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Evidence for the removal of CFC-11, CFC-12, and CFC-113 at the groundwater–surface water interface in the Everglades

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Abstract

Poor agreement between $^3H/^3He$ ages and CFC-11 and CFC-12 ages suggests that CFCs may not be conservative tracers in the Everglades National Park. $^3H/^3He$ ages were used to calculate the expected concentration of CFC-11 and CFC-12 in groundwater from wells 2 to 73 m deep. The expected concentrations of CFCs were compared to the measured concentrations and plots of the % CFC-12 and CFC-11 remaining offered no evidence that significant CFC removal was occurring in the groundwater at depths ≥2 m, suggesting that CFC removal occurs at shallower depths. Except where CFC contamination was suspected, CFC-11, CFC-12 and CFC-113 concentrations in fresh surface water were nearly always below solubility equilibrium with the atmosphere. Measurements of CFC-11, CFC-12 and CFC-113 in pore water indicate a 50–90% decrease in concentration 5 cm below the groundwater–surface water (GW–SW) interface. In the same 5 cm interval CH_4 concentrations increased by 300–1000%. This suggested that CFCs were removed at the GW–SW interface, possibly by methane-producing bacteria. CFC derived recharge ages should therefore be viewed with caution when recharging water percolates through anoxic methanogenic sediments.

Keywords: Chlorofluorocarbons; Groundwater; Biodegradation; Tracers; Tritium

1. Introduction

Chlorofluorocarbons (CFCs)-11, -12 and -113 have been successfully used to determine groundwater recharge ages in many studies. Relatively good agreement between individual CFC ages (Katz et al., 2001; Plummer et al., 1998; Katz et al., 1995; Reilly et al., 1994; Busenberg and Plummer, 1992) and ages derived from other tracers, such as $^3H/^3He$ and ^{85}Kr has been reported (Katz et al., 2001; Plummer et al., 1998; Ekwurzel et al., 1994; Szabo et al., 1996) in oxic groundwaters. In these studies the essential assumption that CFCs are conservative in aquifer systems seems to have been met. On the other hand

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several studies have shown that CFC-11 yields older recharge ages than CFC-12 in anoxic aquifers and have suggested that CFC-11 may be degraded under anoxic conditions (Katz et al., 2001; Plummer et al., 1998; Katz et al., 1995; Cook et al., 1995; Dunkle et al., 1993). Oster et al. (1996) have used $^3H/^3He$ ages to predict CFC-11 and CFC-12 concentrations in two shallow unconfined aquifers in the Rhine Valley. They have shown that CFC-11 and CFC-12 are below expected concentrations with CFC-11 degraded at a rate ~10 times faster than CFC-12. Goode et al. (1999) have concluded that CFC-11, CFC-12 and CFC-113 were degraded in shallow anoxic groundwater in New Hampshire. More recently it has been shown that ages derived from all three CFCs yield consistently older ages than $^3H/^3He$ ages in an anoxic aquifer located in Ohio (Rowe et al., 1999). These authors speculated that methanogenic microbial degradation of the CFCs under anoxic conditions could account for the age differences. It has also been shown in laboratory studies that anoxic water saturated sediments have the potential to degrade CFC-11, CFC-12 and CFC-113 (Lovely and Woodward, 1992; Bauer and Yavitt, 1996; Lesage et al., 1992).

In this paper we present evidence that shows CFC-11, -12 and -113 are removed as the CFCs are transported with recharging water through unconsolidated carbonate marl sediments that overlie the carbonate rock aquifer. Furthermore we show data that suggest methanogenic bacteria may be responsible for the CFC removal. The present study differs from previous studies by showing that the CFC degradation occurs at the GW–SW interface, with samples collected in a zone that lies only 5 cm below this interface.

2. Hydrogeology

Groundwater flow beneath Everglades National Park (ENP) occurs within a shallow aquifer termed the Surficial Aquifer System (SAS, Fig. 1). The lithologic and hydrologic characterization of the Surficial Aquifer is described in detail by Fish and Stewart (1991) and Reese and Cunningham (2000). The SAS consists of Miocene to Holocene age siliciclastic and carbonate sediments and varies in thickness from 50 to 82 m. It contains two named carbonate rock aquifers (Gray Limestone Aquifer and Biscayne Aquifer) separated by siliciclastic sediments (Fig. 1). Low permeability sediments of the Hawthorn Group form the base of the SAS. The Hawthorn Group consists of clay-rich sands and mudstones (Reese and Cunningham, 2000).

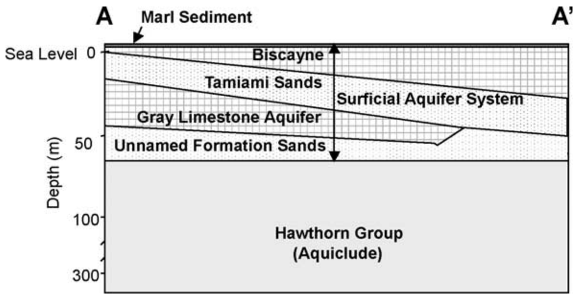

Fig. 1. Generalized hydrogeologic framework beneath ENP adapted from Fish and Stewart (1991) and Reese and Cunningham (2000). Line A-A′ is shown on Fig. 2.

