S9 (S)	0.03739	2.83	7.27	25.58
5/13/2003	S9 (S)	0.09287	2.99	7.58	27.81
6/19/2003	S9 (S)	0.0387	3.05	7.23	26.31
7/22/2003	S9 (S)	0.02848	2.8	7.14	26.08
Average	S9 (S)	0.04	2.23	7.42	26.08

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S9 (M)	0.02263	0.88	7.56	25.7
11/26/2002	S9 (M)	0.01754	0.84	7.48	25.3
12/10/2002	S9 (M)	0.0211	0.99	7.48	25.6
12/10/2002	S9 (M)	0.0211	0.99	7.48	25.6
1/10/2003	S9 (M)	0.00126	0.06	7.49	25.09
3/5/2003	S9 (M)	0.01687	0.63	. 7.55	26.62
4/10/2003	S9 (M)	0.01558	1.02	7.32	26.03
5/13/2003	S9 (M)	0.02463	1.29	7.37	27.62
6/19/2003	S9 (M)	0.00943	1.06	7.05	27.11
7/22/2003	S9 (M)	0.01194	0.94	7.25	25.67
Average	S9 (M)	0.02	0.87	7.40	26.03

Groundwater Data Tables

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S10 (S)	0.69568	34.8	7.4	27.3
11/26/2002	S10 (S)	0.623	31.1	7.41	27
12/10/2002	S10 (S)	0.54536	35.5	7.29	27.1
1/10/2003	S10 (S)	0.01771	0.96	7.42	25.48
2/17/2003	S10 (S)	0.43028	36	7.23	25.45
3/5/2003	S10 (S)	0.67693	36.9	7.39	26.38
4/10/2003	S10 (S)	1.03079	55	7.38	27.02
5/13/2003	S10 (S)	0.82918	37.4	7.44	27.49
6/19/2003	S10 (S)	0.41728	41.5	7.02	29.9
7/22/2003	S10 (S)	0.53618	40.4	7.21	27.62
Average	S10 (S)	0.58	34.96	7.32	27.07

Date	Location	NH ₃	NH_4^+	pН	Temp
11/26/2002	S10 (M)	0.24527	15.5	7.3	27.2
1/10/2003	S10 (M)	0.03214	2.12	7.3	26.58
10/30/2002	S10 (M)	0.29786	14.9	7.4	27.3
12/10/2002	S10 (M)	0.34109	21.9	7.29	27.3
2/17/2003	S10 (M)	0.15219	12.5	7.18	27.36
3/5/2003	S10 (M)	0.16808	11.3	7.23	28.62
4/10/2003	S10 (M)	0.31606	19.62	7.26	28.79
5/13/2003	S10 (M)	0.31067	18.8	7.22	30.51
6/19/2003	S10 (M)	0.21628	26.6	6.95	29.13
7/22/2003	S10 (M)	0.32167	27.5	7.17	27.11
Average	S10 (M)	0.24	17.07	7.23	27.99

Groundwater Data Tables

Well Cluster S 11

Date	Location	NH ₃	NH_4^+	рН	Temp
10/30/2002	S11 (S)	0.16599	4.92	7.51	31.4
11/26/2002	S11 (S)	0.16175	6.01	7.43	30.7
12/10/2002	S11 (S)	0.74833	34.1	7.36	30.01
1/10/2003	S11 (S)	0.51654	21.1	7.44	28.95
2/17/2003	S11 (S)	0.95307	63.4	7.22	29.11
3/5/2003	S11 (S)	0.90132	54.75	7.24	29.78
4/10/2003	S11 (S)	0.62994	43	7.2	29.4
5/13/2003	S11 (S)	0.69999	45	7.21	29.95
6/19/2003	S11 (S)	0.09573	8.56	7.05	30.46
7/22/2003	S11 (S)	0.39703	22	7.26	30.47
Average	S11 (S)	0.53	30.28	7.29	30.02

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S11 (M)	1.44174	42.9	7.51	31.4
11/26/2002	S11 (M)	0.58393	40.1	7.1	32.7
12/10/2002	S11 (M)	0.77746	46.8	7.16	32.63
1/10/2003	S11 (M)	0.02833	1.65	7.18	32.44
2/17/2003	S11 (M)	0.63544	66.3	7.14	25.23
3/5/2003	S11 (M)	0.83928	59.5	7.11	31.88
4/10/2003	S11 (M)	1.03191	68.1	7.15	31.59
5/13/2003	S11 (M)	0.88707	70.3	7.04	32.6
6/19/2003	S11 (M)	0.77743	73.8	6.93	33.66
7/22/2003	S11 (M)	0.69167	56.7	7.01	33.12
Average	S11 (M)	0.77	52.62	7.13	31.73

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Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S12 (S)	0.02654	1.26	7.39	28.4
11/26/2002	S12 (S)	0.01212	1.09	7.13	27.7
12/10/2002	S12 (S)	0.01072	1.29	7.02	27.1
1/10/2003	S12 (S)	0.03007	1.43	7.45	26.39
2/17/2003	S12 (S)	0.10777	2.23	7.84	25.78
3/5/2003	S12 (S)	0.01571	0.99	7.31	26.91
4/10/2003	S12 (S)	0.03713	2.1	7.06	25.54
5/13/2003	S12 (S)	0.07817	1.28	7.88	27.97
6/19/2003	S12 (S)	0.00528	1.01	6.84	26.38
7/22/2003	S12 (S)	0.00706	0.83	7.01	27.78
Average	S12 (S)	0.03	1.35	7.29	27.00

Date	Location	NH ₃	NH4 ⁺	pН	Temp
10/30/2002	S12 (M)	0.00577	0.28	7.38	28.4
11/26/2002	S12 (M)	0.0076	0.32	7.47	27.5
12/10/2002	S12 (M)	0.01267	0.5	7.52	26.8
1/10/2003	S12 (M)	0.01394	0.37	7.69	27.03
2/17/2003	S12 (M)	0.00619	0.34	7.4	25.94
3/5/2003	S12 (M)	0.00726	0.16	7.78	26.81
4/10/2003	S12 (M)	0	0	7.3	25.14
5/13/2003	S12 (M)	0	0	7.66	27.16
6/19/2003	S12 (M)	0.00251	0.31	7.05	25.76
7/22/2003	S12 (M)	0.00373	0.22	7.34	26.88
Average	S12 (M)	0.01	0.25	7.46	26.74

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Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S13 (S)	0.10431	3.49	7.63	25.6
11/26/2002	S13 (S)	0.04408	3.5	7.23	26.2
12/10/2002	S13 (S)	0.04754	4.12	7.21	25.6
1/10/2003	S13 (S)	0	0	7.64	25.22
2/17/2003	S13 (S)	0.03206	3.71	7.08	25.71
3/5/2003	S13 (S)	0.12174	2.58	7.85	25.1
4/10/2003	S13 (S)	0.09455	4.67	7.38	28.15
5/13/2003	S13 (S)	0.10416	4.68	7.52	24.92
6/19/2003	S13 (S)	0.06339	5.73	7.19	25.65
7/22/2003	S13 (S)	0.06049	6.25	7.14	25.37
Average	S13 (S)	0.07	3.87	7.39	25.75

Date	Location	NH ₃	NH₄⁺	pН	Temp
10/30/2002	S13 (M)	0.11687	3.91	7.63	25.6
11/26/2002	S13 (M)	0.0561	3.01	7.43	25.3
12/10/2002	S13 (M)	0.05581	3.94	7.3	25.6
1/10/2003	S13 (M)	0.02263	1.01	7.5	25.67
2/17/2003	S13 (M)	0.01101	0.32	7.7	25.36
3/5/2003	S13 (M)	0.05204	2.47	7.47	25.76
4/10/2003	S13 (M)	0.07166	4.13	7.36	26.56
5/13/2003	S13 (M)	0.10659	4.44	7.54	25.36
6/19/2003	S13 (M)	0.03594	5.32	6.98	25.46
7/22/2003	S13 (M)	0.06637	5.28	7.25	25.52
Average	S13 (M)	0.06	3.38	7.42	25.62

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S14 (S)	0.75578	5.96	7.29	28.9
11/26/2002	S14 (S)	0.5291	33.5	7.26	28.5
12/10/2002	S14 (S)	0.02001	1.4	7.21	28.7
1/10/2003	S14 (S)	0.44977	25.6	7.32	27.24
2/17/2003	S14 (S)	0.47721	31	7.29	27.13
3/5/2003	S14 (S)	0.30785	51.75	7.23	28.88
4/10/2003	S14 (S)	0.24821	84.3	7.21	29.42
5/13/2003	S14 (S)	0.47356	28.6	7.27	28.86
6/19/2003	S14 (S)	0.06433	7.51	6.93	30.57
7/22/2003	S14 (S)	0.44718	31.4	7.21	28.65
Average	S14 (S)	0.38	30.10	7.22	28.69

