
Determination of vertical and horizontal pathways of injected fresh wastewater into a deep saline aquifer (Florida, USA) using natural chemical tracers

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Abstract Two deep-well injection sites in south Florida, USA, inject an average of 430 million liters per day (MLD) of treated domestic fresh wastewater into a deep saline aquifer 900m below land surface. Elevated levels of NH_3 (highest concentration $939\mu\text{mol}$) in the overlying aquifer above ambient concentrations (concentration less than $30\mu\text{mol}$) were evidence of the upward migration of injected fluids. Three pathways were distinguished based on ammonium, chloride and bromide ratios, and temperature. At the South District Wastewater Treatment Plant, the tracer ratios showed that the injectate remained chemically distinct as it migrated upwards through rapid vertical pathways via density-driven buoyancy. The warmer injectate (mean 28°C) retained the temperature signal as it vertically migrated upwards; however, the temperature signal did not persist as the injectate moved horizontally into the overlying aquifers. Once introduced, the injectate moved slowly horizontally through the aquifer and mixed with ambient water. At the North District Wastewater Treatment Plant, data provide strong evidence of a one-time pulse of injectate into the overlying aquifers due to improper well construction. No evidence of rapid vertical pathways was observed at the North District Wastewater Treatment Plant.

Keywords Waste disposal · Deep well injection · Carbonate rocks · Confining units · Ammonia · Temperature · USA

Introduction

Deep well injection of treated municipal wastewater into non-potable aquifers has been used as an alternative to discharge of wastewater to surface waters for many decades. There are 430 permitted municipal wastewater deep injection wells in the United States, with 163 in Florida alone (USEPA 2008). These deep aquifers tend to be saline, and the discharge of fresh wastewater into them has raised concerns of geochemical reactions as a result of the mixing of the two waters, as well as the buoyant transport of the wastewater upwards into overlying aquifers. Confined brackish aquifers in Florida have been used extensively for aquifer storage and recovery (ASR) of potable freshwater (Arthur et al. 2001; Renken et al. 2005), and deeper saline aquifers have been used for disposal of waste fluids such as oil brines, industrial water and municipal wastewater (Meyer 1989a; Meyer 1989b). ASR in Florida has been extensively studied as part of the Comprehensive Everglades Restoration Plan (Reese 2002; Mirecki 2004; Mirecki 2006), however little research has been published regarding the fate and transport of the treated wastewater into deep saline aquifers (Meyer 1989a; Haberfeld 1991, Maliva and Walker 1998; Bloetscher et al. 2005; Bloetscher and Muniz 2006; Maliva et al. 2007).

Miami-Dade County Water and Sewer Department (MDWASD), located in southern Florida, currently discharges 430 million liters per day (MLD) of treated domestic wastewater into a saline deep aquifer at two locations in the county. Deep well injection has been in use in Miami-Dade County since the late 1960s. The injection facilities are located in the north and south of the county, separated by 44 km (Fig. 1). The South District Wastewater Treatment Plant (SDWWTP) site was placed into service in 1983, and is currently permitted for the disposal of 367 MLD of treated wastewater. The North District Wastewater Treatment Plant (NDWWTP) site was placed into service in 1997, and is permitted for 90 MLD.

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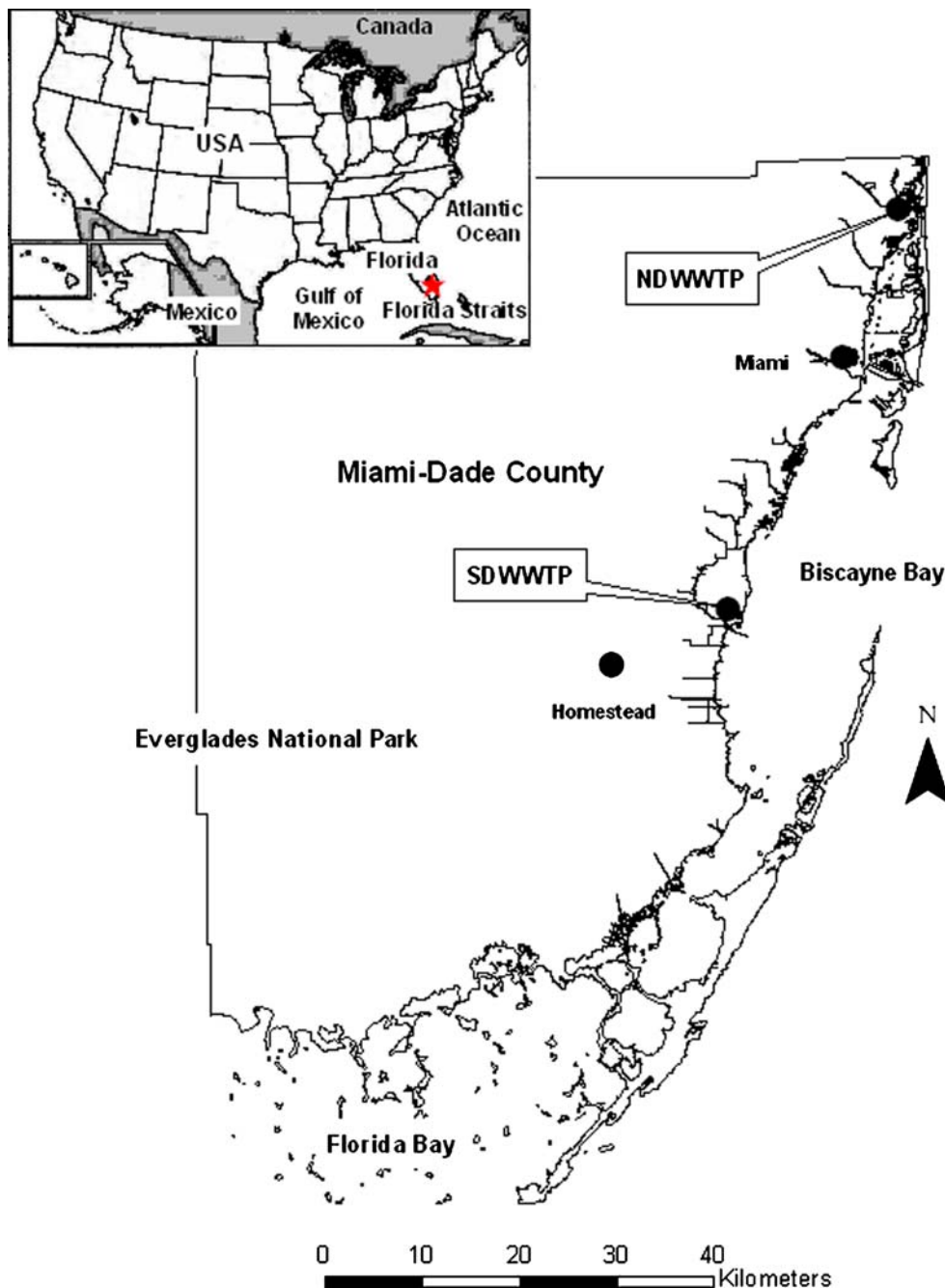
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Fig. 1 Location of the *NDWWTP* and the *SDWWTP* study sites



Both facilities treat domestic wastewater to above secondary drinking water standards, and discharge the treated wastewater into United States Environmental Protection Agency (USEPA) Class I injection wells. The treated wastewater is injected into the Boulder Zone, a highly transmissive interval in the deep saline non-potable Lower Floridan Aquifer. The Boulder Zone has been thought to be hydrologically separated from overlying aquifers by a 335-m-thick confining unit. During the installation of additional monitoring wells at the SDWWTP in 1994, ammonia-nitrogen ($\text{NH}_3\text{-N}$) was detected at 442 m depth in the overlying aquifer at a concentration of 411 micromoles per liter (μmol), above reported background levels of 29 μmol

(BC&E/CH2M Hill 1977). The detection of $\text{NH}_3\text{-N}$ in the aquifers above the Boulder Zone has raised doubts regarding the efficacy of the confining unit and the resultant water quality impact to overlying aquifers, as these aquifers are used as alternative water supplies via storage of freshwater (ASR) and blending with potable surficial aquifer water.

Research has focused on ASR in south Florida (Arthur et al. 2001; Reese 2002; Mirecki 2004; Mirecki 2006; Reese and Richardson 2008); however, few studies have been conducted regarding the transport and fate of injected effluent into the Boulder Zone, and typically these had to do with the relative risk of deep well injection versus ocean outfall disposal of municipal waste (Englehardt et

al. 2001; USEPA 2003; Bloetscher et al. 2005; Bloetscher and Muniz 2006). Recently, researchers have studied the transport mechanisms of the observed migrated injectate, and have suggested density-driven buoyant transport mechanism along natural or anthropogenic vertical fractures in the lower aquifers (Maliva and Walker 1998; McNeill 2000; McNeill 2002; Maliva et al. 2007; Walsh and Price 2008). The objective of this study was to determine migration pathways of injected treated wastewater at two facilities in Miami-Dade County, Florida (SDWWTP and NDWWTP) using historical time series data and major ion data collected as part of this study. The methodology developed for this study used chloride (Cl^-), bromide (Br^-) and NH_3 as tracers. This methodology provided a method for estimating transport pathways, and involved no additional collection of data other than what was typically required under federal and state regulatory programs.

