Degradation rates of CFC-11, CFC-12 and CFC-113 in anoxic shallow aquifers of Araihazar, Bangladesh

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Abstract

Chlorofluorocarbons CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and CFC-113 ($CCl_2F–CClF_2$) are used in hydrology as transient tracers under the assumption of conservative behavior in the unsaturated and saturated soil zones. However, laboratory and field studies have shown that these compounds are not stable under anaerobic conditions. To determine the degradation rates of CFCs in a tropical environment, atmospheric air, unsaturated zone soil gas, and anoxic groundwater samples were collected in Araihazar upazila, Bangladesh. Observed CFC concentrations in both soil gas and groundwater were significantly below those expected from atmospheric levels. The CFC deficits in the unsaturated zone can be explained by gas exchange with groundwater undersaturated in CFCs. The CFC deficits observed in $^3H/^3He$ dated groundwater were used to estimate degradation rates in the saturated zone. The results show that CFCs are degraded to the point where practically no (<5%) CFC-11, CFC-12, or CFC-113 remains in groundwater with $^3H/^3He$ ages above 10 yr. In groundwater sampled at our site CFC-11 and CFC-12 appear to degrade at similar rates with estimated degradation rates ranging from ~0.25 yr^{-1} to ~6 yr^{-1}. Degradation rates increased as a function of reducing conditions. This indicates that CFC dating of groundwater in regions of humid tropical climate has to be carried out with great caution.
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1. Introduction

Chlorofluorocarbons (CFCs) CFC-11 (CCl_3F), CFC-12 (CCl_2F_2) and CFC-113 ($CCl_2F–CClF_2$) are chemical compounds that have been produced industrially since the 1930s (e.g., Siegemund et al., 1988). Until the late 1980s, the atmospheric concentrations of these compounds increased monotonically. In recent years, however, their atmospheric concentrations have stabilized or declined as a consequence of the Montreal protocol.

Starting in the 1970s, CFCs have been used as a dating tool in oceanographic research (e.g., Hahne et al., 1978; Gammon et al., 1982; Thiele et al., 1986; Bullister and Weiss, 1988; Schlosser et al., 1991; Haine

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and Richards, 1995; Boenisch et al., 1997; Pickart and Smethie, 1998; Schlosser et al., 1999; Smethie and Fine, 2001). Soon thereafter, they also have been applied to groundwater studies (Thompson and Hayes, 1979; Busenberg and Plummer, 1992; Cook and Solomon, 1995; Oster et al., 1996; Szabo et al., 1996; Plummer et al., 2001). However, whereas CFC based groundwater ages can be applied in a more or less straightforward manner in many aquifers, point source contamination of groundwater with CFCs, degradation of the CFCs in groundwater, or excess CFCs in soil gas due to locally or regionally elevated atmospheric CFC levels can complicate the application of these tracers (Oster et al., 1996; Ho et al., 1998; Santella et al., 2003). Degradation of CFCs has been reported under anoxic conditions (Lesage et al., 1990; Bullister and Lee, 1995; Cook et al., 1995; Oster et al., 1996; Shapiro et al., 1997; Böhlke et al., 1997; Sharpiro et al., 1998; Plummer et al., 1998a,b; Plummer et al., 2000; Happell et al., 2003; Hinsby et al., 2007). Laboratory studies indicate that the degradation of CFCs is likely due to sulfate-reducing or methane forming microbes (Lesage et al., 1992; Lovley and Woodward, 1992; Sonier et al., 1994; Bauer and Yavitt,

1996; Oremland et al., 1996). The degradation mechanism of CFCs is likely to be dechlorination (Khalil and Rasmussen, 1989; Lovley and Woodward, 1992; Sonier et al., 1994; Deipser and Stegmann, 1997; Shapiro et al., 1997). Whereas the general features of CFC degradation have been revealed in recent studies, uncertainty remains with respect to the degradation rates of the individual CFCs. For example, whereas Oster et al. (1996) found an apparent rate of CFC-11 degradation about 10 times faster than the apparent rate of CFC-12 degradation in compost, sediments, and pond water, a CFC degradation study in the anoxic Framvaren Fjord (Shapiro et al., 1997) revealed first-order CFC-11 degradation rates ranging from $6–9 \text{ yr}^{-1}$, and CFC-12 degradation rates ranging from $0.01–0.03 \text{ yr}^{-1}$ i.e., at this site CFC-11 was removed from the water column at rates that exceeded those for CFC-12 by more than 2 orders of magnitude. The general degree of reactivity of CFCs under anoxic conditions seems to be CFC-11>CFC-113>CFC-12 (Höhener et al., 2003).