The Biscayne Aquifer forms the top of the SAS, and is the principle source of water supply for residences of South Florida. The Biscayne Aquifer is an unconfined carbonate aquifer rated as one of the most productive in the world with measured transmissivities in excess of 93,000 $m^2\,d^{-1}$, and estimated hydraulic conductivity between 4500 and 12,200 $m\,d^{-1}$ (Fish and Stewart, 1991). The high transmissivity and conductivity are due to the karstic character of the aquifer. The Biscayne Aquifer forms an eastward thickening wedge from a feather edge in the northwest corner of Shark Slough to over 65 m thick along the southeastern coastline (Fig. 2). In many portions of ENP, the Biscayne Aquifer is overlain by marl and peat deposits. In the areas that we sampled, the carbonate rock of the SAS is covered by an unconsolidated $CaCO_3$ marl sediment that ranges from ~5 to 100 cm in depth.

The dominant topographic feature in ENP is an area referred to as the Rocky Glades, which ranges in elevation from 1.5 to 2.5 m. The Rocky Glades separate the two main waterways within ENP, Shark Slough and Taylor Slough (Fig. 2). Shark Slough is the larger of the two sloughs and flows southward toward the Gulf of Mexico. Taylor Slough flows south and discharges into Florida Bay. The sloughs are slow moving bodies of water dominated by expanses of sawgrass marshes and tree islands in what is called

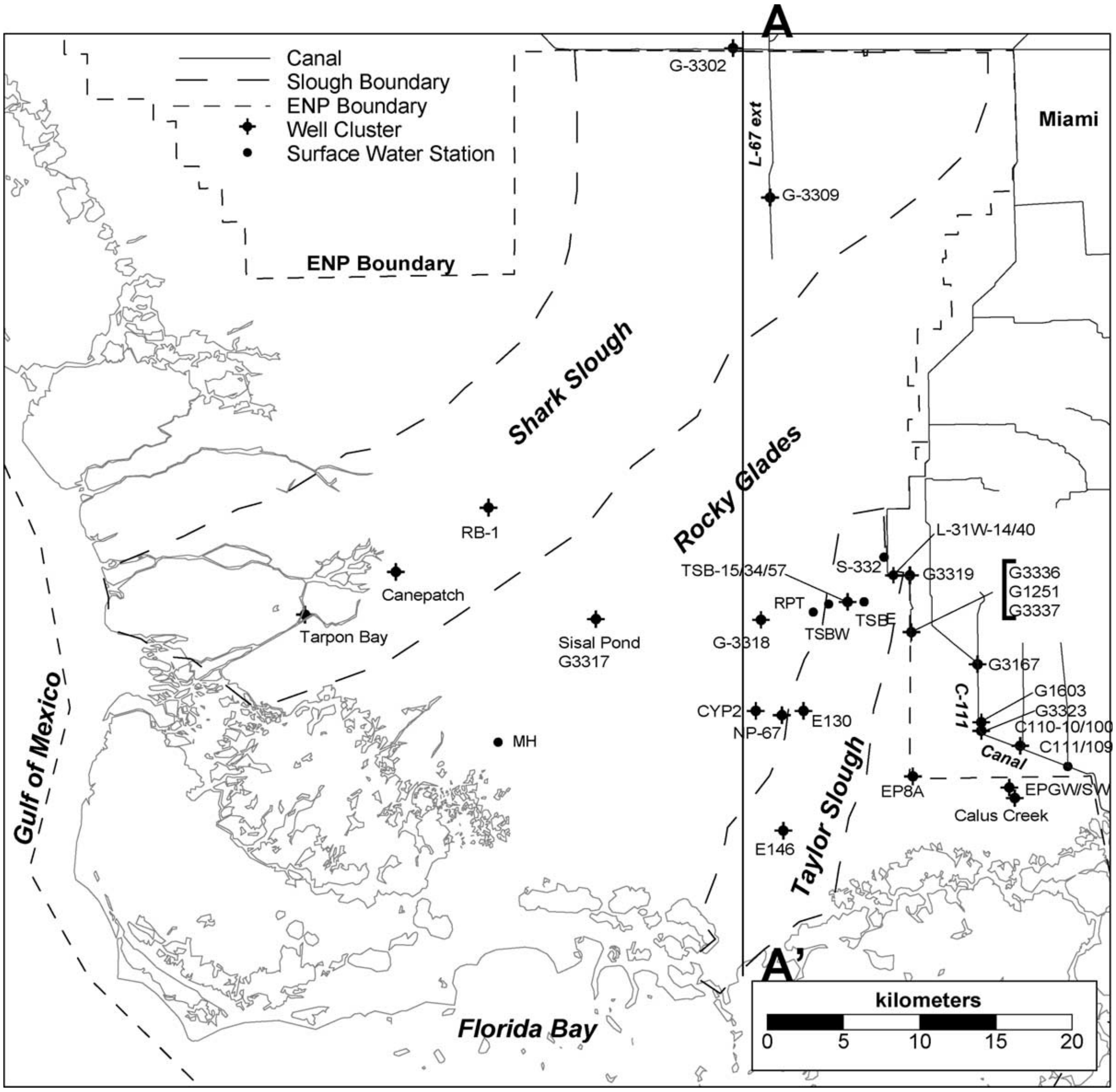

Fig. 2. Site map showing sampling locations. Circles represent surface water sampling only. Circles with crosses represent well clusters of one to four groundwater wells and surface water sampling. Pore water samples were obtained from TSB, TSBE, TSBW, RPT, CYP2, and NP-67. Cross-section A-A′ is shown on Fig. 1.

the 'River of Grass'. The boundaries of the sloughs are poorly defined due to the low topography of the area and varying lateral extent with water levels.