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S14 (M)	0.10355	43.5	7.29	28.9
11/26/2002	S14 (M)	0.15587	13	7.16	27.8
12/10/2002	S14 (M)	0.0176	1.38	7.16	28.7
1/10/2003	S14 (M)	0.03172	1.91	7.35	27.07
2/17/2003	S14 (M)	0.71848	61.2	7.13	28.49
3/5/2003	S14 (M)	0.78348	20.5	7.28	27.1
4/10/2003	S14 (M)	1.2651	25.7	7.09	26.98
5/13/2003	S14 (M)	0.94272	74.3	7.13	29.63
6/19/2003	S14 (M)	0.41483	53.5	6.92	29.44
7/22/2003	S14 (M)	0.45969	40.3	7.13	28.07
Average	S14 (M)	0.49	33.53	7.16	28.22

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S15 (S)	0.0248	1.22	7.45	25.9
11/26/2002	S15 (S)	0.18144	10.5	7.36	26.5
12/10/2002	S15 (S)	0.03242	1.8	7.36	27.1
1/10/2003	S15 (S)	0.07105	1.68	7.76	26.43
2/17/2003	S15 (S)	0.03	1.6	7.44	25.06
3/5/2003	S15 (S)	0.02987	0.88	7.68	25.82
4/10/2003	S15 (S)	0.01567	0.64	7.55	25.32
5/13/2003	S15 (S)	0.03534	1.13	7.63	26.26
6/19/2003	S15 (S)	0.00603	1.19	6.84	25.94
7/22/2003	S15 (S)	0.01584	1.2	7.25	26.22
Average	S15 (S)	0.04	2.18	7.43	26.06

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S15 (M)	0.00915	0.45	7.45	25.9
11/26/2002	S15 (M)	0.01113	0.69	7.36	25.5
12/10/2002	S15 (M)	0.01263	0.68	7.41	25.9
1/10/2003	S15 (M)	0.02547	0.6	7.78	25.83
2/17/2003	S15 (M)	0.02963	0.93	7.66	25.55
3/5/2003	S15 (M)	0.01009	0.35	~ 7.6	26.06
4/10/2003	S15 (M)	0.0459	0.84	7.93	24.66
5/13/2003	S15 (M)	0.00542	0.32	7.36	26.21
6/19/2003	S15 (M)	0.00382	0.47	7.06	25.47
7/22/2003	S15 (M)	0.00558	0.42	7.27	25.67
Average	S15 (M)	0.02	0.58	7.49	25.68

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S16 (S)	0.12604	9.92	7.24	26
11/26/2002	S16 (S)	0.0456	1.28	7.69	26.2
12/10/2002	S16 (S)	0.09502	10.7	7.08	26.1
1/10/2003	S16 (S)	0.18913	8.11	7.5	26.25
2/17/2003	S16 (S)	0.12728	15.6	7.08	24.89
3/5/2003	S16 (S)	0.15907	7.97	7.44	25.96
4/10/2003	S16 (S)	0.07778	10.34	7.05	24.71
5/13/2003	S16 (S)	0.15231	12.4	7.1	30.16
6/19/2003	S16 (S)	0.00047	0.09	6.8	27.58
7/22/2003	S16 (S)	0.08906	11.5	7.04	25.45
Average	S16 (S)	0.11	8.79	7.20	26.33

Date	Location	NH ₃	NH_4^+	pН	Temp
10/30/2002	S16 (M)	0.155	12.2	7.24	26
11/26/2002	S16 (M)	0.09119	11.9	7.04	25.3
12/10/2002	S16 (M)	0.08562	11.8	7.01	25.5
1/10/2003	S16 (M)	0.05604	4.07	7.29	25.52
2/17/2003	S16 (M)	0.06346	9.23	7	25.06
3/5/2003	S16 (M)	0.09958	7.74	7.24	26.18
4/10/2003	S16 (M)	0.06178	11.43	6.91	24.57
5/13/2003	S16 (M)	0.13234	14.4	7	29.25
6/19/2003	S16 (M)	0.06502	12.7	6.8	27.4
7/22/2003	S16 (S)	0.07589	11.5	6.96	25.78
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Average	S16 (S)	0.09	10.70	7.05	26.06











SU-1					
Date	Location	pН	Temp	NH_4^+	NH ₃
Oct-02	SU-1	7.6	30	7.18	0.27
Nov-02	SU-1	7.61	23.7	3.89	0.10
Dec-02	SU-1	7.7	26.25	4.46	0.16
Jan-03	SU-1	7.94	16.93	0.46	0.01
Feb-03	SU-1	7.67	22.56	3.05	0.08
Mar-03	SU-1	8.16	28.59	0.08	0.01
Apr-03	SU-1	8.26	23.36	0	0.00
May-03	SU-1	7.96	31.27	0	0.00
Jun-03	SU-1	7.03	26.87	2.84	0.02
Jul-03	SU-1	7.74	31.67	0	0.00
Average		7.767	26.12	2.196	0.07

SU-2

Date	Location	pН	Temp	NH ₄	NH ₃
Oct-02	SU-2	7.66	28.5	1.58	0.06
Nov-02	SU-2	7.43	22.4	2.25	0.03
Dec-02	SU-2	7.47	25.19	0.22	0.00
Jan-03	SU-2	7.61	16.53	0.49	0.01
Feb-03	SU-2	7.07	22.37	4.6	0.03
Mar-03	SU-2	7.46	26.91	3.63	0.08
Apr-03	SU-2	7.92	22.45	3.49	0.16
May-03	SU-2	7.21	31.08	4.08	0.07
Jun-03	SU-2	6.72	27.42	5.58	0.02
Jul-03	SU-2	6.98	31.6	4.05	0.04
Average		7.353	25.445	2.997	0.05

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Date	Location	pН	Temp	NH_4^+	NH ₃
Oct-02	SU-3	8.04	28.8	0.23	0.02
Nov-02	SU-3	7.5	22.7	0.36	0.01
Dec-02	SU-3	7.63	25.19	0.2	0.01
Jan-03	SU-3	7.6	16.43	0.16	0.00
Feb-03	SU-3	7.22	27.05	0.43	0.01
Mar-03	SU-3	6.64	28.19	0.32	0.00
Apr-03	SU-3	6.86	21.71	0.1	0.00
May-03	SU-3	7.44	30.29	0.22	0.01
Jun-03	SU-3	6.75	27.29	0.57	0.00
Jul-03	SU-3	7.36	30.12	0.42	0.01
Average		7.304	25.777	0.301	0.01

SU-4					
Date	Location	pН	Temp	NH_4^+	NH ₃
Oct-02	SU-4	7.37	29.3	22.2	0.48
Nov-02	SU-4	7.86	21.6	1.1	0.04
Dec-02	SU-4	7.21	27.01	30.6	0.39
Jan-03	SU-4	7.13	18.53	48.9	0.28
Feb-03	SU-4	7.13	23.1	70.25	0.57
Mar-03	SU-4	7.41	27.74	44.6	0.94
Apr-03	SU-4	7.42	24.74	58.7	1.03
May-03	SU-4	7.5	30.11	39.1	1.20
Jun-03	SU-4	6.81	28.42	21.6	0.12
Jul-03	SU-4	7.11	30.19	25.2	0.32
Average		7.295	26.074	36.225	0.54

SU-5

Date	Location	рН	Temp	NH ₄	NH ₃
Oct-02	SU-5	7.75	29.2	2.54	0.13
Nov-02	SU-5	7.81	21.8	1.19	0.04
Dec-02	SU-5	7.82	25.16	1.16	0.05
Jan-03	SU-5	7.77	16.04	0.92	0.02
Feb-03	SU-5	8.22	21.21	1.04	0.08
Mar-03	SU-5	7.9	28.18	0.48	0.03
Apr-03	SU-5	6.84	23.95	1.36	0.01
May-03	SU-5	7.6	31.88	2.41	0.10
Jun-03	SU-5	7.01	29.15	0	0.00
Jul-03	SU-5	7.6	29.26	0.25	0.01
Average		7.632	25.583	1.135	0.05

SU-Series Statistics

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SDLSW Series Data Tables

Date	Temperature (C')	рН	NH ₃ (mg/L) Surface
10/21/2002	22.68	7.69	0.070
11/26/2002	23.90	7.79	0.030
12/12/2002	24.42	7.80	0.050
1/22/2003	23.21	8.12	0.010
2/24/2003	23.54	8.12	0.090
3/19/2003	28.64	7.83	0.080
4/2/2003	23.32	7.72	0.030
5/12/2003	31.29	7.28	0.040
6/24/2003	27.97	7.22	0.000
7/23/2003	30.70	6.90	. 0.000
Average	25.97	7.65	0.040

2 SDLSW - Surface

2 SDLSW - Bottom

Date	Temperature (C')	рН	NH ₃ (mg/L) Bottom
10/21/2002	21.79	7.71	0.090
11/26/2002	23.10	7.80	0.030
12/12/2002	24.60	7.73	0.060
1/22/2003	17.00	7.77	0.010
2/24/2003	23.21	8.12	0.040
3/19/2003	28.08	8.05	0.130
4/2/2003	22.80	7.85	0.040
5/12/2003	30.84	7.40	0.060
6/24/2003	28.02	7.40	0.000
7/23/2003	30.74	7.24	0.000
Average	25.02	7.71	0.046