The objective of this study is to determine the stability of CFCs over a range of redox conditions in the shallow aquifers in Araihazar upazila (Fig. 1),
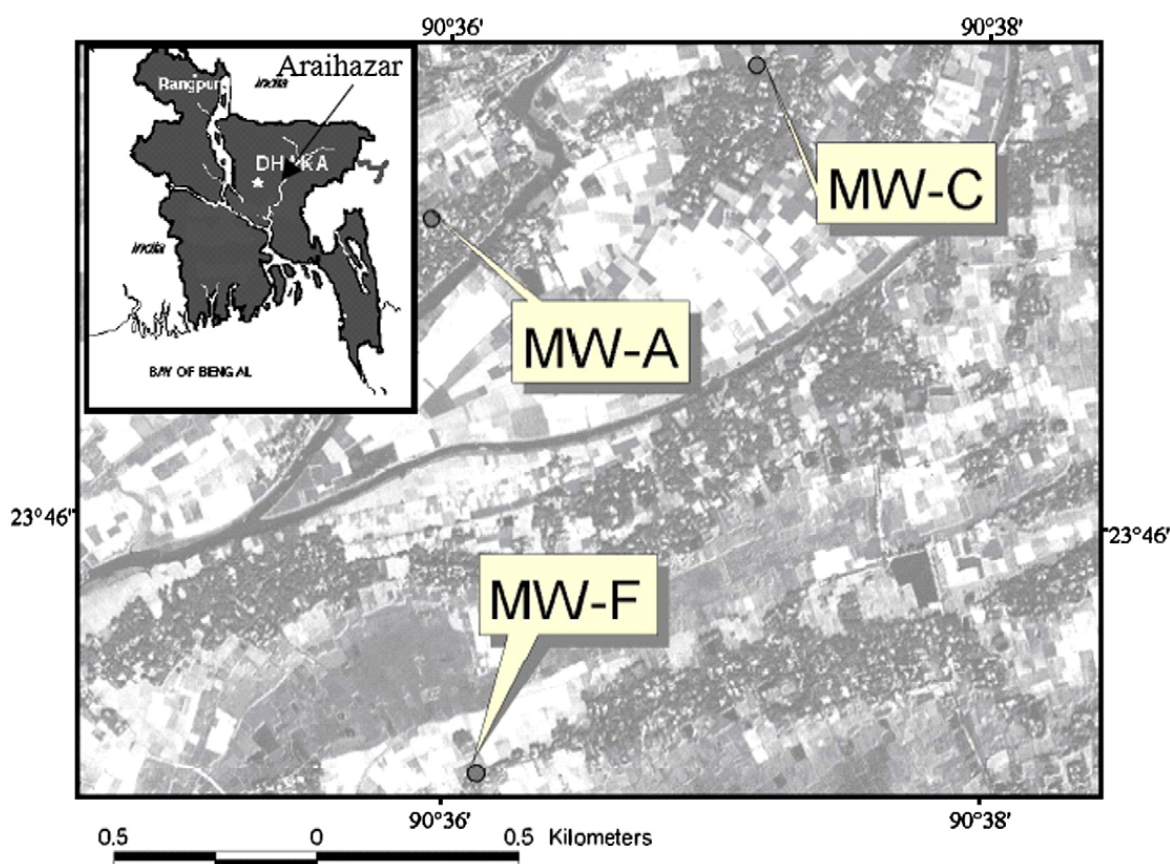

Fig. 1. Locations of the three multi-level wells MW-A, MW-C, and MW-F, where groundwater and soil gas samples were collected for CFC analyses. Inset shows the location of the Araihazar study area.

Bangladesh (90.6°E, 23.7°N), a site of Columbia University's long-term health, earth science, engineering, and social science study of elevated arsenic concentrations in drinking water (van Geen et al., 2002; van Geen et al., 2003).