South Florida experiences a subtropical monsoon-type climate, with most rainfall occurring in the summer months from mid-May through mid-October, except during El Niño years, when the winter and spring months have above normal rainfall with slightly cooler than normal temperatures. Water levels within ENP vary seasonally (between 0 and 1.5 m), with the highest water levels typically recorded in September during the wet season, and the lowest water levels recorded in April near the end of the dry season (Fish and Stewart, 1991). Groundwater and surface water are hydraulically connected, and across much of ENP their levels equate. During high water level conditions, groundwater levels rise above the land surface across most of the Everglades, including the Rocky Glades, thereby obscuring the boundaries between Shark and Taylor Sloughs. During low water conditions groundwater levels drop below the land surface in most areas and very slow moving to standing water occurs in limited areas of the sloughs and in depressions in the bedrock of the Rocky Glades. Canals located along the northern and eastern boundaries of ENP are cut into the limestone bedrock of the Biscayne Aquifer and contain water all year. The canals serve as areas of both groundwater recharge and discharge depending upon their location and seasonal water level conditions (Genereux and Slater, 1999).

3. Sampling and analytical methods

Three types of water samples were collected during this investigation. Groundwater samples were collected from wells completed in the SAS. Pore water samples were collected from the marl sediment overlying the carbonate rock. Surface water samples were collected from ponds, canals, and sloughs. Groundwater from 47 wells, 2 to 73 m deep and surface water were collected yearly between 1997 and 1999. Pore water, surface water and groundwater samples at selected sites were collected in 2000 and 2001.

Prior to groundwater sampling for CFCs, ^{3}H, ^{3}He, ^{4}He and Ne, each well was purged with either a submersible pump equipped with Teflon-lined polyethylene tubing or a peristaltic pump equipped with Viton tubing. Samples for noble gases (^{3}He, ^{4}He, and Ne) were collected in copper tubes. These tubes were crimped in the field to prevent contact with the atmosphere. Tritium samples were collected in 1 l amber glass bottles that were pre-filled with dry argon. Samples for CFCs were collected in 100 cm^3 glass syringes that were rinsed then completely filled with the sample water and inspected to have no air bubbles. Duplicate samples for CFCs were collected from most wells. When present, surface water was collected adjacent to each well for CFC analysis. At the time of sampling, water temperature, conductivity and salinity was determined in the field using an Orion SCT meter. Salty surface water samples for CFC analysis were collected in Florida Bay in January of 1999.

Pore water samples for CFC, CH_4 and He/Ne analysis were collected using a 1 m long stainless steel probe (6.4 mm O.D. × 1.6 mm I.D.) with one end plugged and ground to a point. Immediately above the point is a series of small holes drilled over a 1 cm range. This arrangement results in a sampling resolution of ~5 cm. After the probe is inserted into the $CaCO_3$ marl sediment to the desired depth, a syringe (100 ml glass for CFCs and He/Ne, 60 ml plastic for CH_4) equipped with a three-way polycarbonate stopcock is used to withdraw a sample. The three-way stopcock allows the syringe to be flushed and filled without detaching it from the probe, and also prevents air from getting into the probe while flushing the syringe. Immediately after collecting a He/Ne sample in the glass syringe, the water was transferred to a copper tube, which was then crimp-sealed. A depth profile was obtained by inserting the probe to the 5 cm depth, taking a sample and then successively inserting the probe deeper.

Tritium concentrations were determined by the helium in-growth method or by electrolytic enrichment followed by gas proportional counting. Helium-3 concentrations were determined by mass spectrometry (Clarke et al., 1976). The CFC concentrations were measured, within 24 h of sample collection, using a custom built purge and trap capillary column gas chromatograph modified from similar systems described in Bullister and Weiss (1988) and Happell et al. (1996). All CFC concentrations are reported on the SIO 1998 absolute calibration scale (Prinn et al., 2000). Apparent ^{3}H/^{3}He ages and CFC ages were calculated using standard techniques (Solomon and Cook, 2000; Plummer and Busenberg, 2000).

Methane concentration in surface, pore or groundwater samples was determined by drawing 30 ml of water into a 60 ml syringe. An equal amount of N_2 was added to the syringe and CH_4 was extracted using the headspace equilibration technique (McAuliffe, 1971). Methane concentrations were determined within a few hours of collection on a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 3.2 mm by 2 m stainless steel Porapak Q column.

4. Results and discussion

4.1. Comparison between $^3H/^3He$ ages and CFC ages in groundwater

The present study has evolved from an earlier one (Price, 2001) that characterized the shallow groundwater in the ENP. In that study, observed CFC ages were found to be older than the $^3H/^3He$ ages on the same samples (Fig. 3), hence the extension of work to explain the disparity. Here, by tracer age we mean the apparent age. Implicit in this are the assumptions that no gas loss occurs after recharge and that the observed tracer age distribution is a result of piston flow. We do not discuss the appropriateness of a particular groundwater flow model because the true ages are not of interest in this study. Incidentally, while theoretical evidence (Maloszewski and Zuber, 1982; 1983) suggests that the piston flow model (PFM) may not be appropriate for a karst aquifer, Katz et al. (2001) conclude that PFM yields the best fit to CFC and $^3H/^3He$ age observations in the karstic system of north-central Florida. The key question is whether the difference in apparent CFC and $^3H/^3He$ ages is an artifact of differential diffusion and/or dispersive loss for ^3He and the CFC. Two earlier studies in unconfined surficial aquifers in the eastern USA show that $^3H/^3He$ and CFC ages agree within the analytical uncertainties (Ekwurzel et al., 1994; Szabo et al., 1996). Therefore we attribute the age difference to non-dispersive loss of CFCs.