Natural inorganic tracers have been used extensively in water resources investigations to trace groundwater flow paths and calculate mixed water ratios (Langmuir 1997; Davis et al. 1998; Herczeg and Edmunds 2000). Cl^- and Br^- commonly are used as they tend to be conservative, and their ratios may also give information as to the source and pathways of water. Studies have been conducted in south Florida (Shinn et al. 1994; Paul et al. 1997; Corbett et al. 2000; Böhlke et al. 2003) and elsewhere (Kaehler and Belitz 2003; Clark et al. 2004), tracing treated wastewater in surficial aquifers, but NH_3 was not used as a tracer as it does not behave conservatively in oxic waters. In this study, a novel application of Cl^- , Br^- and NH_3 as conservative tracers of injectate was developed as part of mixing models to distinguish pathways between the deep aquifers. Cl^- is a natural anion in the Floridan aquifer system, and its principal source is seawater, as there are no evaporite minerals to provide an additional source (Sprinkle 1989; Reese 1994). The seawater source of Cl^- in south Florida is thought to be the result of either incomplete flushing of Pleistocene seawater and brackish water intrusion, and/or the result of the cyclic flow based on thermal upwelling of Holocene intruded seawater (Kohout 1965; Sprinkle 1989; Reese 1994). Bromide (Br^-) behaves similar to Cl^- in groundwater systems (Davis et al. 1998), and in south Florida the source of Br^- in groundwater is similar to that of Cl^- although its natural abundances are orders of magnitude less than Cl^- . The only source of the NH_3 is the injectate and, therefore, it was used to trace transport pathways of the injected wastewater.

Geologic and hydrogeologic framework

The Floridan aquifer system (FAS) in southeastern Florida is defined by a vertically continuous sequence of permeable carbonate rocks of Cenozoic age that are hydraulically connected in varying degrees (Miller 1986). The aquifer matrix consists of carbonate and dolomitic limestones, dating from the Paleocene to the Oligocene

epochs. Overlying the FAS are the impermeable sediments of the late Oligocene to Pliocene age Hawthorn Group, a 180-m-thick confining layer of clays, siltstones and silty limestones. The Hawthorn Group separates the Upper Floridan Aquifer from the late Pliocene and Pleistocene formations making up the Surficial Aquifer System which includes the Biscayne Aquifer in south Florida (Fig. 2). The Biscayne Aquifer is an unconfined surficial aquifer and is the major source of potable water in south Florida (Fish and Stewart 1991).

The Floridan Aquifer contains several highly permeable and less permeable zones, with zones of highest permeabilities typically occurring at or near unconformities and usually parallel to the bedding planes (Meyer 1989a). Previous studies (Miller 1986; Reese 1994) grouped the Floridan aquifer system into three hydrostratigraphic units (Fig. 2), the Upper Floridan Aquifer (UFA), the Middle Confining Unit (MCU), and the Lower Floridan Aquifer. Recently the MCU in south Florida has been divided into the MC1 and MC2 (Fig. 2), separated by the Avon Park permeable layer (Reese and Richardson 2008), which in south Florida had previously been identified as the Middle Floridan Aquifer. The Upper Floridan Aquifer contains relatively fresh water, less than $10,000 \text{ mg L}^{-1}$ total dissolved solids (TDS). The Lower Floridan Aquifer, consists of seminconfining or leaky micritic limestone and dolomite layers that contain groundwater with compositions approaching seawater (approximately $30,000 \text{ mg L}^{-1}$ TDS). A dolomite confining unit (DCU), a thin confining unit below the MC2, was characterized at the study site by McNeill (McNeill 2000, 2002). This DCU lies above the permeable zone commonly known as the Boulder Zone within the Oldsmar Formation of the Lower Floridan Aquifer. The FAS outcrops along the Straits of Florida, providing a hydraulic connection to the sea (Kohout 1965; Miller 1986; Reese 1994). Transmissivities in the Upper Florida Aquifer range from 929 to $2.3 \times 10^4 \text{ m}^2 \text{ day}^{-1}$ (Meyer 1989a; Reese 1994) while transmissivities in the Boulder Zone range from $2.97 \times 10^5 \text{ m}^2 \text{ day}^{-1}$ to $2.32 \times 10^6 \text{ m}^2 \text{ day}^{-1}$.

Site descriptions

The NDWWTP and the SDWWTP consist of deep injection wells that penetrate down to approximately 855 m. The upper 755 m of each well is cased to the top of the Boulder Zone. The bottom 100 m of each injection well is an open hole in the Boulder Zone. Nine such injection wells and three multi-zoned and dual-zoned monitoring wells were constructed between 1977 and 1981 at the SDWWTP (Fig. 3). The multi-zone test well BZ cluster (BZ-1 through 4) was constructed in 1977, and consisted of four telescoping monitoring wells, the deepest of which was BZ-4, cased to the top of the Boulder Zone; the shallowest BZ-1 open to the UFA at a depth of 312 m. The remaining monitoring wells were constructed both at the SDWWTP and NDWWTP using a dual zone design, with an inner steel casing drilled to the deeper interval, and the outer steel casing open to the upper interval. For

Series	Geologic unit	Hydrogeologic unit (HU)		Approximate Thickness (meters)	Base of HU (m bls)**	number of monitoring wells
Holocene and Pleistocene	Various*	Surficial Aquifer System	Biscayne Aquifer	40	40	
Pliocene	Tamiami Formation		Lower Tamiami Aquifer			
Miocene and late Oligocene	Hawthorn Group	Intermediate Aquifer system	Confining Unit	256	296	16
			Upper Floridan Aquifer (UFA)	33	329	
Early Oligocene	Suwanee Limestone	Floridan Aquifer system	Middle Confining Unit (MC1)	107	436	16
Eocene	Avon Park Formation		Avon Park Permeable Zone (APPZ)	39	475	
			Middle Confining Unit (MC2)	272	747	
			Lower Floridan Aquifer (LFA)	106	853	
			Boulder Zone (BZ)	77	930	
	Oldsmar Formation					

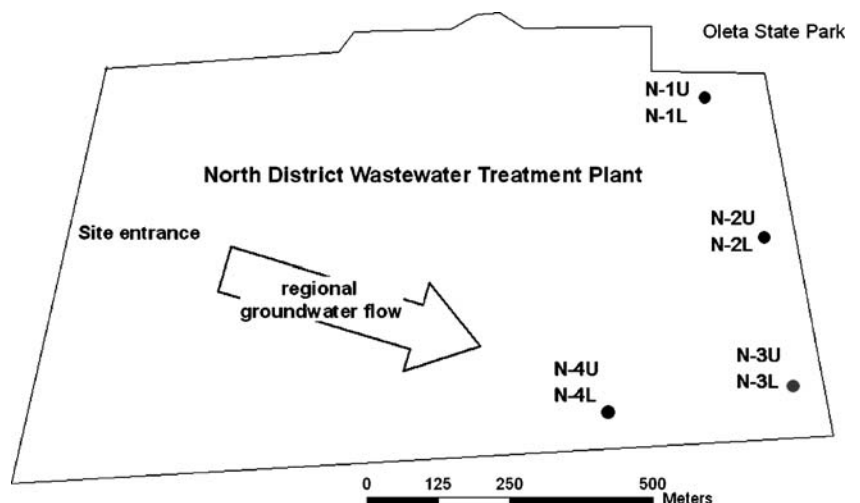
* includes Miami Limestone, Fort Thompson Formation, Anastasia Formation, Key Largo Limestone
 ** meters below land surface

Fig. 2 Geologic and hydrogeologic framework of NDWWTP and the SDWWTP, modified from Reese and Richardson 2008. Well diagram on the right shows the number of wells open to the indicated hydrogeologic unit used for this study

this report, well nomenclature indicates the open interval of the dual-casing: “U” represents the upper monitoring interval and “L” represents the lower monitoring interval. Wells 1 and 2 were dual-cased to monitor water quality in the UFA (~300 m), and the lower confining units (~550 m; CH2MHill 1981). In 1994 NH₃ was detected above ambient levels in the confining unit at the BZ well cluster (BZ-2 depth 488 m), and subsequent investigations by the utility found a leak due to corrosion of the casing in this cluster (MDWASD 1995). The lower three monitoring intervals of the BZ well cluster were plugged in 1995 to stop the upward migration of injectate through the casing hole, and the confining unit (488 m) monitoring interval was redrilled. From 1995–1996 nine injection wells and

thirteen dual-zoned monitoring wells were constructed on the SDWWTP. These monitoring wells were cased to the Avon Park Permeable zone (APPZ) and the MC2, with open holes in the formations approximately 30 m. During the construction of the monitoring wells, NH₃ concentrations above ambient levels were found throughout the site. Elevated NH₃ concentrations were found in the northwest corner of the site in the MC1 interval in several wells, but not in the lower MC2 interval of these wells. Elevated levels were found in the MC2 interval in the south side of the site. As a result of the detected NH₃ in the confining units, the EPA required purging of the wells that showed elevated concentrations NH₃ (Starr et al. 2001) in an attempt to remove the NH₃ loading in the

Fig. 3 Well locations at the SDWWTP



impacted intervals. Discontinuous purging of approximately 2100 L/min commenced from 1997 to 2000, for the northwest wells (5U, 6U, 7U, 8U, 15U and 16U) of the APPZ interval, and the south wells (11L and 12L) of the MC2 (MDWASD 2000).