2. Hydrogeological setting

Over the last 5–7 kyr of the Holocene, between 20 and 80 m of alluvial silt, sand, gravel, and clay have accumulated across the Ganges–Brahmaputra–Meghna delta (Goodbred and Kuehl, 1999; Goodbred and Kuehl, 2000; BGS and DPHE, 2001; Goodbred et al., 2003). These relatively young deposits are typically separated from older, presumably Pleistocene, formations by one or several clay layers. Such a Pleistocene formation, the Madhupur Terrace (Fergusson, 1863), has been uplifted and affects the geology of the Araihazar study site (Fig. 1). Indeed, the thickness of Holocene sediments increases from only 15 m in the western portion of Araihazar to 150 m a few kilometers to the east (van Geen et al., 2003). The Holocene shallow aquifer materials range from silt to fine sands, with hydraulic conductivities between 9 and 38 m d^{-1} (Horneman, 2006). The vertical hydraulic conductivities vary from 10^{-3} to ~1 m d^{-1} (Zheng et al., 2005). The elevation of the groundwater table fluctuates seasonally over a range of ~4 m in Araihazar, reaching a maximum in the monsoon season (July), and a minimum at the end of the dry season (March). The ^{3}H/^{3}He estimated groundwater ages in the Holocene aquifers range

from less than <1 yr in the uppermost part of the aquifer to >40 yr in groundwater below 25 m that is practically ^{3}H-free (Stute et al., 2007).

Samples were collected for CFCs from nests of monitoring wells at three locations in Araihazar that have been characterized previously (Horneman et al., 2004). Although the sites are less than 3 km apart, their surface geomorphology is different and affects the rate of local recharge. The Holocene aquifer extends to a depth of 16 and 27 m at sites MW-C and MW-F, respectively. At both sites, sandy aquifer material essentially extends to the surface and the recharge rates derived from ^{3}H/^{3}He age profiles are elevated (~0.5 m yr^{-1} at MW-F and 1.1 m yr^{-1} at MW-C; Stute et al., 2007). At site MW-A, the Holocene aquifer is capped by ~2 m of silty surface soil and, consequently, the recharge rate derived from the ^{3}H/^{3}He age profile is only ~0.11 m yr^{-1}.

3. Methods

3.1. Sample collection

Three sets of well nests constructed of 2 in. PVC with a 0.9 m galvanized iron pipe at the surface (sites MW-A, C, and F; see Fig. 1) were sampled for CFCs and ^{3}H/^{3}He in January 2003 at depths ranging from 5.7 to 26.4 m below the surface (Table 1). The screens were 0.9 m long at site MW-A and 1.5 m at sites MW-C and MW-F. Atmospheric air at site MW-A and soil gas in the

Table 1
Overview of sampled depth intervals at the three multi-level wells, measured groundwater CFC concentrations and ^{3}H/^{3}He estimated ages

Site	Depth	CFC-11	CFC-12	CFC-113	^{3}H/^{3}He age
	m	pmol kg^{-1}	pmol kg^{-1}	pmol kg^{-1}	yr
MW-A	**7.4**	**0.110/0.112**	**0.168/0.215**	**0.015/0.011**	**3.54 ± 0.27**
	10.5	**<0.03/0.043**	**0.075/0.076**	0.011/0.013	**10.77 ± 0.24**
	13.4	0.056	0.018	<0.01	20.29 ± 2.29
	16.1	0.068/<0.03	0.026/0.016	<0.01/<0.01	31.66 ± 0.94
MW-C	**5.7**	**<0.03/0.032**	**0.132/0.134**	<0.01/<0.01	**−0.53 ± 0.47**
	9.3	**<0.03/<0.03**	**0.026/0.027**	0.014/<0.01	**0.8**
	12.4	<0.03/<0.03	<0.01/<0.01	<0.01/<0.01	2.60 ± 0.40
	15.4	0.034/<0.03	<0.01/<0.01	<0.01/<0.01	2.77 ± 0.29
MW-F	**6.9**	**0.363/0.280**	**0.509/0.482**	**0.032/0.025**	**0.79 ± 0.40**
	12.2	**0.039/0.058**	**0.018/<0.01**	<0.01/<0.01	**2.79** [a]
	16.2	0.034/<0.03	0.041/0.035	<0.01/<0.01	5.28 ± 0.28
	20.4	<0.03/<0.03	<0.01/<0.01	<0.01/<0.01	29.1 ± 1.10
	26.4	<0.03/<0.03	<0.01/<0.01	<0.01/<0.01	>40