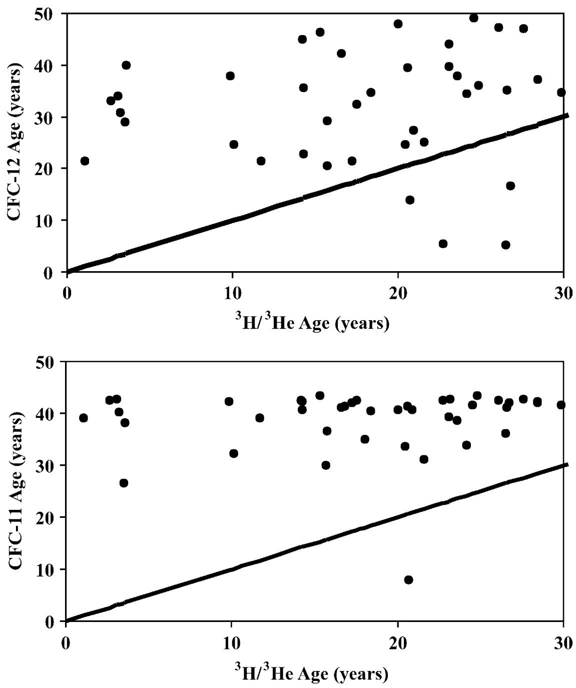

Fig. 3. $^3H/^3He$ age versus CFC-12 age (top panel) and $^3H/^3He$ age versus CFC-11 age (bottom panel). Although $^3H/^3He$ ages older than 30 years were observed we only present ages younger than 30 years because Price (2001) has concluded that samples older than 30 years have been significantly affected by dispersion by comparing total ^3H ($^3H + {}^3He$) in the groundwater samples with ^3H in Miami rainfall. The solid line in both panels is the one to one line. A majority of the points that fall above these lines indicating that the corresponding CFC age was older than the $^3H/^3He$ age. This suggests that the CFCs were not conservative. Several points in each graph fall below the lines suggesting that there may be slight CFC contamination in these samples.

Assuming that the $^3H/^3He$ ages of ≤ 30 years were correct, the amount of CFC-12 and CFC-11 expected to be in a groundwater sample was calculated from the appropriate atmospheric time history (Prinn et al., 2000), recharge temperature (26 °C), and solubility function (Warner and Weiss, 1985). The percentage amount of CFC-12 or CFC-11 remaining in a groundwater sample was then calculated from the expected and measured concentrations. The percent of each CFC remaining was then plotted against the $^3H/^3He$ age (Fig. 4A and B). A logarithmic decrease in the percent CFC remaining with increasing recharge age would suggest pseudo-first order CFC removal within the groundwater as has been shown for CCl_4 removal within a Long Island aquifer (Happell and Wallace, 1998). It was not possible to fit any type of line that had a slope significantly different from zero to either % CFC-12 remaining (Fig. 4A) or the % CFC-11 remaining (Fig. 4B), suggesting that significant removal was not occurring within the groundwater of the SAS below the marl sediment-carbonate rock interface.

4.2. Removal of CFC-12, CFC-11 and CFC-113 at the groundwater–surface water interface

Since the study gives no evidence to suggest significant CFC removal in the groundwater beneath the marl sediment-carbonate rock interface, CFC removal was either occurring in the shallow groundwater in the marl sediments or in the surface water. It is unlikely that CFC removal is occurring in

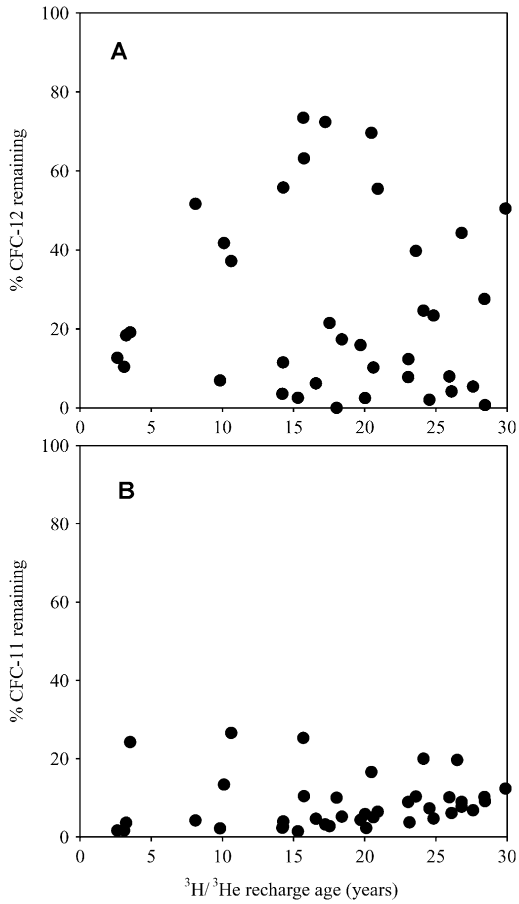

Fig. 4. % CFC-12 (A) and CFC-11 (B) remaining as a function of $^3H/^3He$ derived recharge age. The samples were collected from wells that ranged in depth from 2 to 73 m. The expected CFC-12 and CFC-11 concentration in each sample was calculated from the $^3H/^3He$ derived recharge age and the atmospheric time history and solubility of the CFCs. The expected and measured CFC concentrations were then used to calculate the % CFC remaining. These figures suggest that no significant degradation of CFC-12 or -11 occurs within groundwater samples collected from ≤ 2 m deep because it was not possible to fit any type of line that had a slope significantly different from zero to the data.