SDLSW Series Data Tables

8 SDLSW - Surface

Date	Temperature (C')	pН	NH ₃ (mg/L) Surface
10/21/2002	22.70	7.62	0.040
11/26/2002	23.90	7.70	0.040
12/12/2002	24.92	7.88	0.070
1/22/2003	17.98	7.85	0.010
2/24/2003	23.11	8.07	0.020
3/19/2003	28.79	8.04	0.150
4/2/2003	22.47	7.92	0.050
5/12/2003	31.05	7.06	0.020
6/24/2003	29.91	7.10	0.000
7/23/2003	30.45	6.89	0.000
Average	25.53	7.61	0.040

8 SDLSW - Bottom

Date	Temperature (C')	рН	NH ₃ (mg/L) Bottom
10/21/2002	22.48	7.63	0.040
11/26/2002	23.40	7.69	0.050
12/12/2002	24.63	7.78	0.050
1/22/2003	16.82	7.87	0.010
2/24/2003	22.81	8.10	0.020
3/19/2003	28.25	8.14	0.160
4/2/2003	22.42	7.95	0.050
5/12/2003	30.84	7.32	0.040
6/24/2003	29.88	7.30	0.010
7/23/2003	30.49	7.26	0.000
Average	25.20	7.70	0.043

SDLSW Series Data Tables

10 SDLSW - Surface

Date	Temperature (C')	pН	NH ₃ (mg/L) Surface
10/21/2002	23.56	7.73	0.460
11/26/2002	26.00	7.19	0.340
12/12/2002	26.56	7.08	0.170
1/22/2003	21.96	7.12	0.260
2/24/2003	24.67	7.26	0.490
3/19/2003	28.74	7.25	0.230
4/2/2003	23.08	7.49	0.740
5/12/2003	30.51	7.63	0.890
6/24/2003	26.72	6.76	0.040
7/23/2003	30.48	6.98	0.350
Average	26.23	7.25	0.397

10 SDLSW - Bottom

Date	Temperature (C')	рН	NH ₃ (mg/L) Bottom
10/21/2002	23.51	7.68	0.380
11/26/2002			
12/12/2002	26.44	7.06	0.210
1/22/2003	21.06	7.09	0.150
2/24/2003	24.33	7.22	0.380
3/19/2003	28.74	7.25	0.130
4/2/2003	22.83	7.24	0.220
5/12/2003	30.96	7.50	0.630
6/24/2003	26.83	6.89	0.100
7/23/2003	30.45	7.21	0.370
Average	26.13	7.24	0.286
SDLSW Series Data Tables 100

11 SDLSW - Surface

Date	Temperature (C')	рН	NH ₃ (mg/L) Surface
10/21/2002	24.42	7.17	0.030
11/26/2002	23.40	7.64	0.020
12/12/2002	25.24	7.85	0.080
1/22/2003	16.61	7.79	0.010
2/24/2003	23.59	8.15	0.040
3/19/2003	28.92	7.90	0.130
4/2/2003	23.17	6.52	0.000
5/12/2003	30.96	7.50	0.070
6/24/2003	28.28	7.33	0.000
7/23/2003	29.37	7.14	0.120
Average	25.40	7.50	0.050

SDLSW Series Data Tables

12 SDLSW - Surface

Date	Temperature (C')	pН	NH ₃ (mg/L) Surface
10/21/2002	22.72	8.48	0.020
11/26/2002	23.10	8.30	0.010
12/12/2002	24.33	8.39	0.020
1/22/2003	17.17	8.39	0.010
2/24/2003	22.94	8.36	0.010
3/19/2003	29.54	8.31	0.010
4/2/2003	22.05	8.37	0.000
5/12/2003	30.74	8.38	0.000
6/24/2003	28.05	7.41	0.000
7/23/2003	31.03	7.23	0.000
Average	25.17	8.16	0.008

12 SDLSW - Bottom

Date	Temperature (C')	pН	NH ₃ (mg/L) Bottom
10/21/2002	22.04	8.28	0.070
11/26/2002	23.10	8.34	0.010
12/12/2002	24.13	7.40	0.000
1/22/2003	16.33	8.42	0.010
2/24/2003	22.77	8.34	0.010
3/19/2003	28.35	8.78	0.010
4/2/2003	21.15	8.31	0.000
5/12/2003	30.61	8.03	0.010
6/24/2003	28.22	7.41	0.000
7/23/2003	30.90	7.24	0.000
Average	24.76	8.06	0.012

Appendix A

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FS 2200. Groundwater Sampling

1. INTRODUCTION AND SCOPE

1.1. Use these Standard Operating Procedures to collect groundwater samples. They are designed to ensure that the collected samples will be representative of water in the aquifer or target formation and that the samples have not been altered or contaminated by the sampling and handling procedures. These procedures apply to permanently and temporarily installed monitoring wells, wells with installed plumbing, remedial groundwater treatment systems and excavations where groundwater is present. Use of alternative, FDEP-approved and properly documented procedures (e.g., Corporate SOP, ASTM Standards, alternative equipment, etc.) is acceptable if they meet the intent (e.g., sample representativeness and integrity) of this standard (see FA 1000).

1.2. The topics in this SOP include equipment and supply selection, equipment construction materials, and purging and sampling techniques.

- 1.3. Use the following FDEP SOPs in conjunction with FS 2200:
 - FA 1000 Regulatory Scope and Administrative Procedures for Use of DEP SOPs
 - FC 1000 Cleaning/Decontamination Procedures
 - FD 1000 Documentation Procedures
 - FQ 1000 Field Quality Control Requirements
 - FS 1000 General Sampling Procedures
 - FS 2000 General Aqueous Sampling
 - FT 1000 Field Testing and Measurement

1.4. Groundwater samples may be collected from a number of different configurations. Each configuration is associated with a unique set of sampling equipment requirements and techniques:

1.4.1. <u>Wells without Plumbing</u>: These wells require that equipment be brought to the well to purge and sample unless dedicated equipment is placed in the well.

1.4.2. <u>Wells with In-Place Plumbing</u>: Wells with in-place plumbing do not require that equipment be brought to the well to purge and sample. In-place plumbing is generally considered permanent equipment routinely used for purposes other than purging and sampling, such as for water supply. They are generally found at wellfields, industrial facilities, and private residences. See FS 2300 for procedures to sample potable water wells.

1.4.3. <u>Air Strippers or Remedial Systems</u>: These types of systems are installed as remediation devices. Sample these wells like drinking water wells (see FS 2300).

FS 2201. Equipment and Supplies

Use groundwater purging and sampling equipment constructed of only non-reactive, non-leachable materials that are compatible with the environment and the selected analytes. In selecting groundwater purging and sampling equipment, give consideration to the depth of the well, the depth to groundwater, the volume of water to be evacuated, the sampling and purging technique, and the analytes of interest. Refer to Tables FS 1000-1, FS 1000-2, FS 1000-3 and FS 2200-1 for selection of appropriate equipment.

Additional supplies such as reagents, preservatives, and field measurement equipment may be necessary.

1. FLOW CONTAINER: FDEP recommends using a flow-through cell or container when collecting measurements for purging stabilization. The design must ensure that fresh formation water continuously contacts the measuring devices and does not aerate the sample or otherwise affect the groundwater properties.

². PUMPS: All pumps or pump tubing must be lowered and retrieved from the well slowly and carefully to minimize disturbance to the formation water. This is especially critical at the air/water interface. Avoid the

uspension of sediment particles (turbidity) at the bottom of the well or adhered to the well casing during sitioning of the pump or tubing.

2.1. Above-Ground Pumps

2.1.1. <u>Variable Speed Peristaltic Pump</u>: Use a variable speed peristaltic pump to purge groundwater from wells when the static water level in the well is no greater than 20-25 feet below land surface (BLS). If the water levels are deeper than 18-20 feet BLS, the pumping velocity will decrease.

2.1.1.1. A variable speed peristaltic pump can be used for normal purging and sampling (see FS 2213 and FS 2221), sampling low permeability aquifers or formations (see FS 2222) and collecting filtered groundwater samples (see FS 2225, section 1).

2.1.1.2. Most analyte groups can be sampled with a peristaltic pump if the tubing and pump configurations are appropriate. See Table FS 1000-3 for proper tubing selection and pump configurations.

2.1.2. <u>Variable Speed Centrifugal Pump</u>: A variable speed centrifugal pump can be used to purge groundwater from 2-inch and larger internal diameter wells. **Do not use** this type of pump to collect groundwater samples.

2.1.2.1. When purging is complete, do not allow the water that remains in the tubing to fall back into the well. Install a check valve at the end of the purge tubing, and withdraw the tubing slowly from the well while the pump is still running.

2.1.2.2. See Table FS 1000-3 for proper tubing selection and allowable analyte groups.

2.2. Submersible Pumps

2.2.1. <u>Variable Speed Electric Submersible Pump</u>: A variable speed submersible pump can be used to purge and sample groundwater from 2-inch and larger internal diameter wells.