Injection well construction started at the NDWWTP in 1996. Four injection wells were constructed into the Boulder Zone, and four dual-zoned monitoring wells were constructed to the UFA and the APPZ intervals (Fig. 4). In 1996, effluent was injected in two completed injection wells while one injection well was still under construction, resulting in injectate backflowing into an open borehole at an uncased injection well for 5 days. Several months after the construction of the wells had been completed, NH₃ concentrations were observed to increase in the APPZ interval of the monitoring wells on site. The utility was required to purge the APPZ interval wells for a period of 1 year from 2003–2004 (MDWASD 2005).

Methodology

Historical data were collected and checked for quality assurance for the NDWWTP and SDWWTP. Data were available from 1983 through 2007 for the SDWWTP, and 1996–2007 for the NDWWTP. Data studied as part of this research included pressure, temperature, pH, Cl⁻, sulfate (SO₄²⁻), NH₃ and nitrate (NO₃⁻). The historical data were compiled from the utility monthly operating reports available sporadically from 1983. Non-detects that had been entered as a zero value were updated to the detection level of the parameter. Summary statistics including mean, median, standard deviation, maximum and minimum were applied to each of the wells' time series data to assess water-quality changes over time, and used to compare to ambient water quality data at other locations in south Florida. Most water quality for the Floridan Aquifer in south Florida had been collected as regulatory requirements, which usually included chemical analyses that are used for drinking water quality, and therefore did not include major ion data. Residence time in the Floridan

aquifer system in south Florida is on the order of thousands of years (Meyer 1989a), and it was assumed that due to the depth of the aquifer water quality was in equilibrium and there would be no other cause of perturbations to ambient water quality other than migration of injectate. Time series data that showed large variation over time would indicate non-equilibrium conditions, and therefore not ambient conditions. Abrupt changes in water quality and pressure were observed in the time series data in wells that were purged in 1997. These changes were not observed in wells that were not purged. These changes in water quality and pressure were interpreted as being the result of cross connections developed in the dual zone casings of some of the purged wells, and review of borehole videos of these wells taken in 2004 confirmed holes in the casings of these wells. It could not be determined which interval the data collected from these wells represented after the cross connections developed; therefore, data were discarded from the historical series analysis based on the month it was ascertained the cross connection developed, and the summary statistics were recalculated for these wells.

Floridan Aquifer water samples were collected at the NDWWTP and SDWWTP during 2006 and 2007 as part of this study for major ions and nitrogen species. Thirty-two monitoring wells were sampled at the SDWWTP, and water-quality samples were collected from these wells from the UFA, the APPZ, and the MC2. At the NDWWTP, samples were collected from four monitoring wells representing the UFA and four wells in the APPZ. Temperature, pH, dissolved oxygen, and conductance were taken from water samples in the field using a YSI 556 MPS. The YSI instrument was calibrated per the manufacturer's instructions prior to each sampling event. All wells were purged for at least 24 h prior to sampling to ensure at least three well volumes were evacuated. The wells were sampled through a closed system using a low flow cell and tygon tubing through a disposable, high capacity 0.45 μmol in-line filter. Water samples were analyzed for the anions Br⁻, Cl⁻, F⁻, NO₃⁻, NO₂⁻, and SO₄²⁻ on a DIONEX ion chromatography system. HCO₃⁻ and CO₂⁻ were analyzed via manual titration. NH₃ was analyzed on a LACHAT analyzer 800, with NH₄⁺ then calculated based on pH and temperature of the sample using the NH₃ result (Stumm and Morgan 1996). Cations (Ca²⁺, Mg²⁺, K⁺, Na⁺ and Sr²⁺) were analyzed by inductively coupled plasma (ICP).

Results

The mean historical data are summarized in Table 1 for the SDWWTP, and Table 2 for the NDWWTP. Dissolved oxygen, NO₃⁻ and NO₂⁻ had similar results for both the SDWWTP and NDWWTP sites for the aquifer intervals. NO₃⁻ concentrations were either detected at very low concentrations, or below detectable levels. NO₂⁻ levels were below 1 micromole/L (μmol) for all aquifer intervals and in the injectate at the NDWWTP and SDWWTP sites for the historical time series. The injectate had a mean value

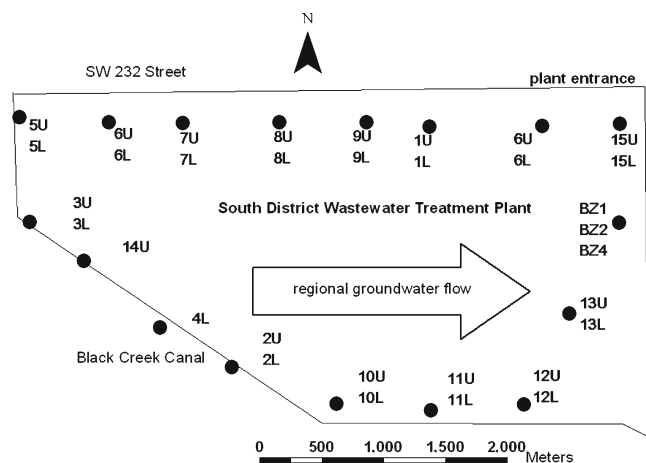


Fig. 4 Well locations at the NDWWTP

Table 1 Mean values for historical time series: SDWWTP. *mbls* meters below land surface

Geologic formation	Hydrostratigraphic formation	Well ID	Open interval mbls	Period of record	Temp °C	pH	NH ₃ µmol	Cl ⁻ mmol	SO ₄ ²⁻ mmol	NO ₃ ⁻ µmol
Pleistocene	Biscayne Aquifer	Injectate (S-EFF)	Surface	5/91-12/07	27.7	6.6	889	2	0.3	10.9
Undifferentiated Hawthorn/Avon Park Limestone	Upper Floridan Aquifer (UFA)	1U	299-332	9/83-12/07	24.0	7.9	12	21	3.2	0.2
		2U	299-311	7/83-12/07	24.4	7.9	13	21	3.2	0.3
		3U	299-320	2/91-12/07	24.3	7.9	10	23	3.2	0.3
		BZ1	306-316	7/83-12/07	24.2	7.6	12	22	3.1	0.2
		13U	451-475	2/96-12/07	23.9	7.7	62	108	4.8	0.3
		5U	454-484	5/94-11/02	24.1	7.6	492	108	4.9	0.3
		6U	454-483	5/94-12/07	24.1	7.6	545	76	3.0	0.3
		7U	454-482	6/94-1/98	24.5	7.4	526	73		
		8U	454-480	8/94-6/02	24.0	7.7	216	106	4.1	0.2
		9U	454-484	1/95-12/07	23.9	7.7	64	111	4.3	0.2
Avon Park Limestone	Avon Park Permeable Zone (APPZ)	10U	454-485	2/96-12/07	24.0	7.6	35	105	4.2	0.2
		11U	454-484	2/96-12/07	24.0	7.6	118	106	4.3	0.2
		14U	454-480	2/96-12/07	23.9	7.4	320	99	4.3	0.2
		15U	454-480	2/96-12/07	23.1	7.5	296	106	5.3	0.3
		16U	454-485	2/96-12/07	23.1	7.6	330	109	4.8	0.2
		12U	456-487	2/96-2/04	24.9	7.6	100	111	4.2	0.2
		BZ2	481-507	7/83-12/07	25.4	7.5	106	133	5.6	0.2
		2L	501-510	7/83-12/07	24.3	7.4	12	199	2.6	0.2
		4L	519-561	12/91-12/07	24.0	7.3	12	510	19.3	0.4
		13L	530-562	2/96-12/07	23.7	7.5	55	508	22.8	0.9
Middle Confining Unit (MC2)	Middle Confining Unit (MC2)	3L	540-577	1/91-12/07	24.0	7.3	7	529	21.9	1.0
		5L	546-576	5/94-11/02	23.9	7.4	6	528	21.6	0.4
		6L	546-576	5/94-10/05	23.7	7.4	30	526	22.7	0.3
		7L	550-571	6/94-1/98	24.2	7.1	10	536		
		8L	546-576	8/94-6/02	23.7	7.4	5	541	24.8	0.4
		9L	546-573	1/95-12/07	23.4	7.4	5	534	22.6	0.4
		10L	546-576	3/96-12/07	23.8	7.6	141	429	20.4	0.5
		11L	546-576	2/96-11/99	23.8	7.6	417	193	9.3	0.2
		12L	546-576	2/96-12/07	25.4	7.4	676	57	3.0	0.3
		15L	546-576	2/96-1/04	23.1	7.5	12	531	25.2	0.4
Oldsmar Formation Boulder Zone	Lower Floridan Aquifer	16L	546-576	2/96-12/07	22.9	7.4	6	532	21.9	0.4
		1L	561-587	7/83-12/07	23.8	7.3	6	539	23.9	0.4
		BZ4	853	07/83-8/94	24.9	7.2	634	3		