Replicate samples are separated by "/". CFC values below detection limit are marked with <0.01 for CFC-12 and CFC-113 and <0.03 for CFC-11. The depth intervals marked with bold at each site are used for calculating the CFC degradation rates.
^{3}H/^{3}He ages from Stute et al. (2007).
Depth intervals, CFC measurements, and tritium–^{3}He ages used to estimate CFC degradation rates are in bold.
[a] Age is based on linear regression between two neighboring samples.

unsaturated zone within 20 m distance of all three sites were sampled for CFC measurement in January 2005. To avoid CFC contamination during sampling, only copper, brass, and stainless steel tubing/connectors were used. A submersible stainless steel pump (Rediflo 2, Grundfos, Ks, U.S.A.) was used for sample collection. Before sampling, the wells were purged until pH, conductivity, temperature, and oxidation–reduction potential (ORP) readings (U22XD, Horiba, CA, U.S.A.) had stabilized.

3.2. Tritium–^{3}He sampling and analysis

^{3}H samples were collected in 250 mL glass bottles and samples for helium isotopes were collected in copper tubes in January 2003. The samples were analyzed by mass spectrometry (e.g., Clarke et al., 1976; Ludin et al., 1998). The ^{3}H/^{3}He results (for summary of values used in this study, see Table 1) are discussed in Stute et al. (2007). The agreement between the historic atmospheric ^{3}H concentrations for Bangladesh (Stute, 2001), and the measured ^{3}H + ^{3}He concentrations as a function of the apparent ^{3}H/^{3}He groundwater ages at MW-A, MW-C, and MW-F gives confidence in the tritium–^{3}He ages (Stute et al., 2007).

3.3. CFC sampling and analysis

A total of 13 groundwater samples with replicates were collected for CFC analysis (4 levels at site MW-A, 4 at site MW-C, and 5 at site MW-F; Table 1). The samples were stored in flame sealed ampoules as described by Busenberg and Plummer (1992). The nitrogen gas used to flush the sampling apparatus was tested and found to be CFC-free at the Lamont-Doherty Earth Observatory (LDEO) and subsequently shipped to Bangladesh. To avoid degassing during sample collection, the sampling line was pressurized by holding the overflow tube ~2 m above the sampling level and visually checking that no bubbles appeared in the ampoules.

The samples were stored in the dark and shipped via air to LDEO where they were refrigerated until their analysis. The samples were analyzed for CFC-11, CFC-12, and CFC-113 over a period of 2 days, approximately 1 month after collection, using a purge and trap system interfaced to a gas chromatograph (Hewlett Packard HP 6890 series GC system; Smethie et al., 2000). Based on the blanks, the detection limit for CFC-12 and CFC-113 was determined to be ~0.01 pmol kg^{-1}. However, the system had a CFC-11 memory when running the groundwater samples. To counter this memory effect, blank samples consisting of quantitatively degassed water (>99%) were

run after one to three sample measurements to monitor and correct for the memory effect as well as purge the system. Despite measurement of the blank samples, the detection limit of CFC-11 was ~0.03 pmol kg^{-1}, three times higher than those for CFC-12 and CFC-113.

Three soil gas profiles consisting of a total of 12 samples were collected in January 2005 using 1 L Cali-5-Bond™ pillow gas sampling bags (Calibrated Instruments, Inc., McHenry, MD) each equipped with one double O-ring valve. The profiles were collected with a soil gas probe (AMS Manual Soil Gas Vapor Probe). Sampling depths ranged from 0.5 to 3 m with a typical sampling interval of 0.5 m. In addition, two atmospheric air samples were collected on January 5 and 6, 2005 at site MW-A.

Storage tests of the gas sampling bags at LDEO with CFC-free gas and standard gas with known CFC-11, CFC-12, and CFC-113 concentrations showed no measurable change in concentrations over time periods of two weeks. A 200 mL glass syringe was used to pump soil gas through the soil probe into the bags. The bags were flushed 4 times with 50 mL of soil gas from the depth interval of interest before a total of ~360 mL air was collected in each bag. Including the flushing of the tubing of the probe, a total of 1000 mL air was drawn for sampling. Assuming an air filled porosity of 0.3, the sampling affected a sphere with a radius of 0.14 m. Nylon tubing (1/8″ ID) and 3-way valves (Cole Parmer) were used to connect the gas sampling bags with the 200 mL glass syringe. The soil gas samples were analyzed at LDEO approximately three weeks after collection on the same system as the groundwater samples.