2.2.1.1. A variable speed submersible pump can be used for normal purging and sampling (see FS 2213 and FS 2221), sampling low permeability aquifers or formations (see FS 2222) and collecting filtered groundwater samples (see FS 2225, section 1).

2.2.1.2. Make sure that the pump housing, fittings, check valves and associated hardware are constructed of stainless steel. Make sure that any other materials are compatible with the analytes of interest. See Table FS 1000-3 for restrictions.

2.2.1.3. Install a check valve at the output side of the pump to prevent backflow.

2.2.1.4. If purging and sampling for organics:

- The entire length of the delivery tube must be Teflon, Polyethylene or Polypropylene (PP) tubing.
- The electrical cord must be sealed in Teflon, Polyethylene or PP and any cabling must be sealed in Teflon, Polyethylene or PP, or be constructed of stainless steel.
- All interior components that contact the sample water (impeller, seals, gaskets, etc.) must be constructed of stainless steel or Teflon.

2.2.2. <u>Variable Speed Bladder Pump</u>: A variable speed positive displacement bladder pump (no-gas contact) can be used to purge and sample groundwater from 3/4-inch and larger internal diameter wells.

2.2.2.1. A variable speed bladder pump can be used for normal purging and sampling (see FS 2213 and FS 2221), sampling low permeability aquifers or formations (see FS 2222) and collecting filtered groundwater samples (see FS 2225, section 1).

2.2.2.2. The bladder pump system is composed of the pump, the compressed air tubing, the water discharge tubing, the controller and a compressor or compressed gas supply.

2.2.2.3. The pump consists of a bladder and an exterior casing or pump body that surrounds the bladder and two (2) check valves. These parts can be composed of various materials, usually

combinations of polyvinyl chloride (PVC), Teflon, Polyethylene, PP and stainless steel. Other materials must be compatible with the analytes of interest. See Table FS 1000-3 for restrictions.

- 2.2.2.4. If purging and sampling for organics:
 - The pump body must be constructed of stainless steel and the valves and bladder must be Teflon, Polyethylene or PP.
 - The entire length of the delivery tube must be Teflon, Polyethylene or PP.
 - Any cabling must be sealed in Teflon, Polyethylene or PP, or be constructed of stainless steel.

2.2.2.5. Permanently installed pumps may have a PVC pump body as long as the pump remains in contact with the water in the well.

3. BAILERS:

3.1. <u>Purging</u>: FDEP does not recommend using bailers for purging unless no other equipment can be used or purging with a bailer has been specifically authorized by an FDEP program, permit, contract or order (see Table FS 2200-3). Use a bailer if there is non-aqueous phase liquid (free product) in the well or non-aqueous phase liquid is suspected to be in the well. If in doubt about the appropriateness of using a bailer at a site or during a particular sampling event, contact the appropriate FDEP program or project manager. If a bailer is used, follow FS 2213, section 4, with no deviations.

3.2. <u>Sampling</u>: Bailers may be used to routinely collect some analyte groups or under specific circumstances for other analyte groups (see Table FS 2200-3).

3.3. Construction and Type:

3.3.1. Bailers must be constructed of materials compatible with the analytes of interest. See Table FS 1000-3 for restrictions.

3.3.1.1. Stainless steel, Teflon, Polyethylene and PP bailers may be used to sample all analytes.

- 3.3.2. Use disposable bailers when sampling grossly contaminated sample sources.
- 3.3.3. FDEP recommends using dual check valve bailers when collecting samples.
- 3.3.4. Use bailers with a controlled flow bottom when collecting volatile organic samples.
- 3.3.5. Use bailers that can be pressurized when collecting filtered samples for metals.

3.4. <u>Contamination Prevention</u>:

- 3.4.1. Keep the bailer wrapped (foil, butcher paper, etc.) until just before use.
- 3.4.2. Use protective gloves to handle the bailer once it is removed from its wrapping.
- 3.4.3. Handle the bailer by the lanyard to minimize contact with the bailer surface.

4. LANYARDS

4.1. Lanyards must be made of non-reactive, non-leachable material. They may be cotton twine, nylon, stainless steel, or may be coated with Teflon, Polyethylene or PP.

4.2. Discard cotton twine, nylon, and non-stainless steel braided lanyards after sampling each monitoring well.

4.3. Decontaminate stainless steel, coated Teflon, Polyethylene and PP lanyards between monitoring wells (see FC 1003). They do not need to be decontaminated between purging and sampling operations.

FS 2210. GROUNDWATER PURGING

FS 2211. Water Level and Purge Volume Determination

Collect representative groundwater samples from the aquifer. The amount of water that must be purged from a well is determined by the volume of water and/or field parameter stabilization.

1. GENERAL EQUIPMENT CONSIDERATIONS

1.1. Selection of appropriate purging equipment depends on the analytes of interest, the well diameter, transmissivity of the aquifer, the depth to groundwater and other site conditions.

1.2. Use a pump to purge the well unless no other equipment can be used or there is non-aqueous phase liquid in the well or non-aqueous phase liquid is suspected to be in the well.

1.3. Bailers may be used if approved by an FDEP program, or if bailer use is specified in a permit, contract or FDEP order (see Table FS 2200-3). If used, bailers must be of appropriate type and construction, and the user must follow the procedure outlined in FS 2213, section 4, with no deviations. If in doubt about the appropriateness of using a bailer at a site or during a particular sampling event, contact the appropriate FDEP program or project manager. FDEP does not recommend using bailers because improper bailing:

1.3.1. Introduces atmospheric oxygen which may precipitate metals (i.e., iron) or cause other changes in the chemistry of the water in the sample (i.e., pH)

1.3.2. Agitates groundwater which may bias volatile and semi-volatile organic analyses due to volatilization

1.3.3. Agitates the water in the aquifer and resuspends fine particulate matter

1.3.4. Surges the well loosening particulate matter in the annular space around the well screen

1.3.5. May introduce dirt into the water column if the sides of the casing wall are scraped

2. INITIAL INSPECTION

2.1. Verify the identification of the monitoring well by examining markings, sign plates, placards or other designations.

2.2. Remove the well cover and remove all standing water around the top of the well casing (manhole) before opening the well cap.

2.3. Inspect the exterior protective casing of the monitoring well for damage and document the results of the inspection if there is a problem.

2.4. It is recommended that you place a protective covering around the well head. Replace the covering if it becomes soiled or ripped.

2.5. Inspect the well lock and determine whether the cap fits tightly. Replace the cap if necessary.

3. WATER LEVEL MEASUREMENTS: Use an electronic probe or chalked tape to determine the water level.

3.1. Decontaminate all equipment before use.

3.2. Measure the depth to groundwater from the top of well casing to the nearest 0.01 foot and always measure from the same reference point or survey mark on the well casing. If there is no reference mark, measure from the north side of the casing.

3.3. Record the measurement and the reference point.

3.4. Electronic Probe

3.4.1. Follow the manufacturer's instructions for use.

3.4.2. Record the measurement.

3.5. <u>Chalked Line Method:</u> This method is not recommended if collecting samples for organic or inorganic parameters.

3.5.1. Lower chalked tape into the well until the lower end is in the water (usually determined by the sound of the weight hitting the water).

3.5.2. Record the length of the tape relative to the reference point (see section 3.2 above).

3.5.3. Quickly remove the tape from the well.

3.5.4. Record the length of the wetted portion to the nearest 0.01 foot.

3.5.5. Determine the depth to water by subtracting the length of the wetted portion (see section 3.5.3 above) from the total length (see section 3.5.2 above). Record the result.

4. WATER COLUMN DETERMINATION

Do not determine the total depth of the well by lowering the probe to the bottom of the well before purging and sampling. If the well must be sounded, delay purging and sampling activities for at least 24 hours after the well was sounded or for a time sufficient to meet the purge stabilization criterion for turbidity. Alternatively, collect samples before sounding the well.

4.1. Subtract the depth to the top of the water column from the total well depth to determine the length of the water column.

4.2. The total well depth depends on the well construction. Some wells may be drilled in areas of sinkhole or karst formations or rock leaving an open borehole. Attempt to find the total borehole depth in cases where there is an open borehole below the cased portion.

5. WELL WATER VOLUME

5.1. Calculate the total volume of water in gallons in the well using the following equation:

V = (0.041)d x d x h

Where: V = volume in gallons

d = well diameter in inches

h = height of the water column in feet

5.2. The total volume of water in the well may also be determined with the following equation by using a casing volume per foot factor (Gallons per Foot of Water) for the appropriate diameter well:

V = [Gallons per Foot of Water] x h

Where: V = volume in gallons

h = height of the water column in feet

Casing Internal Diameter	Approximate Gallons per Foot of Water		
0.75"	. 0.02		
1"	0.04		
1.25"	0.06		
2"	0.16		
3"	0.37		
4"	0.65		
5"	1.02		
6"	1.47		
12"	5.88		

5.3. Record all measurements and calculations in the field records.

6. PURGING EQUIPMENT VOLUME

6.1. Calculate the total volume of the pump, associated tubing and container that is used for in situ measurements (flow container), if used, using the following equation:

V = p + ((0.041)d x d x l) + fc

Where: V = volume in gallons

p = volume of pump in gallons

d = tubing diameter in inches

I = length of tubing in feet

fc = volume of flow cell in gallons

7. When collecting samples from multiple wells on a site, if the groundwater elevation data are to be used to construct groundwater elevation contour maps, all water level measurements must be taken within the same 24-hour time interval unless a shorter time period is required by a FDEP program. If the site is tidally influenced, complete the water level measurements within the time frame of an incoming or outgoing tide.