the oxygenated surface water because CFC degradation has only been observed in anoxic water (Katz et al., 2001; Rowe et al., 1999; Plummer et al., 1998; Dunkle et al., 1993; Bauer and Yavitt, 1996; Oster et al., 1996; Cook et al., 1995; Katz et al., 1995; Lesage et al., 1992; Lovely and Woodward, 1992). If the atmosphere was the only source of CFCs to the surface water and the CFCs behaved conservatively, then the surface water CFC concentrations should be near solubility equilibrium with the atmosphere at the time of sampling. A total of 77 fresh surface water samples for CFC-11 and CFC-12 analysis were collected as part of this study. One of these samples was above solubility equilibrium (supersaturated) for CFC-11 and 10 were supersaturated for CFC-12. This suggests that the atmosphere was not the only source of CFC-11 and CFC-12 in these supersaturated samples. All of the supersaturated CFC-11 and CFC-12 surface water samples were from canals, where the dumping of automobiles, refrigerators, and other CFC containing equipment is a common occurrence. The remaining samples (76 for CFC-11 and 67 for CFC-12) were at or below solubility equilibrium (undersaturated). The average saturation values ($\pm\sigma_s$) for these samples were 70.6 ± 1.5% for CFC-11 and 75.6 ± 1.7% for CFC-12. Similar results were observed for CFC-113, although 26 of the 77 samples appeared to be supersaturated either from non-atmospheric sources or because of an interfering peak in the chromatogram. The remaining 51 undersaturated samples had an average saturation of 61.4 ± 2.6%. The CFC undersaturated surface water appears to be broadly distributed throughout ENP and CFC undersaturations were observed in both the dry and wet seasons.

Possible explanations for the CFC undersaturation in the surface water include the discharge of old groundwater, or a loss of CFCs at the GW–SW interface. It is important to note that CFC adsorption onto sediment particles cannot explain the surface water undersaturations because adsorption is a reversible process. At steady state, the rate of CFC sorption is going to be equal to the rate of CFC desorption, and the surface water will eventually reach equilibrium with the atmosphere. In order for the surface water to remain undersaturated there must be an irreversible process removing the CFCs.

Older groundwater discharging to the surface water could explain the undersaturated values, but it is unlikely that discharge was occurring at all the sites we sampled. Price (2001) used an ^{18}O balance to get an average discharge rate of $0.7 \pm 1.4\ \mathrm{cm\,d^{-1}}$ between December 1997 and September 1999 for the area just south of Taylor Slough Bridge (TSB). A chloride mass balance in the same area over the same time gave an average recharge rate of $0.7 \pm 10.1\ \mathrm{cm\,d^{-1}}$. The relatively large uncertainties in the average discharge rates suggest large variability in the discharge rate and monthly data suggest there are times when discharge occurs, other times when recharge occurs and that the net advective exchange is zero over this time period. Harvey et al. (2000) also found that there was little advective exchange of groundwater in the area just south of TSB during the same time period using chloride mass balance, and that there was a net loss of surface flow between the headwaters of Taylor Slough (S332 structure) and TSB suggesting recharge in the area north of TSB. Price (2001) measured water level elevations 16 times between December 1997 and August 1998 at the TSB well site and found no measurable difference in groundwater levels from the surface water during most times, when there was a small difference the surface water elevation was greater than the head levels in the wells indicating a potential for recharge flow (Price, 2001) at TSB.

Assuming steady-state conditions, zero wind speed, and no horizontal surface water movement, a conservative estimate of the discharge of low CFC groundwater needed to maintain the CFC surface water undersaturations was made. The average flux of each CFC across the water–air interface was calculated with

$$F_g = k(C_w - C_s) \tag{1}$$

where C_w was the measured CFC concentration in the surface water in pmol m^{-3}, C_s was the concentration of CFC expected in the surface water that is in equilibrium with the atmosphere in pmol m^{-3}, k was the air–water exchange coefficient (piston velocity) in m d^{-1} (Happell et al., 1995) and F_g was the flux of CFC leaving box in pmol m^{-2} d^{-1}. At steady state and no horizontal exchange, the fluxes of CFCs entering the surface water from the atmosphere would be equal to the fluxes leaving at the GW–SW interface. Assuming that these removal fluxes were only due to the dilution of the surface water by low CFC concentration groundwater and using an average groundwater concentration below 10 cm for each CFC, groundwater discharge estimates were 11, 10 and 14 cm d^{-1} for CFC-11, CFC-12 and CFC-113.