Table 2 Mean values for historical time series: NDWWTP. *mbl/s* meters below land surface

Geologic formation	Hydrostratigraphic formation	Well ID	Open interval mbls	Period of record	Temp °C	pH	NH ₃ μmol	Cl ⁻ mmol	SO ₄ ²⁻ mmol	NO ₃ ⁻ μmol	Revised period of record ^a	Temp °C	pH	NH ₃ μmol	Cl ⁻ mmol	SO ₄ ²⁻ mmol		
Pleistocene	Biscayne Aquifer	Injectate (N-EFF)	Surface	7/97–12/07	28.4	6.5	819.3	20.0	0.5	37.9								
Avon Park Limestone Eocene	Upper Floridan Aquifer (UFA)	N-1U	354–385	1/97–12/07	23.1	7.6	18.8	73.7	3.5	0.2								
		N-2U	351–384	3/96–12/07	23.0	7.8	17.7	66.2	3.6	2.1								
		N-3U	354–379	3/96–12/07	22.9	7.8	17.3	65.8	3.6	2.0								
		N-4U	354–379	4/96–12/07	23.1	7.6	18.1	68.4	3.5	0.8								
	Avon Park Permeable Zone (APPZ)	N-1L	430–461	4/96–12/07	21.9	7.3	261.2	368.2	32.8	1.0		34/96–7/97	22.4	7.2	19.3	461.7		
		N-2L	431–459	3/96–12/07	22.3	7.6	168.4	397.9	15.6	2.2		3/96–8/98	22.9	7.8	17.7	455.7	16.6	
		N-3L	430–460	3/96–12/07	22.2	7.6	131.4	409.4	15.8	1.0		3/96–12/98	23.0	7.7	19.1	454.8	14.9	
		N-4L	430–460	4/96–12/07	22.4	7.2	190.3	380.4	15.2	1.6		4/96–12/98	22.3	7.5	23.7	440.5		

of NO₃⁻ of 37.9 μmol at the NDWWTP, and 10.9 μmol at the SDWWTP for the historical time series. Dissolved oxygen was detected at concentrations less than 1.0 mg L⁻¹ for all aquifer intervals. Dissolved oxygen concentrations for the injectate at both the NDWWTP and the SDWWTP had results above 3 mg L⁻¹.

Historical time series results: SDWWTP

The historical period of record data for the freshwater injectate samples from the SDWWTP (identified as S-EFF) were available from 1991 through 2007 (Table 1). Temperature ranged from 21.8 to 31.1 °C, with a mean of 27.7 °C. Mean pH in the historical time series was 6.6. NH₃ ranged from 146.8–1,849.6 μmol, with a mean of 889 μmol. NH₃ varied seasonally and increased with time (Fig. 5). Cl⁻ concentrations averaged 2 millimoles/L (mmol), with a very small range and standard deviation, indicative of the freshwater source of the injectate. Historical data from the SDWWTP for the UFA (wells BZ1, 1U, 2U and 3U) were available from 1983 through 2007. Temperature averaged 24 °C, with no significant difference observed between the wells. The range of pH was from 7.6 to 8.2 in the UFA. Chloride averaged between 21 and 23 mmol, while NH₃ means ranged between 10 and 13 μmol. The summary statistics for the water-quality samples collected from the UFA showed consistent values, with no discernable variation over time. Historical data from wells open to the APPZ at the SDWWTP (wells 5U, 6U, 7U, 8U, 9U, 10U, 11U, 12U, 13U, 14U, 15U, 16U) were available from 1994 through 2007. Mean temperatures ranged between 23.1 and 24.9 °C in these wells. There was little variation observed in the pH in the APPZ samples, but the mean pH of 7.6 was lower than the mean pH in the UFA. Almost all of the wells showed variation in NH₃ concentrations over time. Mean values of NH₃ in these wells ranged from 35 μmol in well 10U to 545 μmol in well 6U. Well 6U showed an increasing trend with time in NH₃ that was observed to be similar to the increasing trend of NH₃ in the injectate (Fig. 5). The spread between the 5th and 95th percentile was the greatest in wells 6U and 12U. Only wells 9U, 10U and 13U showed little variation in NH₃ over time. Mean concentrations of Cl⁻ in wells 6U and 7U were 76 and 73 mmol. Wells in the MC2 were open to intervals varying in depth from 481 to 551 m. Mean temperature values ranged from 22.9 to 24.2 °C in all wells, with the exception of a mean value of 25.4 °C in wells BZ2 and 12L. Mean pH values ranged from 7.3 to 7.6. Mean NH₃ concentrations showed two groupings. Wells BZ2, 10L, 11L and 12L exhibited concentrations of 106, 141, 417 and 676 μmol, respectively. The remainder of the wells exhibited mean NH₃ concentrations of less than 55 μmol. Cl⁻ concentrations for wells 10L, 11L and 12L were 429, 193, and 57 mmol respectively; the remainder of the wells had mean concentrations greater than 508 mmol (exception is BZ-2, whose Cl⁻ concentration of 133 mmol reflects the shallower depth of this well with the open interval in the lower brackish water zone of the Floridan

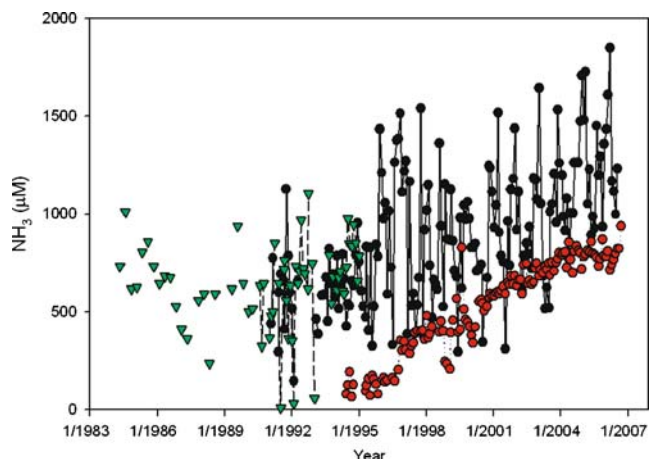


Fig. 5 Time series NH_3 data from the injectate (black circle), BZ-4 (green triangle) and well 6U (red circle) at the SDWWTP site. The apparent seasonal variation observed in the injectate is a result of increased flows during the wet season and storm events. The increasing trends with time correlate to increased injection over time due to growth in population in Miami-Dade County

Aquifer). Data collected from well 12L were similar to data collected for wells for 6U and 7U. These wells had high NH_3 concentrations, with low Cl^- and SO_4^- concentrations. Historical data were available for the Boulder Zone interval (well BZ4) from 1983 through 1994. The mean pH and temperature values were 7.2 and 24.9°C respectively. Mean NH_3 concentration was 634 μmol , and showed apparent seasonal variation and increasing trend over time, and was similar to the injectate historical time series (Fig. 5). The mean Cl^- concentration was 3 mmol, similar to the mean Cl^- concentration of 2 mmol for the injectate.

Historical time series results: NDWWTP

The historical period of record data for freshwater injectate samples (N-Eff) at the NDWWTP were available from 2002 through 2007. Temperature ranged from 22 to 34°C, with a mean of 28°C. The mean pH was similar to the SDWWTP injectate at 6.5. NH_3 ranged from 210–3764 μmol , with a mean of 819 μmol and a large standard deviation, indicative of the apparent seasonality similar to the SDWWTP. Cl^- concentrations ranged from 0.8 mmol to 113.1 mmol, with a mean 20 mmol, slightly higher than the mean concentration of the SDWWTP injectate. Historical data were available from 1996 through 2007 for wells open to the UFA (N-1U, N-2U, N-3U and N-4U). Mean temperature averaged 23°C in these wells, with no significant difference observed between the wells. Mean values of pH ranged from 7.6 to 7.8. Cl^- mean concentrations ranged between 66.2 and 73.7 mmol. NH_3 mean concentrations ranged between 17 to 18 μmol . Concentrations for the UFA water-quality samples for the NDWWTP showed consistent values, with no discernable variation over time. Historical data were available from 1996 through 2007 for wells open to the APPZ (N-1L, N-2L, N-3L, and N-4L). Temperature mean values were

22°C. Analysis of historical NH_3 data indicates increasing concentrations of NH_3 starting in late 1997 (Fig. 6). NH_3 concentrations appeared to have reached a peak concentration of 408 μmol in well N-1L in July 2001, and steadily declined thereafter to concentrations ranging from 200 to 250 μmol . Wells N-2L, N-3L and N-4L show similar patterns as well N-1L, but with lowered and delayed peak concentration values. NH_3 concentrations are observed to increase scatter after 2003, which corresponds to when purging commenced at the NDWWTP. Once purging ceased in 2004, NH_3 concentrations in wells varied between 150–300 μmol . The Cl^- mean concentrations ranged from 368 to 409 mmol. Cl^- in these wells exhibited variation over time, and analysis of the time series indicated that as NH_3 concentrations increased, Cl^- concentrations decreased (Fig. 6). The time series data for the lower wells were revised to remove data after NH_3 concentrations were observed to increase in each well in order to determine ambient concentrations in the APPZ. Revised NH_3 mean concentrations ranged from 18–24 μmol ; Cl^- mean concentrations ranged from 441–461. Very little variation was observed in NH_3 and Cl^- mean concentrations after the time series data were removed.