3.4. Methane and hydrogen analyses

In 2005, nine samples with replicates were collected in 50 mL glass crimp vials using rubber stoppers with no headspace at sites MW-A and MW-F for dissolved methane (CH$_4$) and H$_2$ gas analyses. To avoid breakdown of methane during storage, the samples were poisoned with 0.1 mL of saturated HgCl$_2$ solution (Fisher Scientific). The samples were analyzed at Princeton University approximately five days after collection by introducing an N$_2$ gas headspace and letting the water re-equilibrate with the headspace. The re-equilibrated headspace was then analyzed by a Kappa 5 Gas Chromatograph (Tracer Analytical, Ca.; Lin et al., 2005). Also, an additional 9 (50 cm to 200 cm depth) soil gas samples collected in January 2005 (MW-A: 2 samples; MW-C: 4 samples; MW-F: 3 samples) were analyzed for CH$_4$ on the same instrument.

3.5. Iron and sulfur analyses

The Fe(II)/Fe(tot) ratios of the leachable fraction of the sediments, dissolved iron, dissolved sulfate, and dissolved reduced sulfur were measured at the three sites. Dissolved reduced sulfur and iron-complexed sulfide was measured on site immediately after sample collection in January 2003 using a differential pulse
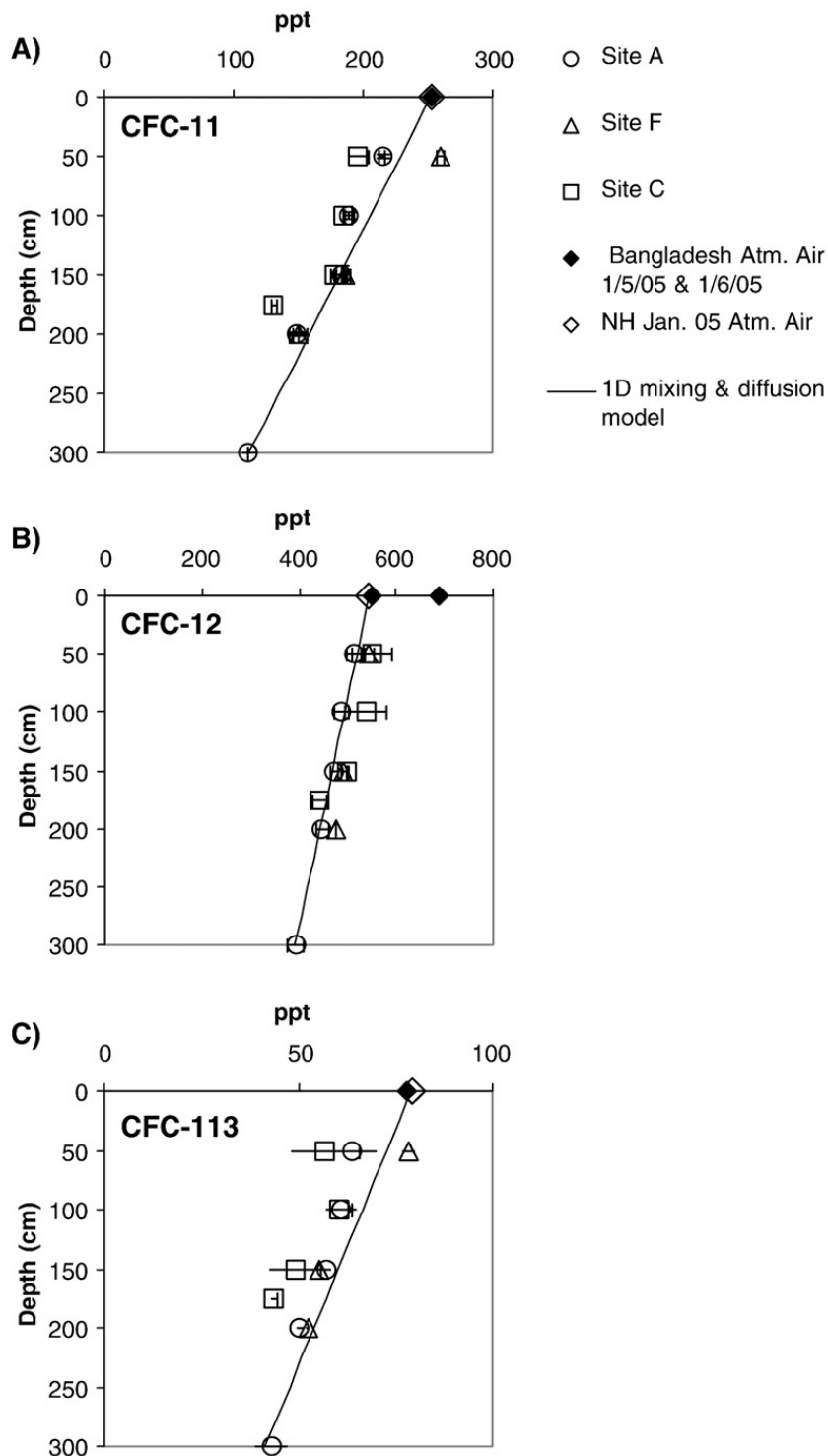