A groundwater discharge flux of 10–14 cm d^{-1} averaged over the whole area of the ENP is needed if discharging groundwater were the only processes keeping the surface water undersaturated. These estimates are 3–5 times greater than estimates obtained from other studies (Harvey et al., 2000; Price, 2001), and require the whole area of the ENP to be a discharge zone, which also conflicts with the conclusions of Harvey et al. (2000) and Price (2001). While discharging groundwater could explain some of the surface water CFC undersaturations, it cannot explain the magnitude and spatial extent of the observed undersaturations. Therefore, some other processes must be responsible for the surface water undersaturations. We hypothesize that CFC removal was occurring at the GW–SW interface, where anoxic conditions exist and this removal was occurring at a rate faster than CFC equilibration with the atmosphere resulting in CFC undersaturated surface water. Removal at this interface would allow CFCs to be removed from the surface water in the absence or presence of advective (recharge or discharge) flow.

Initial pore water CFC concentration profiles were obtained from two sites within ENP, one adjacent to the TSB well nest and the other ~0.5 km east of TSB

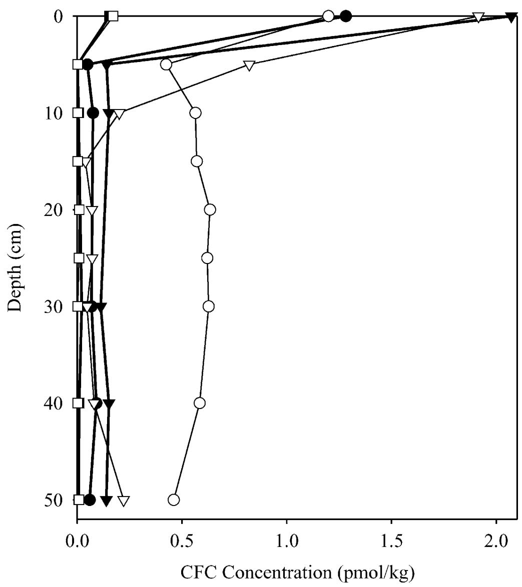

Fig. 5. CFC-11 (triangles), CFC-12 (circles), and CFC-113 (squares) in surface and pore water at the TSB well site (closed symbols, thick lines) and TSBE (open symbols, thin lines) on 10/12/00. The surface water at both sites was ~50 cm deep at the time of sampling. The 0 cm concentrations are surface water samples drawn from within 2 cm of the GW–SW interface. Surface water saturations were 77, 82 and 64% for CFC-11, CFC-12 and CFC-113, respectively, at TSB and 71, 77, 76%, respectively, at TSBE. The largest decrease in CFC concentration occurs between the surface water and 5 cm deep in the sediment pore water.

(TSBE) (Fig. 5). All of the CFCs were undersaturated in the surface water at both of these sites. Both of these profiles indicated that CFC-11, CFC-12 and CFC-113 concentrations decreased with depth in the pore water, with ~90% of the loss occurring between the surface water (0 cm) and 5 cm deep in the sediment. Below the 5 cm depth the CFC pore water concentrations remained relatively constant. This supports our hypothesis that CFC removal was occurring at the GW–SW interface.

Additional pore water profiles were obtained at TSB (Fig. 6) and at NP-67 well site (Fig. 7) and CYP-2 well site (Fig. 7). Similar to the first two pore water profiles, CFC concentrations in the surface water were undersaturated and the CFC pore water concentrations decreased with depth in the sediment, with the largest decrease occurring between the surface water and 5 cm deep in the sediment. Below 5 cm the CFC concentrations remained relatively constant. Again this indicates that CFC removal was occurring at the GW–SW interface. Furthermore, CH_4 concentrations increased between the surface water and 10 cm deep in the sediment and remained relatively constant below 10 cm. The largest increase in CH_4 concentration occurred between the surface water and 5 cm deep in the pore water, and was coincident with the largest decrease in CFC concentrations.

The surface water depth at the TSB site (Fig. 6) was 50 cm. Surface water samples for CFCs and CH_4 were taken just below the surface water–atmosphere interface and just above the GW–SW interface. The concentrations of CFC-11, CFC-12, CFC-113 and CH_4 were relatively constant throughout the water