FS 2212. Well Purging Techniques

The selection of the purging technique and equipment is dependent on the hydrogeologic properties of the aquifer, especially depth to groundwater and hydraulic conductivity. The intent of proper purging is to stabilize the water level in the well and minimize the hydraulic stress to the hydrogeologic formation.

Every attempt must be made to match the pumping rate with the recharge rate of the well before evaluating the purging completion criteria.

A flowchart which summarizes purging procedure options is in Figure FS 2200-2.

Equipment selection must comply with construction and configuration requirements specified in Table FS 2200-1 and the discussions in FS 2201.

1. MEASURING THE PURGE VOLUME: The volume of water that is removed during purging must be recorded. Therefore, you must measure the volume during the purging operation.

1.1. Collect the water in a graduated container and multiply the number of times the container was emptied by the volume of the container, or

1.2. Estimate the volume based on pumping rate. This technique may be used only if the pumping rate is constant. Determine the pumping rate by measuring the amount of water that is pumped for a fixed period of time or use a flow meter.

1.2.1. Calculate the amount of water that is discharged per minute:

 $D = \frac{Measured amount}{T}$

Total time in minutes

1.2.2. Calculate the time needed to purge one (1) well volume or one (1) purging equipment volume:

Time =
$$\frac{V}{D}$$

Where: V = well volume determined from FS 2211, section 5, or purging equipment volume D = discharge rate calculated in section 1.2.1. above

1.2.3. Make new measurements (see section 1.2.1 above) each time the pumping rate is changed, or

1.3. Use a totalizing flow meter.

1.3.1. Record the reading on the totalizer prior to purging.

1.3.2. Record the reading on the totalizer at the end of purging.

1.3.3. Subtract the reading on the totalizer prior to purging from the reading on the totalizer at the end of purging to obtain the volume purged.

- 1.4. Record in the field records the times that purging begins and ends.
- 2. STABILIZATION MEASUREMENT FREQUENCY

Begin to record stabilization measurements after pumping the minimum volume as prescribed below. Every attempt must be made to match the pumping rate with the recharge rate of the well before evaluating the purging criteria.

If the well screened interval is not known, use option 2.1 below.

2.1. <u>Wells with Fully Submerged Screen and Pump or Intake Tubing Placed at the Top of the Water</u> <u>Column (conventional purge)</u>: Purge a minimum of one (1) well volume prior to collecting measurements of the field parameters. Allow at least one quarter (1/4) well volume to purge between subsequent measurements.

2.2. <u>Wells with Fully Submerged Screen and Pump or Intake Tubing Placed Within the Screened Interval</u> (minimizing purge volume): Purge until the water level has stabilized (well recovery rate equals the purge rate), then purge a minimum of one (1) volume of the pump, associated tubing and flow container (if used) prior to collecting measurements of the field parameters. Take measurements of the field parameters no sooner than two (2) to three (3) minutes apart. Purge at least three (3) volumes of the pump, associated tubing and flow container, if used, prior to collecting a sample.

2.3. <u>Wells with a Partially Submerged Well Screen:</u> Purge a minimum of one (1) well volume prior to collecting measurements of the field parameters. Take measurements of the field parameters no sooner than two (2) to three (3) minutes apart.

3. PURGING COMPLETION: DEP recommends the use of a flow-through container to measure the stabilization parameters discussed below. Alternatively, measure all parameters *in situ* by inserting measurement probes into the well at the depth appropriate for the purging option. Purging is considered complete if the criteria in section 3.1, 3.2 or 3.3 below are satisfied. Make every attempt to satisfy the criteria in section 3.1. Every attempt must be made to match the pumping rate with the recharge rate of the well before evaluating the purging criteria.

3.1. Three (3) consecutive measurements of the five (5) parameters listed below must be within the stated limits. The measurements evaluated must be the last three consecutive measurements taken before purging is stopped. The range between the highest and the lowest values for the last three measurements of temperature, pH and specific conductance cannot exceed the stated limits. The last three consecutive measurements of dissolved oxygen and turbidity must all be at or below the listed thresholds.

- Temperature: ± 0.2° C
- pH: <u>+</u> 0.2 Standard Units
- Specific Conductance: ± 5.0% of reading
- Dissolved Oxygen: <a>
- Turbidity: ≤20 NTU

Document and report the following, as applicable, except that the last four (4) items only need to be submitted once:

- Purging rate.
- Drawdown in the well, if any.
- · Pump or tubing intake placement.
- · Length and location of the screened interval.
- A description of the process and the data used to design the well.
- The equipment and procedure used to install the well.
- The well development procedure.
- Pertinent lithologic or hydrogeologic information.

3.2. If the criteria in section 3.1 above for dissolved oxygen and/or turbidity cannot be met, then three (3) consecutive measurements of the five (5) parameters listed below must be within the stated limits. The measurements evaluated must be the last three consecutive measurements taken before purging is stopped. The range between the highest and the lowest values for the last three measurements cannot exceed the stated limits.

Temperature: + 0.2° C

pH: ± 0.2 Standard Units

- Specific Conductance: ± 5.0% of reading
- Dissolved Oxygen: <u>+</u> 0.2 mg/L or 10%, whichever is greater
- Turbidity: <u>+</u> 5 NTUs or 10%, whichever is greater

Additionally, document and report the following, as applicable, except that the last four (4) items only need to be submitted once:

- Purging rate.
- Drawdown in the well, if any.
- · Pump or tubing intake placement.
- · Length and location of the screened interval.
- A description of conditions at the site that may cause the Dissolved Oxygen to be high and/or Dissolved Oxygen measurements made within the screened or open hole portion of the well with a downhole dissolved oxygen probe.
- A description of conditions at the site that may cause the Turbidity to be high and any procedures that will be used to minimize Turbidity in the future.
- · A description of the process and the data used to design the well.
- The equipment and procedure used to install the well.
- The well development procedure.
- · Pertinent lithologic or hydrogeologic information.

If from review of the submitted data the Department determines that both the elevated Dissolved Oxygen and Turbidity measurements are due to naturally occurring conditions, then only the first four (4) items are required to be submitted in future reports. However, if the Department cannot determine if the Dissolved Oxygen or Turbidity is elevated due to naturally occurring conditions, then in addition to the first four (4) items, a description of the conditions at the site that may have caused the affected parameter(s) to be high is required to be submitted in future reports.

3.3. If the stabilization parameters in either section 3.1 or 3.2 cannot be met, and all attempts have been made to minimize the drawdown, check the instrument condition and calibration, purging flow rate and all

tubing connections to determine if they might be affecting the ability to achieve stable measurements. All measurements that were made during the attempt must be documented. The sampling team leader may decide whether or not to collect a sample or to continue purging after five (5) well volumes (conventional purge section 2.1 or 2.3 above) or five (5) volumes of the screened interval (minimizing purge volumes in section 2.2 above).

Further, the report in which the data are submitted must include the following, as applicable, except that the last four (4) items only need to be submitted once:

- · Purging rate.
- Pump or tubing intake placement.
- Length and location of the screened interval.
- Drawdown in the well, if any.
- A description of conditions at the site that may cause the Dissolved Oxygen to be high and/or Dissolved Oxygen measurements made within the screened or open hole portion of the well with a downhole dissolved oxygen probe.
- A description of conditions at the site that may cause the turbidity to be high and any procedures that will be used to minimize turbidity in the future.
- A description of the process and the data used to design the well.
- The equipment and procedure used to install the well.
- The well development procedure.
- Pertinent lithologic or hydrogeologic information.

If from review of the submitted data the FDEP determines that both the elevated Dissolved Oxygen and Turbidity measurements are due to naturally occurring conditions, then only the first four (4) items are required to be submitted in future reports. However, if the FDEP cannot determine if the Dissolved Oxygen or Turbidity is elevated due to naturally occurring conditions, then in addition to the first four (4) items, a description of the conditions at the site that may have caused the affected parameter(s) to be high is required to be submitted in future reports.

3.4. One fully dry purge (not recommended). This criterion applies only if purging was attempted per FS 2212, FS 2213, and section 3.4.1 below, and if it is impossible to balance the pumping rate with the rate of recharge at very low pumping rates (< 100 mL/minute).

3.4.1. If wells have previously and consistently purged dry, when purged according to FS 2212 and FS 2213, and the current depth to groundwater indicates that the well will purge dry during the current sampling event, minimize the amount of water removed from the well by using the same pump to purge and collect the sample:

3.4.1.1 Place the pump or tubing intake within the well screened interval.

3.4.1.2 Use very small diameter Teflon, Polyethylene or PP tubing and the smallest possible pump chamber volume to minimize the total volume of water pumped from the well and to reduce drawdown.