Major ion data collection results

Major ions were collected for this study from 2006–2007 (Table 3). Data from wells at the SDWWTP site that exhibited cross connections were removed from this analysis. Data collected from the SDWWTP UFA exhibited very little variation between wells, and were similar to the historical time-series data, with low cation and anion concentrations. For the APPZ wells, NH_4^+ mean concentrations could be combined into three groups: wells 9U, 10U and 13U with NH_4^+ mean concentrations of 60, 67 and 143 μmol respectively; wells 14U and 16U with 497 and 439 μmol ; and well 6U 823 μmol . Cation and anion mean concentrations showed a similar grouping as the NH_4^+ concentration grouping, with well 6U consistently grouping independently, and with increasing NH_4^+ concentrations correlating to decreasing ion concentrations. The MC2 mean NH_4^+ concentrations could also be combined into three groups: well 12L at a mean NH_4^+ concentration of 765 μmol ; wells BZ-2, 10L and 13L NH_4^+ at mean concentrations 176, 200 and 108 μmol respectively; the remainder wells at NH_4^+ concentrations below 10 μmol . Cation and anion concentrations could be combined in the same 3 groups as the NH_4^+ groups, with lower ion mean concentrations observed for BZ-2, 10L and 13L, and much lower ion concentrations observed in well 12L. As with well 6U in the MC1, well 12L in the MC2 consistently grouped independently.

The NDWWTP wells open to the UFA (351–385 m) exhibited very little variation in field measurements and mean concentrations between wells, and were similar to the historical time series. The interval (430–461 m) in the APPZ at the NDWWTP also showed little variation, with mean NH_4^+ concentrations (215–295 μmol) and mean

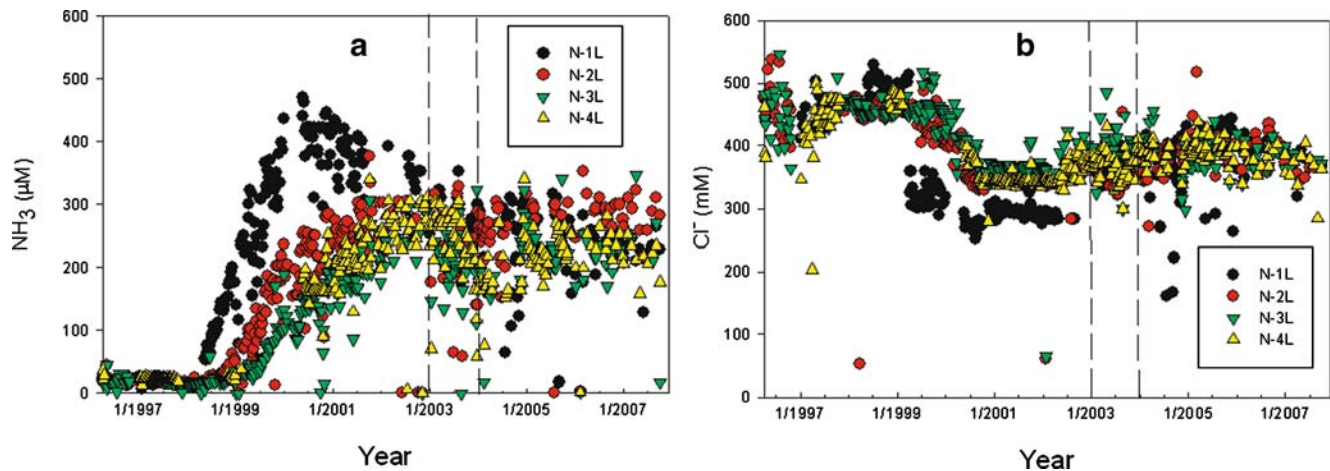


Fig. 6 Graph **a** shows the NH_3 data time series for the wells in the APPZ interval at the NDWWTP. The *dashed lines* indicate the purging time from 2003 through 2004. NH_3 concentrations are observed to increase in well *N-1L* similar to contaminant breakthrough curves. Well *N-1L* was the closest well to the uncased injection well when injectate backflowed into the APPZ. NH_3 concentrations for wells *N-2L*, *N-3L*, and *N-4L* appear to be similar and show a similar increase after 1999. Variability is seen in the data after 2003. Graph **b** shows Cl^- concentrations in well *N-1L* clustered at approximately 300 mmol, and an abrupt decrease to less than 300 mmol is seen. Cl^- concentrations in wells *N-2L*, *N-3L*, and *N-4L* are very similar, and show a decrease in concentrations after 1999 until 2000, when concentrations appear to stabilize. Cl^- concentrations start to increase slightly and become variable after 2003. All four wells show similar concentrations of both NH_3 and Cl^- after 2004

concentrations of Cl^- (371–386 mmol) varying little between wells.

Ternary diagram

The typical Cl^-/Br^- ratio for seawater is about 290 (Davis et al. 1998), and most of the Cl^-/Br^- ratios at both sites were within that range, with no discernable differences. Quite often the addition of a third water-quality member could enhance the understanding of the data, and this was the case with using NH_4^+ as the third end-member. NH_4^+ , Cl^- and Br^- data were plotted on a ternary diagram, with data normalized to 100%. Typical seawater and freshwater NH_4^+ , Cl^- and Br^- values after Hem (1985) were also plotted for comparison. Water quality at the NDWWTP clustered into three distinct groups, with two groups based on depth of the interval sampled and the third the injectate (Fig. 7). The ambient aquifer data plot close to seawater. The injectate data plotted off in the lower left hand corner due to the large NH_4^+ concentrations. At the SDWWTP, three aquifer groupings were observed. Ambient well data from the MC2 plotted similar to seawater. Ambient well data from the UFA plotted slightly towards freshwater. Data from wells that showed elevated NH_4^+ plotted in a line towards the injectate, with groundwater data from 6U and 12L plotting very close to the injectate. This line represents the evolution of the water quality of these wells towards the injectate water quality, and does not show any evolution of more saline water into the higher intervals in the aquifer.

Mixing end-member models

End-member mixing models of wells 6U, 12L and 10L represented the results obtained for all wells at the

SDWWTP (Fig. 8). Well 6U and 12L showed the progressive freshening of water and increasing NH_3 concentrations towards the injectate end-member (Fig. 8). There was little mixing from the saline end-member towards the brackish end-member in well 6U, and almost all of the mixing was towards the injectate end-member. Both 6U and 12L showed large changes in concentrations from their original end-members over time. Well 10L showed a different pattern than 6U and 12L, with gradual freshening of the saline water towards the injectate end-member. The mixing was towards the lower range of the injectate end-member, and there were no large changes in concentrations of either NH_3 or Cl^- from the saline end-member. Well *N-1L* at the NDWWTP end-member mixing model showed a different pattern than the SDWWTP (Fig. 9). Clustering of the NH_3/Cl^- ratios were distinguished based on time. The NH_3/Cl^- ambient ratio can clearly be seen on Fig. 9, and lies along the saline end-member. As the concentrations of NH_3 increased in time to the peak concentration, the NH_3/Cl^- ratios showed two distinct clusters. Initially, the NH_3/Cl^- ratio showed gradual increasing in NH_3 with little change in Cl^- from ambient concentrations. There was a rapid change in the NH_3/Cl^- ratio as NH_3 reached the peak concentrations. Once the peak was reached, the NH_3/Cl^- ratios slowly declined in time.