Fig. 2. A) CFC-11, B) CFC-12 and C) CFC-113 soil gas profiles from sites MW-A, MW-C and MW-F. Also shown are atmospheric CFC concentrations measured 1/5/05 and 1/6/05 and avg. NH atmospheric CFC concentrations January 2005 (NOAA/CMDL, 2005). Lines show the results of the 1-D mixing and diffusion models.

stripping voltammetry method with sub nM detection limit (He et al., 2002). Addition of dissolved sulfide standard resulted in an increase of both reduced sulfur and iron-complexed sulfide peaks. This increase is not linear as one would expect from a standard addition calibration experiment. Therefore, rather than absolute

concentrations, the measured peak areas for reduced sulfur (-0.55 eV) and iron-complex sulfide (-1 eV) are used in this study. The analytical methods for the other parameters used in this study are presented in previous studies describing the geochemistry of the Araihazar study area (Horneman et al., 2004; Zheng et al., 2004).
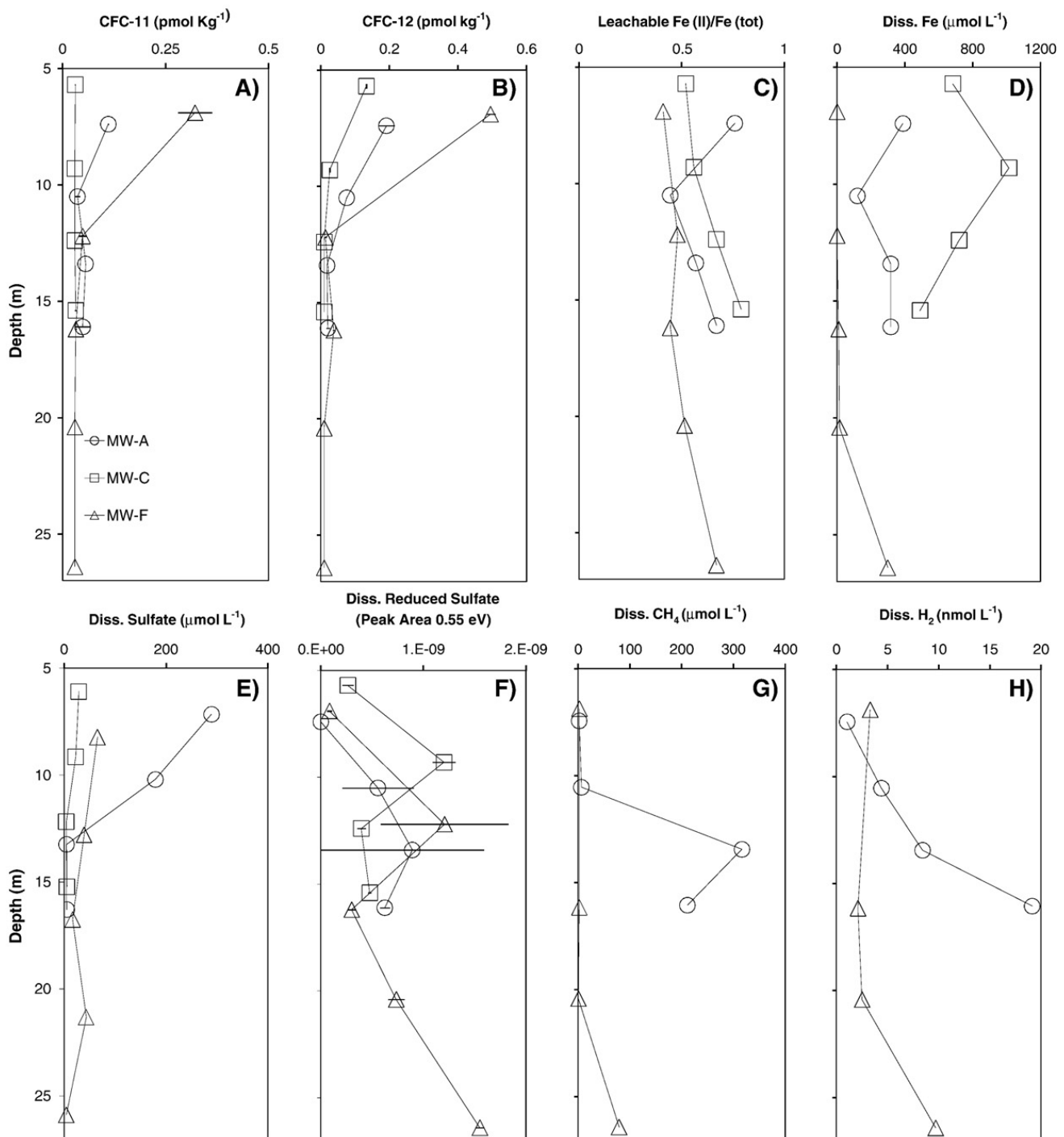