3.4.1.3 Select tubing that is thick enough to minimize oxygen transfer through the tubing walls while pumping.

3.4.1.4 Pump at the lowest possible rate (100 mL/minute or less) to reduce drawdown to a minimum.

3.4.1.5 Purge at least two (2) volumes of the pumping system (pump, tubing and flow cell, if used).

3.4.1.6 Measure pH, Specific Conductance, Temperature, Dissolved Oxygen and Turbidity and begin to collect the samples (see FS 2222).

4. Collect samples immediately after purging is complete. The time period between completing the purge and sampling cannot exceed six (6) hours. If sample collection does not occur within one (1) hour of purging completion, re-measure the five (5) field parameters Temperature, pH, Specific Conductance, Dissolved Oxygen and Turbidity just prior to collecting the sample. If the measured values are not within 10 percent of the previous measurements, re-purge the well. The exception is "dry" wells (see section 3.4 above).

- 5. LANYARDS
 - 1.2. Securely fasten lanyards, if used, to any downhole equipment (bailers, pumps, etc.).
 - 1.3. See FS 2201, section 4, for acceptable lanyard types and use.
 - 1.4. Use bailer lanyards in such a way that they do not touch the ground surface.

FS 2213. Purging Wells Without Plumbing (Monitoring Wells)

1. TUBING/PUMP PLACEMENT

1.1. Do not lower the pump or tubing to the bottom of the well. Pump or tubing placement will be determined by the purging option selected in FS 2212, section 2 above. <u>Minimizing Purge Volume</u>: If the following conditions can be met, position the intake hose or pump at the midpoint of the screened or open hole interval.

- The same pump must be used for both purging and sampling,
- The well screen interval must be less than or equal to 10 feet, and
- The well screen must be fully submerged.

1.2. <u>Conventional Purging</u>: Position the pump or intake tubing in the top one foot of the water column or no deeper than necessary for the type of pump. If purging with a bailer, see section 4 below.

1.3. <u>Partially Submerged Screened Interval:</u> If the well screen or borehole is partially submerged, and the pump will be used for both purging and sampling, position the pump midway between the measured water level and the bottom of the screen. Otherwise position the pump as described in section 1.2 above. If purging with a bailer, see section 4 below.

- 2. NON-DEDICATED (PORTABLE) PUMPS
 - 2.1. Variable Speed Peristaltic Pump
 - 2.1.1. Attach a short section of tubing to the discharge side of the pump and into a graduated container.
 - 2.1.2. Attach one end of a length of new or precleaned tubing to the pump head flexible hose.
 - 2.1.3. Place the tubing per one of the options in FS 2213, section 1 above.
 - 2.1.4. Measure the depth to groundwater at frequent intervals.
 - 2.1.5. Record these measurements.

2.1.6. Adjust the purging rate so that it is equivalent to the well recovery rate to minimize drawdown.

2.1.7. If the purging rate exceeds the well recovery rate, reduce the pumping rate to balance the withdrawal rate with the recharge rate.

2.1.8. If the water table continues to drop during pumping, lower the tubing at the approximate rate of drawdown so that the water is removed from the top of the water column.

2.1.9. Record the purging rate each time the rate changes.

2.1.10. Measure the purge volume by one of the methods outlined in FS 2212, section 1.

2.1.11. Record this measurement.

2.1.12. Decontaminate the pump and tubing between wells (see FC 1000) or only the pump if precleaned tubing is used for each well.

2.2. Variable Speed Centrifugal Pump

2.2.1. Position fuel powered equipment **downwind** and at least 10 feet from the well head. Make sure that the exhaust faces downwind.

2.2.2. Place the decontaminated suction hose so that water is always pumped from the top of the water column.

2.2.3. Equip the suction hose with a foot valve to prevent purge water from re-entering the well.

2.2.4. Measure the depth to groundwater at frequent intervals.

2.2.5. Record these measurements.

2.2.6. Adjust the purging rate so that it is equivalent to the well recovery rate to minimize drawdown.

2.2.7. If the purging rate exceeds the well recovery rate, reduce the pumping rate to balance the withdrawal rate with the recharge rate.

2.2.8. If the water table continues to drop during pumping, lower the tubing at the approximate rate of drawdown so that the water is removed from the top of the water column.

2.2.9. Record the purging rate each time the rate changes.

2.2.10. Measure the purge volume by one of the methods outlined in FS 2212, section 1.

2.2.11. Record this measurement.

2.2.12. Decontaminate the pump and tubing between wells (see FC 1000) or only the pump if precleaned tubing is used for each well.

2.3. Variable Speed Electric Submersible Pump

2.3.1. Position fuel powered equipment **downwind** and at least 10 feet from the well head. Make sure that the exhaust faces downwind.

2.3.2. Carefully position the decontaminated pump per one of the options in FS 2213, section 1 above.

2.3.3. Measure the depth to groundwater at frequent intervals.

2.3.4. Record these measurements.

2.3.5. Adjust the purging rate so that it is equivalent to the well recovery rate to minimize drawdown.

2.3.6. If the purging rate exceeds the well recovery rate, reduce the pumping rate to balance the withdrawal rate with the recharge rate.

2.3.7. If the water table continues to drop during pumping, lower the tubing or pump at the approximate rate of drawdown so that the water is removed from the top of the water column.

2.3.8. Record the purging rate each time the rate changes.

2.3.9. Measure the purge volume by one of the methods outlined in FS 2212, section 1.

2.3.10. Record this measurement.

2.3.11. Decontaminate the pump and tubing between wells (see FC 1000) or only the pump if precleaned tubing is used for each well.

2.4. Variable Speed Bladder Pump

2.4.1. Position fuel powered equipment **downwind** and at least 10 feet from the well head. Make sure that the exhaust faces downwind.

2.4.2. Attach the tubing and carefully position the pump per one of the options in FS 2213, section 1 above.

2.4.3. Measure the depth to groundwater at frequent intervals.

2.4.4. Record these measurements.

2.4.5. Adjust the purging rate so that it is equivalent to the well recovery rate to minimize drawdown.

2.4.6. If the purging rate exceeds the well recovery rate, reduce the pumping rate to balance the withdrawal rate with the recharge rate.

2.4.7. If the water table continues to drop during pumping, lower the tubing or pump at the approximate rate of drawdown so that the water is removed from the top of the water column.

2.4.8. Record the purging rate each time the rate changes.

2.4.9. Measure the purge volume by one of the methods outlined in FS 2212, section 1.

2.4.10. Record this measurement.

2.4.11. Decontaminate the pump and tubing between wells (see FC 1000) or only the pump if precleaned tubing is used for each well.

3. DEDICATED PORTABLE PUMPS: Place dedicated pumps per one of the options in FS 2213, section 1 above.

3.1. Variable Speed Electric Submersible Pump

3.1.1. Position fuel powered equipment **downwind** and at least 10 feet from the well head. Make sure that the exhaust faces downwind.

3.1.2. Measure the depth to groundwater at frequent intervals.

3.1.3. Record these measurements.

3.1.4. Adjust the purging rate so that it is equivalent to the well recovery rate to minimize drawdown.

3.1.5. If the purging rate exceeds the well recovery rate, reduce the pumping rate to balance the withdraw with the recharge rate.

3.1.6. Record the purging rate each time the rate changes.

3.1.7. Measure the purge volume by one of the methods outlined in FS 2212, section 1.

3.1.8. Record this measurement.

3.2. Variable Speed Bladder Pump

3.2.1. Position fuel powered equipment **downwind** and at least 10 feet from the well head. Make sure that the exhaust faces downwind.

3.2.2. Measure the depth to groundwater at frequent intervals.

3.2.3. Record these measurements.

3.2.4. Adjust the purging rate so that it is equivalent to the well recovery rate to minimize drawdown.

3.2.5. If the purging rate exceeds the well recovery rate, reduce the pumping rate to balance the withdraw with the recharge rate.

3.2.6. Record the purging rate each time the rate changes.

3.2.7. Measure the purge volume by one of the methods outlined in FS 2212, section 1.

3.2.8. Record this measurement.

4. BAILERS: FDEP recommends against using bailers for purging except as a last contingency, or if free product is present in the well or suspected to be in the well. However, they may be used if approved by an FDEP program, or specified in a permit, contract or FDEP order (see Table FS 2200-3 and FS 2211, section 1.3). If in doubt about the appropriateness of using a bailer at a site or during a particular sampling event, contact the appropriate FDEP program or project manager.

- 4.1. Minimize handling the bailer as much as possible.
 - 4.1.1. Remove the bailer from its protective wrapping just before use.

4.1.2. Attach a lanyard of appropriate material (see FS 2201, section 4).

4.1.3. Use the lanyard to move and position the bailer.

4.2. Lower and retrieve the bailer slowly and smoothly.

4.2.1. Lower the bailer carefully into the well to a depth approximately a foot above the water column.

4.2.1.1. When the bailer is in position, lower the bailer into the water column at a rate of 2 cm/sec until the desired depth is reached (see section 4.2.2 below).