Discussion

The Floridan aquifer system was sampled by others at different sites in south Florida and these data are summarized in Table 4. Wells identified as WWF were monitoring wells installed as part of the MDWASD ASR system west of the NDWWTP and SDWWTP (CH2M Hill 1998). The ASR systems were not in use during the

Table 3 Mean field parameters and ion concentrations during the 2006–2007 sampling completed as part of this study, *mbls* meters below land surface

Geologic formation	Hydrogeologic unit	Open interval mbls	Well ID	Temp °C	pH	NH ₄ ⁺ μmol	Ca ²⁺ mmol	Mg ²⁺ mmol	Na ⁺ mmol	K ⁺ mmol	Si ²⁺ μmol	Cl ⁻ mmol	SO ₄ ²⁻ mmol	HCO ₃ ⁻ mmol	Br ⁻ μmol	F ⁻ μmol	NO ₃ ⁻ μmol	NO ₂ ⁻ μmol	
SDWWTP																			
Pleistocene	Biscayne Aquifer	Surface	S-EFF	29.0	6.7	1,125	1	0	3	0	7	3	0	4	30	19	7	6	
	UFA	306–316	BZ1	24.2	7.8	6	1	3	25	1	39	21	3	4	40	109	1	1	
Undifferentiated Hawthorn/Ocala Limestone to Avon Park Limestone		299–332	1U	23.6	8.1	6	1	3	24	1	42	22	4	4	56	117	0	1	
		299–320	3U	24.3	7.9	6	1	3	25	1	48	28	4	4	54	119	4	1	
		299–311	2U	25.3	7.9	10	1	3	22	1	43	21	5	4	33	143	1	1	
	APPZ	454–484	9U	23.8	7.7	60	4	10	98	3	99	104	5	3	169	85	0	1	
		454–485	10U	24.8	7.7	67	5	10	85	2	125	112	5	3	174	45	1	0	
		451–475	13U	24.4	7.7	143	4	10	88	3	113	109	5	4	200	119	2	1	
		454–485	16U	23.2	7.7	439	4	9	94	3	75	102	5	5	250	135	1	1	
		454–480	14U	25.0	7.5	497	3	6	66	2	65	70	4	5	115	80	1	1	
	MC2	454–483	6U	25.1	7.5	823	3	5	87	2	32	45	3	7	81	51	1	1	
		501–510	2L	24.8	7.5	9	8	16	148	4	147	194	4	2	305	75	0	1	
		481–507	BZ2	24.1	7.6	176	5	11	121	3	114	128	6	4	217	93	0	1	
		546–573	9L	23.1	7.6	3	11	44	459	12	167	550	24	3	849	211	1	1	
		546–576	16L	22.9	7.5	4	11	41	439	12	175	552	25	4	800	195	0	1	
		540–577	3L	24.1	7.5	4	10	43	440	12	159	522	23	3	834	233	5	1	
		519–561	4L	24.5	7.5	7	11	40	416	12	181	492	21	3	737	234	0	1	
		530–562	13L	24.2	7.5	108	10	36	350	12	174	460	24	3	775	313	2	1	
		546–576	10L	24.7	7.6	200	8	30	285	10	111	369	23	3	588	77	3	0	
		546–576	12L	28.1	7.6	765	3	6	49	2	36	54	4	5	87	35	2	0	
		561–587	1L	23.4	7.5	4	11	64	412	13	161	533	25	3	834	235	1	1	
NDWWTP																			
Pleistocene	Biscayne Aquifer	surface	N-EFF	26.3	6.5	505	2	2	20	1	6	16	1	3	36	10	38	49	
	UFA	354–385	N-FA-1U	22.5	7.8	17	3	8	68	2	155	73	4	1	81	180	0	1	
		351–384	N-FA-2U	22.7	7.8	13	3	7	65	2	121	66	4	1	126	179	2	2	
		354–379	N-FA-3U	21.2	7.9	16	3	7	66	2	133	62	3	1	115	3	2	1	
		354–379	N-FA-4U	20.8	7.9	16	3	7	69	2	147	66	4	1	131	174	1	1	
	APPZ	430–460	N-FA-3L	19.4	7.5	215	9	37	423	11	216	380	17	3	651	537	1	2	
		430–461	N-FA-1L	19.9	7.4	231	7	36	458	11	100	386	20	3	839	422	1	1	
		430–460	N-FA-4L	19.2	7.4	264	9	37	421	11	223	371	19	3	695	463	2	1	
		431–459	N-FA-2L	20.1	7.4	295	8	39	431	12	125	383	22	3	748	486	2	1	

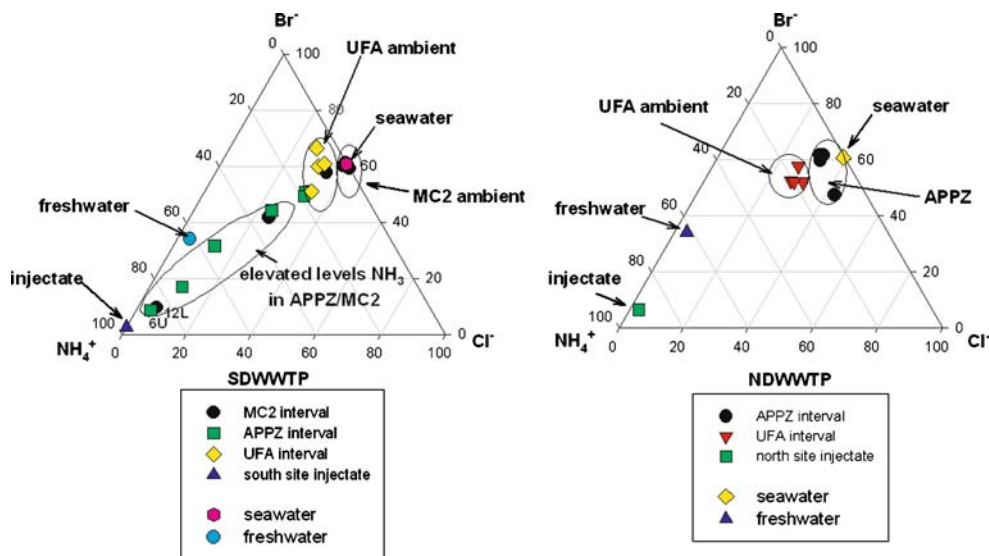


Fig. 7 Ternary diagrams for the NDWWTP and the SDWWTP. NH_4^+ , Cl^- , and Br^- data collected from 2006–2007 were normalized to 100%. Seawater and freshwater values (Hem 1985) were plotted. Ambient water was grouped at the SDWWTP for the MC2 and UFA intervals. Ambient MC2 data plot directly with seawater. UFA ambient plots towards freshwater, reflecting the fresher water quality in the UFA. The injectate data plot at the NH_4^+ end point, indicating the freshwater quality but high NH_4^+ concentration of the injectate. Well data from the APPZ and MC2 intervals that have NH_4^+ concentrations above ambient levels plot in a line towards the injectate end point, with data from wells 6U and 12L plotting very close to the NH_4^+ end point. Data from the SDWWTP plot into distinct groups based on depth in the aquifer, but no line towards the injectate end point is seen

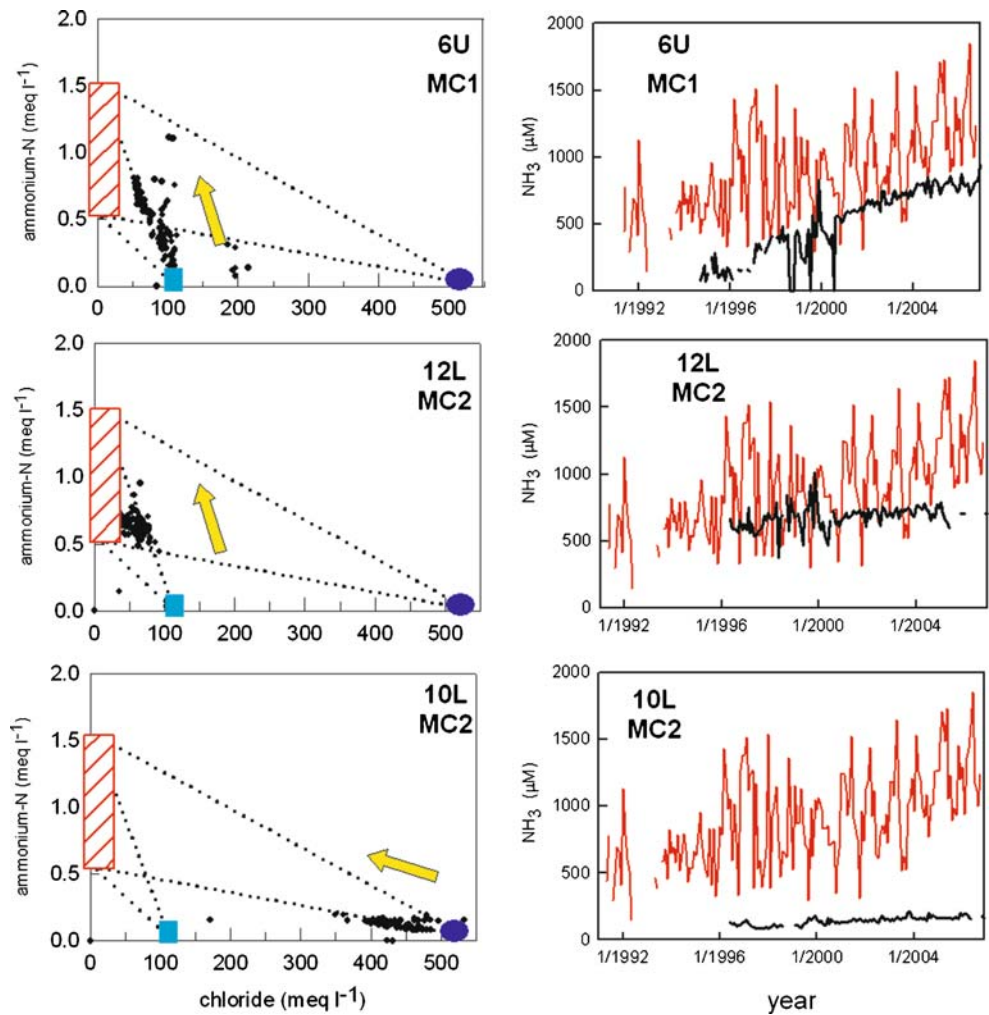
time of this study. Wells designated as “FPL” were test wells installed into the Floridan aquifer system ~10 km south from the SDWWTP (Dames and Moore 1975; Florida Partners 2006). For comparison to the present study, the data from these sites were assumed to represent ambient water-quality concentrations, as no injection activities had occurred at these sites. Wells in this study that exhibited little variation in the time series data and had low NH_3 concentrations, were compared to the data from these other sites. Although direct comparisons were difficult due to the varying aquifer open intervals from which these samples were collected, some generalizations can be made. NH_3 or NH_4^+ concentrations from these wells were below $29\ \mu\text{mol}$. Cl^- concentrations increased with depth of the sampled intervals, and were similar in concentrations to wells in this study of approximately the same aquifer interval. NO_3^- concentrations were below $1\ \mu\text{mol}$, similar to data collected for this study. Based on comparisons with water quality from these other sites, the revised time series water-quality data that had mean NH_3 concentrations below $30\ \mu\text{mol}$ were assumed to be ambient aquifer water, with no influence of injectate. All the wells in the UFA at the SDWWTP were considered ambient, and most of the wells in the MC2 at the SDWWTP were considered ambient with the exception of 10L, 11L and 12L. All of the wells in the APPZ at the SDWWTP had NH_3 concentrations above ambient levels, with well 9U the lowest. Time series data at the NDWWTP indicated that all of the wells open to the UFA were considered ambient, and the data from wells open to the APPZ were ambient prior to the observed increase in NH_3 concentrations.