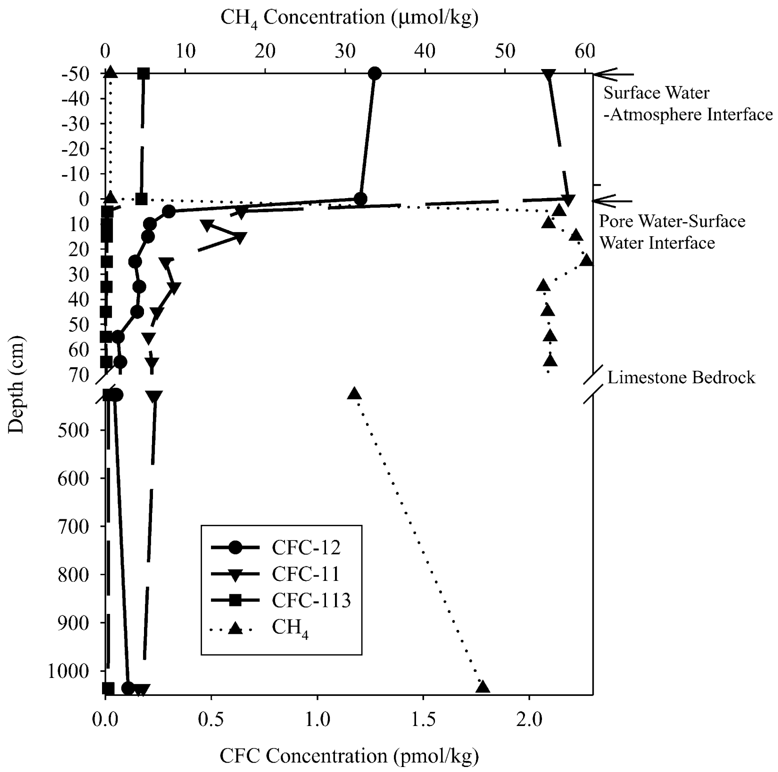

Fig. 6. CFCs and CH_4 in surface, pore and groundwater at the TSB well site on 10/18/00. The surface water appears to be well mixed based on the relatively constant CFC and CH_4 concentrations at the top and bottom of the water column. Surface water saturations were 78, 81 and 75% for CFC-11, CFC-12 and CFC-113, respectively. The largest decrease in CFC concentrations occurs between the surface water and 5 cm deep in the sediment pore water and is coincident with the depth where the largest increase in CH_4 concentration occurs.

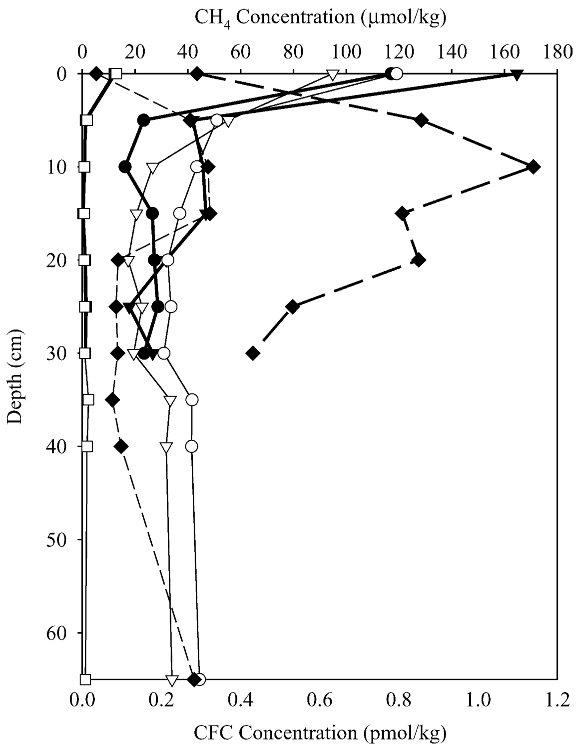

Fig. 7. CFC-11 (triangles), CFC-12 (circles), CFC-113 (squares), and CH_4 (diamonds) in surface and pore water at the NP-67 well site (closed symbols, thick lines) and CYP-2 well site (open symbols, thin lines) on 10/30/00. The surface water was ~20 and 10 cm deep at NP-67 and CYP-2, respectively. The 0 cm concentrations are surface water samples drawn from within 2 cm of the GW–SW interface. Surface water saturations were 39, 48 and 32% for CFC-11, CFC-12 and CFC-113, respectively, at NP-67 and 24, 52 and 37%, respectively, at CYP-2. The largest decrease in CFC concentrations occurs between the surface water and 5 cm deep in the sediment pore water and is coincident with the depth where the largest increase in CH_4 concentration occurs.

column (Fig. 6) suggesting the surface water is well mixed. In addition to the shallow groundwater and surface water samples, deeper groundwater was also sampled from the two shallowest wells (427, 1036 cm) in the TSB well nest. Concentrations of CFCs in the deeper groundwater were very similar to the concentrations found in groundwater sampled between 10 and 65 cm in the sediment column, suggesting that significant removal does not occur in the deeper groundwater. The abrupt decrease in CFC concentrations across the top 5 cm of the sediment is consistent with a majority of the CFC removal occurring at the GW–SW interface.

The hypothesis that a majority of the CFC removal occurs at the GW–SW interface does not require recharge at each pore water sampling site at the time of sampling in order to produce the observed pore water profiles. Recharge has to occur some place in the ENP and may occur at some time at the pore water sampling sites. When and where recharge occurs is when a majority of the CFCs in the groundwater are removed. The shallow groundwater at each individual site could be undergoing local recharge, have been locally recharged in the past, have been recharged someplace else and transported horizontally to the site, or any combination of all three.

It is possible that gas bubbles form by denitrification and methanogenesis in the sediments and ebullition of these bubbles could be stripping some of the CFCs from the shallow groundwater and surface water. It has been shown that ebullition was a relatively rare occurrence during chamber flux measurements of methane emission from Everglades's wetlands (Happell et al., 1993). Samples of surface and pore water were collected to test for the possibility of bubble stripping. CFC, CH_4, He and Ne concentrations were measured in these samples and percent saturations were calculated (Table 1). Similar patterns in CFC and CH_4 concentrations that were observed at the other surface and shallow groundwater sites were observed during this sampling, with the surface water generally undersaturated with CFCs and a large decrease in CFC concentration between the surface water and 5 cm deep in the pore water that was coincident with a large increase in CH_4 concentration. There was one difference in that the CFC-12 concentrations in the surface water from the Taylor Slough area were at or slightly above solubility equilibrium with the atmosphere. If bubble stripping were occurring and causing the undersaturated CFC concentrations, then He and Ne would be undersaturated to an even greater extent due to their lower solubilities. He and Ne were always slightly supersaturated in both surface water and pore water (Table 1), most likely due to the presence of 'excess' air (Heaton and Vogel, 1981), indicating that bubble stripping was not removing significant amounts of any of the trace gases measured. This suggests that other processes are responsible for the CFC undersaturations.