4.2.2. Do not lower the top of the bailer more than one (1) foot below the top of the water table so that water is removed from the top of the water column. Ensure that the length of the bailer does not exceed the length of the water column.

4.2.3. Allow time for the bailer to fill with aquifer water as it descends into the water column.

4.2.3.1. Carefully raise the bailer. Retrieve the bailer at the same rate of 2 cm/sec until the bottom of the bailer has cleared to top of the water column.

4.3. Measure the purge volume by one of the methods outlined in FS 2212, section 1.

4.3.1. Record the volume of the bailer.

4.4. Continue to carefully lower and retrieve the bailer as described above until the purging completion conditions specified in FS 2212, section 3, have been satisfied.

4.4.1. Remove at least one (1) well volume before collecting measurements of the field parameters. Take each subsequent set of measurements after removing at least one quarter (1/4) well volume between measurements.

FS 2214. Purging Wells With Plumbing (production wells or permanently installed pumps equipped with sampling ports or sampling spigots)

Wells with in-place plumbing are commonly found at municipal water treatment plants, industrial water supplies, private residences, etc.

1. CONTINUOUSLY RUNNING PUMPS

- 1.1. Select the spigot that is closest to the pump and before any storage tanks (if possible).
- 1.2. Remove all hoses, aerators and filters (if possible).
- 1.3. Open the spigot and purge at maximum flow.

1.4. If a storage tank is located between the pump and the spigot, purge the volume of the tank, lines and spigot.

1.5. If the spigot is before any storage tank, purge until sufficient volume is removed to flush the stagnant water from the spigot and the tap line to the spigot.

1.6. Reduce the flow rate to \leq 500 mL/minute (a 1/8" stream) or approximately 0.1 gal/minute before collecting samples. When sampling for volatile organic compounds, reduce the flow to \leq 100 mL/minute before collecting the samples.

2. INTERMITTENTLY RUNNING PUMPS

2.1. Open the spigot and purge sufficient volume to flush the spigot and lines and until the purging completion criteria in FS 2212, section 3, have been met.

2.2. Reduce the flow rate to \leq 500 mL/minute (a 1/8" stream) or approximately 0.1 gal/minute before collecting samples. When sampling for volatile organic compounds, reduce the flow to \leq 100 mL/minute before collecting the samples.

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Appendix B

FS 2100. Surface Water Sampling

See also the following Standard Operating Procedures:

- FA 1000 and 2000 Administrative Procedures
- FC 1000 Cleaning/Decontamination Procedures
- FD 1000-9000 Documentation Procedures
- FM 1000 Field Planning and Mobilization
- FQ 1000 Field Quality Control Requirements
- FS 1000 General Sampling Procedures
- FS 2000 General Aqueous Sampling
- FS 2400 Wastewater Sampling
- FT 1000 General Field Testing and Measurement
- 1. INTRODUCTION AND SCOPE

1.1. This section presents standard operating procedures to be used to consistently collect representative surface water samples. Each collection event must be performed so that samples are neither contaminated nor altered from improper handling.

1.2. The following topics include acceptable equipment selection and equipment construction materials; and standard grab, depth-specific and depth-composited surface water sampling techniques. Information regarding sample types and flow- or time-weighted aqueous sampling is found in FS 2420.

2. GENERAL CAUTIONS

When using watercraft, take samples near the bow, away and upwind from any gasoline outboard engine. Orient watercraft so that bow is positioned in the upstream direction.

When wading, collect samples upstream from the body.

Avoid disturbing sediments in immediate area of sample collection.

Collect water samples prior to taking sediment samples when obtaining both from the same area (site).

Consider the representativeness of selected sampling locations, for example, when attempting to characterize a water body that may be stratified or heterogeneous.

Unless dictated by permit, program or order, sampling at or near structures (e.g., dams, weirs or bridges) may not provide representative data because of unnatural flow patterns.

Collect surface water samples from downstream towards upstream.

3. EQUIPMENT AND SUPPLIES

3.1. Use sampling equipment constructed of materials consistent with the analytes of interest. Refer to FS 1000, Tables 1000-1 and 1000-2 for material selection. Select equipment based on the analytes of interest, the specific equipment use and the available equipment. Refer to FS 1000, Table 1000-3 for selection of appropriate equipment.

3.2. For information on sample container size and construction, preservation and holding time requirements, see FS 1000, Tables 1000-4 through 1000-9.

- 3.3. For information on sampling equipment cleaning requirements, see FC 1000.
- 3.4. For information on documentation requirements, see FD 1000.

FS 2110. SURFACE WATER SAMPLING TECHNIQUES

Use the following protocols when collecting surface water samples. Adhere to all general protocols applicable to aqueous sampling detailed in FS 2000 when following the surface water sampling procedures addressed below.

1. MANUAL SAMPLING: Use manual sampling for collecting grab samples for immediate in-situ field analyses. Also use manual sampling in lieu of automatic equipment over extended periods of time for composite sampling, especially when it is necessary to observe and/or note unusual conditions.

1.1. Surface Grab Samples

Collect surface grab samples within the top 12 inches of the water column. Avoid skimming the surface of the water during collection unless specifically required by the sampling plan. Very shallow water bodies may require careful techniques of sample collection to avoid disturbing sediments

Where practical, use the actual sample container as the collection device (direct grab). Sample containers attached to poles are also considered direct grabs.

The use of unpreserved sample containers is encouraged since the same container can be submitted for laboratory analysis after appropriate preservation. This procedure reduces sample handling and potential loss of analytes or contamination of the sample from other sources (e.g., additional sampling equipment, environment, etc.).

1.1.1. Direct Grab Technique

1.1.1.1. Use an unpreserved sample container to collect the sample.

1.1.1.2. Slowly remove the container cap and slowly submerge the container, opening first, into the water.

1.1.1.3. Invert the bottle so the opening is upright and pointing towards the direction of water flow (if applicable). Allow water to run slowly into the container until filled.

1.1.1.4. Return the filled container quickly to the surface.

1.1.1.5. Pour out a small volume of sample away from and downstream of the sampling location. This procedure allows for addition of preservatives and sample expansion. Do not use this step for volatile organics or other analytes where headspace is not allowed in the sample container.

1.1.1.6. Add preservatives, if required, securely cap container, label and complete field notes.

1.1.1.7. If preservatives have been added, invert the container several times to ensure sufficient mixing of sample and preservatives.

1.1.1.8. Check preservation of the sample and adjust pH with additional preservative, if necessary.

1.1.2. <u>Sampling with an Intermediate Vessel or Container</u>: If the sample cannot be collected directly into the sample container to be submitted to the laboratory or if the laboratory provides prepreserved sample containers, use an unpreserved sample container or an intermediate vessel (e.g., beakers, buckets or dippers) to obtain the sample. These vessels must be constructed appropriately including any poles or extension arms used to access the sample location.

1.1.2.1. Rinse the intermediate vessel with ample amounts of site water prior to collecting the first sample. Discard rinsate away from or downstream of the sampling location.

1.1.2.2. After adequate rinsing, fill the intermediate vessel with sample water. Minimize agitation of the sample.

1.1.2.3. Fill sample containers from the intermediate vessel. Minimize agitation during filling. Do not touch the sample container with the intermediate vessel.

1.1.2.4. Leave adequate headspace in the sample container. This procedure allows for addition of preservatives (if required) and sample expansion. Do not use this step for volatile organics or other analytes where headspace is not allowed in the sample container.

1.1.2.5. Add preservatives if required, securely cap container, label and complete field notes.

1.1.2.6. Invert the container several times to ensure sufficient mixing of sample and preservatives.

1.1.2.7. Check preservation of the sample and adjust pH with additional preservative, if necessary.

1.1.3. <u>Pump and Tubing</u>: Use appropriate pumps, equipment and tubing. (See restrictions listed in FS 1000 Tables FS 1000-1 through 1000-3).

Do not collect oil & grease, TRPH or FL-PRO samples with a pump. See FS 2000 for proper collection procedures for extractable organics and volatile organic compounds.

1.1.3.1. Lower tubing to a depth 6-12 inches below water surface, where possible.

1.1.3.2. Pump several tubing volumes through the system to flush the tubing prior to collecting the first sample.

1.1.3.3. Fill individual sample bottles via the discharge tubing, being careful not to remove the inlet tubing from the water.

1.1.3.4. Do not touch the discharge tubing to the sample container.

1.1.3.5. Leave adequate headspace in the sample container. This procedure allows for addition of preservatives (if required) and sample expansion. Do not use this step for volatile organics or other analytes where headspace is not allowed in the sample container.

1.1.3.6. Add preservatives if required, securely cap container, label and complete field notes.

1.1.3.7. Invert the container several times to ensure sufficient mixing of sample and preservatives.

1.1.3.8. Check preservation of the sample and adjust pH with additional preservative, if necessary.

1.2. <u>Depth Grab Samples</u>: Examples of equipment that may be used for depth grab sampling include Kemmerer, Niskin, Van Dorn and similar samplers; pumps with tubing and double check-valve bailers. See restrictions listed in FS 1000 Tables 1000-1, 1000-2 and 1000-3. Do not collect oil & grease, TRPH or FL-PRO samples with a pump. See FS 2000 for proper collection procedures for extractable organics and volatile organic compounds.