Ambient Cl^- concentrations from this study showed brackish, transitional, and saline zones in the Floridan

aquifer system for the SDWWTP and NDWWTP as defined by Reese (1994). Although there were only two sample depths at the NDWWTP, the top of the saline zone at the north appears to be higher than at the SDWWTP. Mean temperatures at the NDWWTP were cooler than at the SDWWTP, with an average of 23°C for both intervals. The NDWWTP lies closer to the Florida Straits, and the cooler temperatures at that site may be due to closer proximity to open seawater. Wells that showed a higher concentration of NH_3 at the SDWWTP showed higher temperatures (example Well 12L), whereas at the NDWWTP, no change in temperature was noted with increasing NH_3 concentrations.

Based on results of this study, introduced nitrogen from the injectate into the Floridan Aquifer is mostly in the form of NH_4^+ . This is consistent with eH-pH diagrams for nitrogen (Stumm and Morgan 1996) where in most natural environments, any ammonia-N would have the form of NH_4^+ (Hem 1985). No relationship was observed in the historical data or data collected as part of this study between NH_3 and NO_3^- . No change from ambient NO_3^- concentrations was observed for wells that had elevated NH_3 concentrations. The reduced form of nitrogen (NH_4^+) was not oxidized once introduced in the anoxic aquifer at either site, and was conserved in the aquifer in this reduced state. Any introduced oxidized form of nitrogen (NO_3^-) from the injectate that was reduced would result in insignificant changes in NH_4^+ concentrations, as NO_3^- concentrations are two to three orders of magnitude less than NH_4^+ . The elevated concentrations of NH_4^+ in the Floridan aquifer at the two sites are interpreted as the result of the upward migration of the injectate. Once introduced into the aquifer, NH_4^+ appeared to have behaved conservatively.

Fig. 8 Graphs on the left are NH_3/Cl^- mixing end-member models for the APPZ and MC2 intervals at the SDWWTP. 6U, 12L and 10L are well identification codes. Arrows indicate increase in time. Hatched red rectangle is injected freshwater end-member, indicating the seasonal range in concentrations. Cyan square is the APPZ brackish water/ambient water end-member; blue circle is the MC2 saline water end-member. Graphs on the right are NH_3 concentrations over time. Solid black lines are concentrations from each well site; red line is injected freshwater concentrations. For wells 6U and 12L, the data plot towards the injectate end-member. Little influence is seen in well 6U from the saline MC2 end-member. Well 10L shows a different evolution of water quality, with data plotting at the saline MC2 end-member and slowly plotting towards the lower end of the injectate end-member



At least two pathways of injectate were distinguished based on the analysis of the natural tracers at the SDWWTP. One pathway at the SDWWTP appeared to have rapid vertical pathways from the Boulder Zone up to the APPZ, with little mixing of ambient waters as it migrated upward. These vertical conduits did not appear

to extend up to the UFA. This pathway is identified at wells 6U and 14U in the APPZ, and well 12L in the MC2. It may be present at well 8U in the APPZ; however, the development of cross connection in well 8U compromised data interpretation. NH_4^+ concentrations in these wells were within the range of injectate NH_4^+ concentrations.

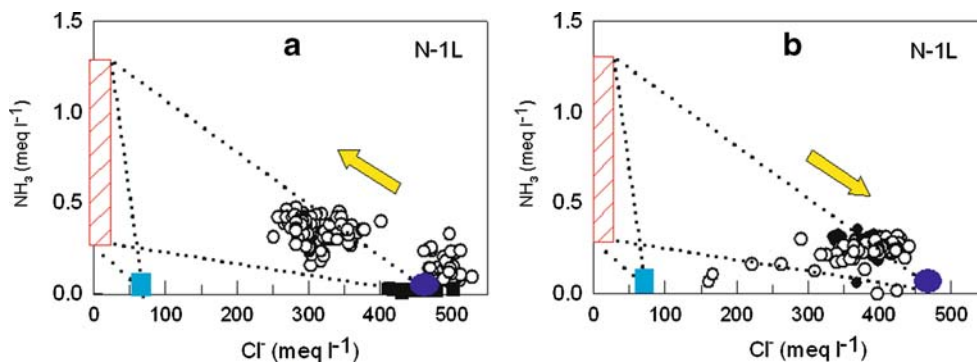


Fig. 9 Graph a is the NH_3/Cl^- mixing end-member model for the APPZ at the NDWWTP for pre-purge data (prior to 2003) for well N-1L. Arrows indicate increase in time. Hatched red rectangle is injected freshwater end-member, indicating the seasonal range in concentrations. Cyan square is the UFA brackish water ambient water end-member; blue circle is the APPZ saline water end-member. The data plot in separate groupings, with the earliest time series plotting around the APPZ saline end-member. The second data cluster plot towards the injectate end-member, but no evolution towards the injectate end-member is seen as was seen for wells 6U and 12L at the SDWWTP. Graph b is the post-purge data plotted for well N-1L. Data plot with time back towards the APPZ saline end-member

Table 4 Historical ambient Floridan Aquifer water quality data

Parameter	Unit	1U ^a	WWF ^b	WWF ^b	FPL PW-3 ^c	FPL test well ^d	9U ^a	FPL test well ^d	2L ^a	3L ^a	FPL test well ^d
		299–332 m	260–305 m	260–308 m	314–380 m	340–410 m	454–484 m	456–517 m	501–510 m	530–562 m	639–701 m
pH		7.9	8.0	7.4	7.5	7.7	7.7	7.5	7.5	7.5	7.0
HCO ₃ ⁻	mmol	0.0				3.2	2.7	3.3	2.1	3.0	2.6
Ca ²⁺	mmol	1.3			1.7	3.7	4.3	6.7	7.8	10.3	19.6
Mg ²⁺	mmol	2.7			2.8	7.3	10.1	15.5	16.0	43.4	55.5
Na ⁺	mmol	24.7			22.2	74.6	98.3	158.2	148.2	438.2	487.2
K ⁺	mmol	0.8			0.8	2.0	2.6	3.8	3.6	11.8	9.7
Cl ⁻	mmol	22.3		70.5	27.1	82.1	104.3	179.4	193.9	521.6	592.3
SO ₄ ²⁻	mmol	4.1	7.5	6.9	0.3	6.9	4.7	13.7	4.2	22.6	30.7
NO ₃ ⁻	μmol	0.3	0.8	0.2		0.2	0.2	0.3	0.2	4.8	0.2
F ⁻	mmol	0.1		0.1		0.1	0.1	0.1	0.1	0.2	0.1
Si	mmol	0.5				0.4	0.2	0.5	0.3	0.3	0.2
Si ²⁺	μmol	41.9				77.6	98.2	184.9	147.2	158.6	
Total P	μmol	3.2	7.1				6.5		6.5	3.2	
NH ₄ ⁺	μmol	5.5	7.2				61.0		11.1	5.5	
NH ₃	μmol		0.8	29.4	12.3						

^aData were collected for this study during 2006–2007 for wells at the SDWWTP

^bData from CH2M Hill 1998

^cData from Florida Partners 2006

^dData from Dames and Moore 1975

Cl⁻ concentrations in these wells were also very close to injectate Cl⁻ concentrations.