Table 1
Concentrations and % saturation values of various gases measured on 12/5/01

Location	Temp. (°C)	Conc. (pmol/kg)			Conc. (μmol/kg)	Conc. (10^{-8} cm^3/g)		% Saturation					
		CFC-12	CFC-11	CFC-113	CH_4	He	Ne	CFC-12	CFC-11	CFC-113	CH_4	He	Ne
TSB wells surface H_2O	25.0	1.62	2.44	0.16	0.66	7.32	27.2	100.2	89.1	69.6	1170.8	164.1	150.5
TSB wells pore H_2O 5 cm	25.5	0.17	0.35	0.03	153	8.34	31.2	10.8	13.1	11.4	270029.3	187.2	172.8
TSB wells pore H_2O 10 cm	25.5	0.11	0.22	0.01	138	7.00	25.0	6.9	8.4	5.7	243273.7	157.2	138.2
TSB wells pore H_2O 20 cm	25.5	0.09	0.17	0.01	126	7.21	25.7	5.6	6.4	3.1	222214.2	162.0	142.4
TSB west surface H_2O	25.7	1.67	2.58	0.17	0.19	6.66	20.9	105.7	97.0	75.4	337.8	149.6	115.8
RPT surface H_2O	26.0	0.84	1.15	0.08	7.76	6.56	18.5	53.6	43.6	37.5	13671.6	147.5	103.0
TSB east surface H_2O	26.0	1.65	2.40	0.17	0.51	6.75	23.7	105.5	91.5	74.8	902.4	151.8	131.4

TSB: Taylor Slough Bridge; RPT: Royal Palm Turnoff.

4.3. Potential CFC removal mechanisms and implications for groundwater dating

The most likely explanation for the data observed in this study was that the CFCs were undergoing biodegradation at the GW–SW interface. Laboratory studies indicate that anoxic methane-producing sediments can consume CFC-11, CFC-12 (Lovely and Woodward, 1992; Bauer and Yavitt, 1996), and CFC-113 (Lesage et al., 1992), although these studies were carried out at CFC concentrations that are at least 1000 times greater than present background concentrations. Khalil and Rasmussen (1990) observed that rice paddies could consume small amounts of atmospheric CFC-11 and CFC-12 using chamber flux measurements. Khalil and Rasmussen (1989) also observed lower CFC-11, CFC-12 and CFC-113 concentrations inside termite mounds compared to air outside the termite mounds. Both of these environments contain methanogenic bacteria. Rowe et al. (1999) have shown that most CFC-11, CFC-12 and CFC-113 derived recharge ages were older than $^3H/^3He$ derived recharge ages in a buried valley aquifer, with the difference between CFC-12 and $^3H/^3He$ ages increasing with increasing CH_4 concentration.

In this study, there was an abrupt decrease in CFC concentrations (50–90%) within the top 5 cm of anoxic sediment, which was coincident with the greatest increase in CH_4 concentration. Similar reductions in CFC-11 and CFC-12 concentrations were observed in an unconfined aquifer in the Rhine Valley, although the depth range (3–4 m), and presumably the time range (~10 years), over which the change occurred was greater than in this study (Oster et al., 1996). Although this is not direct proof that methanogenic bacteria are consuming CFCs in the Everglades, it does support the hypothesis that methanogens are responsible for the observed CFC removal. Additional support of the methanogenic degradation hypothesis for CFC-11 and CFC-12 in the Everglades lies in a comparison of the surface water saturations between freshwater and saltwater samples. CFC-11 (70.6 ± 1.5%) and CFC-12 (75.6 ± 1.7%) were significantly undersaturated in the fresh surface water of the ENP, where methanogenic bacteria can exist at the GW–SW interface. In saltwater systems, methanogenic activity is not present at the GW–SW interface because methanogenic bacteria are out-competed by sulfate-reducing bacteria. Surface water samples ($n = 3$) collected from Florida Bay, a shallow estuarine ecosystem located just south of the land portion of the ENP, were near solubility equilibrium with the atmosphere for CFC-11 (97.9 ± 2.6%) and CFC-12 (105.0 ± 2.4%). Even in saltwater samples CFC-113 was significantly undersaturated (66.1 ± 1.6%), suggesting that the removal pathway for CFC-113 in freshwater may be different than for CFC-11 and CFC-12 or that there may be an additional removal pathway for CFC-113 in Florida Bay.

Rowe et al. (1999) have suggested that CFCs cannot be used as reliable age tools in anoxic groundwater systems, because they are not conserved. This study confirms this conclusion and shows that even though CFC removal may not be significant at depths ≥ 2 m, it does occur as recharging water passes the GW–SW interface where active methanogenesis is occurring. CFC ages should be viewed with caution where recharging water must pass through sediments with active populations of methane-producing bacteria. This would apply to groundwater that receives a majority of its recharge through wetlands, lakes or rivers. The data also raise the interesting possibility that wetlands may be a tropospheric sink for atmospheric CFC-11, CFC-12 and CFC-113.

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