1.2.1. Kemmerer, Niskin and Van Dorn Type Devices

1.2.1.1. Many of these samplers are constructed of plastic and rubber that preclude their use for all volatile and extractable organic sampling. Some newer devices are constructed of stainless steel or are all Teflon or Teflon-coated. These are acceptable for all analyte groups without restriction.

1.2.1.2. Measure the water column to determine maximum depth and sampling depth prior to lowering the sampling device.

1.2.1.3. Mark the line attached to the sampler with depth increments so that the sampling depth can be accurately recorded.

1.2.1.4. Lower the sampler slowly to the appropriate sampling depth, taking care not to disturb the sediments.

1.2.1.5. At the desired depth, send the messenger weight down to trip the closure mechanism.

1.2.1.6. Retrieve the sampler slowly.

1.2.1.7. Rinse the sampling device with ample amounts of site water prior to collecting the first sample. Discard rinsate away from and downstream of the sampling location.

1.2.1.8. Fill the individual sample bottles via the discharge tube. Sample bottles must be handled as described in sections 1.1.3.3 - 1.1.3.8 above.

1.2.2. <u>Double Check-Valve Bailers</u>: Collect samples using double check-valve bailers if the data requirements do not necessitate a sample from a strictly discrete interval of the water column. Bailers with an upper and lower check-valve can be lowered through the water column and water will continually be displaced through the bailer until the desired depth is reached, at which point the bailer is retrieved.

1.2.2.1. Sampling with this type of bailer must follow the same protocols outlined in section 1.2.1 above except that a messenger weight is not applicable.

1.2.2.2. Although not designed specifically for this kind of sampling, a bailer is acceptable when a mid-depth sample is required.

1.2.2.3. Note: This sampler does not perform as well as the devices described above or the pump and tubing described in section 1.2.3 below.

1.2.2.4. As the bailer is dropped through the water column, water is displaced through the body of the bailer. The degree of displacement depends upon the check-valve ball movement to allow water to flow freely through the bailer body.

1.2.2.5. Slowly lower the bailer to the appropriate depth. Upon retrieval, the two check-valves seat, preventing water from escaping or entering the bailer.

1.2.2.6. Rinse the sampling device with ample amounts of site water prior to collecting the first sample.

1.2.2.7. Fill the individual sample bottles via the discharge tube. Sample bottles must be handled as described in sections 1.1.3.3 - 1.1.3.8 above.

1.2.3. <u>Pump and Tubing</u>: Use appropriate pumps, equipment and tubing. (See restrictions listed in FS 1000 Tables 1000-1, 1000-2 and 1000-3). Do not collect oil & grease, TRPH or FL-PRO samples with a pump. See FS 2000 for proper collection procedures for extractable organics and volatile organic compounds.

1.2.3.1. Measure the water column to determine the maximum depth and the sampling depth.

1.2.3.2. Tubing will need to be tied to a stiff pole or be weighted down so the tubing placement will be secure. Do not use a lead or metallic weight if collecting metals samples. Any dense, non-contaminating, non-interfering material will work (brick, stainless steel weight, etc.). The the weight with a lanyard (braided or monofilament nylon, etc.) so that it is located below the inlet of the tubing.

1.2.3.3. Pump several tubing volumes through the system to flush the tubing prior to collecting the first sample.

1.2.3.4. Fill the individual sample bottles via the discharge tube, being careful not to remove the inlet tubing from the water. Do not touch the discharge tubing to the sample container.

1.2.3.5. Leave adequate headspace in the sample container. This procedure allows for addition of preservatives (if required) and sample expansion. Do not use this step for volatile organics or other analytes where headspace is not allowed in the sample container.

1.2.3.6. Add preservatives if required, securely cap container, label and complete field notes.

1.2.3.7. Invert the container several times to ensure sufficient mixing of sample and preservatives.

1.2.3.8. Check preservation of the sample and adjust pH with additional preservative, if necessary.

2. AUTOMATIC SAMPLERS: Use automatic samplers when several sites are to be sampled at frequent intervals or when a continuous sample is required. Composite samplers can be used to collect time composite or flow proportional samples. Use appropriate equipment and tubing. (See restrictions listed in FS 1000 Tables 1000-1, 1000-2 and 1000-3). Do not collect oil & grease, TRPH or FL-PRO samples with automatic samplers unless required by the sampling plan. See FS 2000 for proper collection procedures for extractable organics and volatile organic compounds

The use of automatic samplers for collecting surface water samples will more frequently run into situations where sampling equipment is deployed on-site for a long term or dedicated to the site.

2.1. Installing and Programming the Composite Sampler

2.1.1. Use all new or precleaned pump tubing each time the sampler is brought to the field and set up. If the automatic sampler is deployed in the field for extended periods, it is recommended to replace the tubing at a minimum of every six months. Other replacement schedules may be required, depending on the specific installation and

project requirements. Inspect the tubing each time the composite-sample container is picked up. If there is evidence of loss of elasticity or discoloration or other conditions that would impact the quality of the sample (such as algal growth), or the pumping flow rate, then replace the tubing. Select the tubing for the pump head and sampling train according to the analytes of interest and the allowable construction materials specified in FS 1000 Table FS 1000-1, 1000-2 and 1000-3.

2.1.1.1. Cut the proper length of precleaned Teflon or Tygon tubing.

2.1.1.2. <u>Equipment Blanks</u>: Collect equipment blanks each time the tubing is changed or at a frequency of 5% of the tubing changes, whichever is less. Collect a minimum of one blank each year. Collect the blank by passing analyte-free water through the equipment that is exposed to the sample.

• Composite sample containers may be cleaned either in the field or in a fixed base operation. Demonstrate cleaning effectiveness by collecting equipment blanks on the composite sample containers according to the frequency specified in FQ 1000. Collect sample container equipment blanks by adding analyte-free water to the cleaned sample container, mix the water thoroughly within the container and then pour off an aliquot for analysis.

2.1.1.3. Put the collection sieve and tubing in the appropriate sample location, using conduit if necessary to hold it in place. Ensure the supporting conduit does not contaminate the incoming sample water.

2.1.1.4. Program the sampler per manufacturer's directions and as required in the permit or work plan conditions.

2.1.1.5. Automatic Sampler Security: Place a lock or seal on the sampler to prevent or detect tampering. This procedure, however, does not prevent tampering with the sampler tubing. See additional discussions on sample security in FS 2410, section 2.3.2.

2.2. Sample Acquisition

2.3.1. At the end of each sampling period, stir the contents of the composite jug and siphon the contents (poured if no visible solids) into the respective containers. If the sampler was configured to collect discrete samples ensure that the contents of each container are adequately mixed while pouring the sample into the sample container.

2.3.2. Immediately preserve the sample, if required, securely cap container, label and complete field notes.

2.3. Long Term Deployment of Automatic Composite Samplers: In certain sampling situations, automatic composite samplers are permanently installed at surface water stations and remain in the field for months or even years. Under these conditions, there are specific sampling issues that need to be addressed.

2.3.1. Sample Preservation

2.3.1.1. If the only analyte of interest is Total Phosphorus and the project is unrelated to an NPDES permit, the sample must be chemically preserved with sulfuric acid (H_2SO_4) but it need not be cooled to 4°C with wet ice.

 The acid must be in the container prior to drawing the first composite sample into the container.

When using large (i.e., 3 gallon) composite sample containers, and there is potential for the sample size to vary greatly due to variable flow rates at the site, the volume of acid for preservation should be small (e.g., 1 to 2 mL of 50% H_2SO_4). **Do not over acidify the sample**. Upon sample pick-up, if needed, add additional acid to achieve the proper pH adjustment for preservation.

• If parameters other than total phosphorus are to be analyzed, appropriate additional preservation (e.g., cooling with ice or refrigeration) is required.

2.3.1.2. Deviations from these SOPs concerning preservation and holding times relating to remote and long term deployments due to site specific considerations must be agreed upon by project management.

2.3.2. Cleaning Requirements

2.3.2.1. Clean composite sampler containers after collection of each composite sample using cleaning solutions and procedures specified in FC 1140, sections 5 through 9.

2.3.2.2. Composite sample containers may be cleaned either in the field or in a fixed based operation. Demonstrate cleaning effectiveness by collecting equipment blanks on the composite sample containers according to the frequency specified in FQ 1000. Collect sampler container equipment blanks by adding analyte-free water to the cleaned sample container, mix the water thoroughly within the container and then pour off an aliguot for analysis.

2.3.2.3. Inspect and replace tubing at a minimum of every six months or when applicable, as discussed in section 2.1.1 above. Collect equipment blanks as specified in section 2.1.1.2 above. If the tubing is being replaced for multiple autosamplers at the same time, one equipment blank may be collected on the entire length of replacement tubing. Collect this equipment blank by passing analyte-free water through the entire length of new tubing.

FS 2120. REFERENCES

1. U.S. Environmental Protection Agency, Region 4, <u>Environmental Investigations Standard</u> Operating Procedures and Quality Assurance Manual, May 1996.