The mixing models for these wells show a mixing pathway almost directly towards the injectate end-member, with no mixing from the lower MC2 interval observed for wells 6U and 14U. Wells that showed the highest concentrations of NH₃ at the SDWWTP also showed higher temperatures, with the temperature signal of the warmer injectate observed in well 12L (mean temperature of 28°C) in the data collected in 2006–2007. Well 12L in the MC2 is much closer to the Boulder Zone than the APPZ wells, and higher injectate temperatures persist into the MC2. Perhaps due to the longer travel times to the APPZ the temperature signal was muted but still visible in the APPZ. Ion data for these wells showed freshening of the water quality. These wells showed a density-driven buoyant rapid vertical advective pathway and transport of the injectate as a distinct water body, with little mixing of native waters as it migrated upwards. The rapid pathways could be the result of construction related events such as drifting boreholes, or the result of structural anomalies such as fracturing and karst features that would vertically connect aquifers and provide high hydraulic conductivity transport pathways through confining units. Migration of saline waters from the Lower to Upper Floridan Aquifer as a result of such structural anomalies have been reported for northeastern and central Florida (Flocks et al. 2001; Spechler 2001), where the Floridan aquifer system lies much closer to the surface. Upward fluid migration of injected fluids in a Palm Beach County, Florida, deep well injection facility had been detected above the confining zone between the injection zone and the overlying monitoring zone, and this had been attributed to fractured dolostone comprising the majority of the confining zone strata (Maliva et al. 2007); however, no fracturing of the confining strata at either the NDWWTP or the SDWWTP

has been reported. McNeill suggested that as wells located on the northwest side of the SDWWTP were cased above the DCU in the LFA, this would be a possible cause of the buoyant upward migration of injected fluids through the more permeable units above the DCU through isolated vertical flow paths, bypassing the MC2 (McNeill 2000, 2002).

The second pathway was suggested by the grouping of well data observed in wells 15U, 16U, BZ2, 10L and 11L. The well data from this group had no significant correlation between NH₃ and Cl⁻. The mixing models for these well data showed a slow evolution of water quality towards the lower average of the injectate end-member with time. These wells showed a slight temperature increase, but no clear temperature signal was distinguished in these wells. Ion data did not show a freshening of the water quality, with little difference seen between ambient ion concentrations and concentrations from these wells. Other studies (Böhlke et al. 2006) have indicated that NH₃ transport can be retarded by a factor of 3–6 in an aquifer, with NH₃ persisting in an aquifer after the more mobile constituents were flushed out, if the aquifer remained under suboxic conditions. At the SDWWTP, it appears that there was still NH₃ loading into the aquifer via rapid vertical pathways, with increasing NH₃ concentrations over time. The data from this well grouping may indicate that once NH₃ was introduced into an aquifer interval, it traveled horizontally at a much slower rate, with the freshwater injectate substantially diluted, and not flushed out, as freshwater continued to migrate upwards.

Four discrete injectate plumes were delineated at the SDWWTP based on the transport pathways. The first plume (plume 1 in Fig. 10), located on the northeast of the site, was associated with the BZ-4 well, which provided a pathway up into the APPZ until it was plugged. This

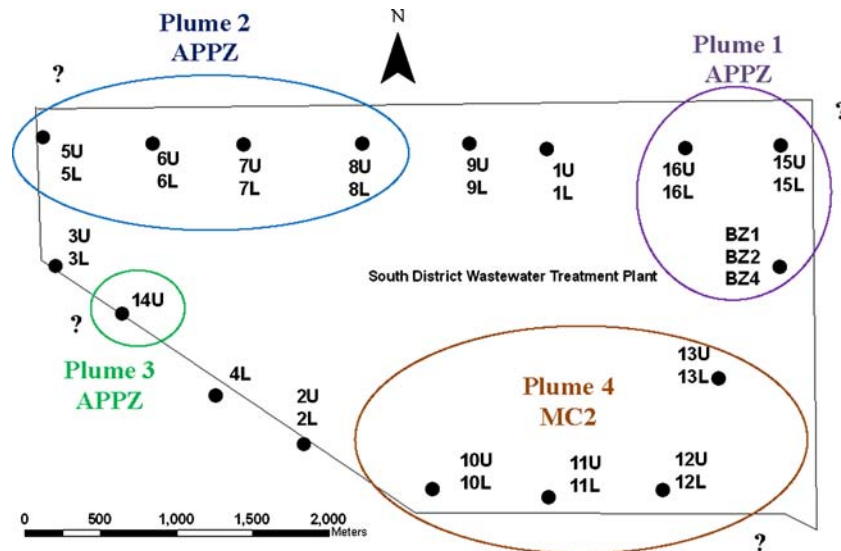


Fig. 10 Location of injectate plumes and their depth interval at the SDWWTP. The source of the plume centered on the BZ well clusters (plume 1) was plugged in 1995. Plumes 2, 3, and 4 are the result of continuing rapid vertical pathways up from the Boulder Zone. The extent of the plumes off site is not known, as indicated by the question marks; however, based on data collected from the site, approximate extent of the plumes on the site can be inferred. The plume in the MC2 is limited to the southeast of the site. The plume located in the northwest of the site is located in the APPZ, and appears to have bypassed the MC2. The plume from the BZ well cluster appears to be limited to the east of the site. The extent of the plume at 14U on site is unknown, as there are no wells that monitor the same aquifer interval in the vicinity of 14U

plume slowly migrated to the surrounding areas mainly via diffusion, as evidenced by slowly increasing NH_3 concentrations, but no change in Cl^- concentrations. The second plume was located on the northwest corner of the site in the APPZ (plume 2). This plume was detected in the APPZ, with no detection of it in the lower MC2, indicating a direct pathway to the APPZ bypassing the MC2. This pathway seemed to persist, with concentrations of NH_3 increasing with time similar to concentration levels of the injectate. This plume was a chemically distinct water body, with little mixing of native waters. The third plume located at well 14U (plume 3) may be a distinct plume, but it may also be in connection with plume 2. No monitoring wells of the same interval as well 14U are in the vicinity, so the extent of this plume could not be determined. The fourth plume was located on the south side of the site in the MC2 (plume 4). All four plumes appeared to have the same initial transport mechanism up from the Boulder Zone through high hydraulic conductivity pathways, with data from plumes 2, 3 and 4 indicating these pathways still persist.

The data collected from the NDWWTP indicate different transport mechanisms than the SDWWTP. The temperature signal of the warmer injectate was not observed in wells with elevated concentrations of NH_4^+ . Water quality showed no evolution towards the injectate plot in the ternary diagram. The mixing model showed two mixing patterns: one towards the injectate end-member before purging, and one towards the ambient end-member once purging ceased. As observed in the time series NH_3 data, NH_3 concentrations were first observed to increase in well N-1L, the well that was within 30 m of the uncased injection well, and concentrations peaked at

341 μmol , well below the mean NH_3 concentration of the injectate. Unlike the increasing NH_3 concentrations observed at the SDWWTP that are the result of rapid vertical migration pathways, once NH_3 concentrations at the NDWWTP peaked, they have since decreased with time. All four NDWWTP lower wells have shown very similar water quality since 2004 when purging ceased at the NDWWTP. Both the time series analysis and the data collected as part of this study in 2006 and 2007 appear to indicate a one-time pulse of injectate water into the APPZ, and this pulse of injectate was still migrating, at the time of this study, through the aquifer in the direction of regional flow. There is no geochemical evidence of a continuing source of NH_3 at the NDWWTP; however, due to retardation as discussed previously, the NH_3 plume may have persisted a long time in the suboxic aquifer (Böhlke et al. 2006).

Conclusions

Chloride, bromide and ammonia were used to understand the pathways and transport mechanisms of injected wastewater into the deep saline Boulder Zone in the Floridan aquifer system. The injectate source was treated freshwater with elevated levels of ammonia. The water quality of the injectate was chemically and physically distinct from ambient Floridan aquifer system water, and these distinctions were used to determine the possible transport pathways. At the SDWWTP, four injectate plumes were identified along with two pathway mechanisms: density-driven buoyant vertical flow, and slower horizontal flow. At the NDWWTP one plume was

identified, and appeared to be a result of a one-time pulse injection. At the SDWWTP, the injectate may first have migrated upwards through discrete vertical pathways from the Boulder Zone to the Middle Confining Unit, with the freshwater injectate migrating upwards through saline water as a chemically distinct water body. The four plumes identified at the SDWWTP appear to have originated via this pathway. Once introduced in the higher aquifer intervals, the transport mechanism appeared to be a horizontal flow with mixing of ambient waters. The rapid vertical pathways did not appear to extend up to the UFA. At the NDWWTP, the elevated levels of NH₃ in the lower Middle Confining Unit appeared to be the result of a construction incident where a pulse of injectate water backflowed into an uncased injection well, providing a pathway to the upper interval. Once introduced into the upper aquifer interval, the plume slowly migrated with the regional flow within the aquifer. No evidence of rapid vertical pathways was observed at the NDWWTP. During the course of this study, it became clear that purging of the wells had unintended consequences for the SDWWTP. Cross connections developed in several wells between the upper and lower monitoring zones either during or after purging, and these cross connections have compromised water-quality data in SDWWTP wells 5, 6, 7, 8, 11, 12, and 15. Although it could not be determined from this study, these cross connections may provide pathways of injectate into layers in the aquifer that had not been previously affected by upward migrating injectate.

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