Fig. 3. CFC concentrations and redox indicators from the three multi-level wells: A) CFC-11 concentrations, B) CFC-12 concentrations, C) leachable Fe(II)/Fe ratios, D) dissolved iron (Horneman et al., 2004), E) dissolved sulfate (Zheng et al., 2004), F) dissolved reduced sulfur quantified by the -0.55 V peak area, G) dissolved methane (only sites MW-A and MW-F), and H) dissolved hydrogen (only sites MW-A and MW-F).

4. Results

4.1. CFCs in local atmosphere and soil gas

The CFC concentrations in the two atmospheric samples have CFC-11 and CFC-113 concentrations within 1% of the average concentrations of the Northern Hemisphere for January 2005 (NOAA/CMDL, 2005; Fig. 2). The same holds for the CFC-12 concentration in the sample collected on January 5, 2005. In the air sample collected on January 6, 2005, however, the CFC-12 concentration is 1.3 times higher than that of the remote atmosphere.

Atmospheric concentrations (~250 ppt) of CFC-11 appear only in the shallow soil gas sample at site MW-F (50 cm, 260 ppt; Fig. 2A). All other soil gas samples have CFC-11 concentrations lower than the remote atmosphere, with the highest deficit seen at site MW-A at 300 cm depth (111 ppt or 56.1% deficit) compared to

average Northern Hemisphere air concentrations). The soil gas CFC-11 concentration gradient ranges from ~41 to 73 ppt m^{-1}. CFC-12 soil gas concentrations are close to atmospheric concentrations at 50 cm depth (94–101%, 513–551 ppt) at all three sites (Fig. 2B). The CFC-12 concentration gradient ranges from 46 to 81 ppt m^{-1} and the concentration is 72–88% of the average Northern Hemisphere (NH) air concentrations at 175–300 cm depth (393–477 ppt). Similarly to CFC-11, the soil gas CFC-113 concentration at 50 cm depth at site MW-F is close to the atmospheric concentrations and deficits were observed in all other samples (Fig. 2C). The CFC-113 concentrations in the 175–300 cm interval range from 54 to 66% of average NH air (~79 ppt), with the lowest concentration found at MW-A (43 ppt; 300 cm depth). The gradient of CFC-113 concentration in the soil air is 8 to 18 ppt m^{-1}. Measurements of CH_4 in the soil gas revealed little variation between the individual samples and the concentrations were ~1 ppm.
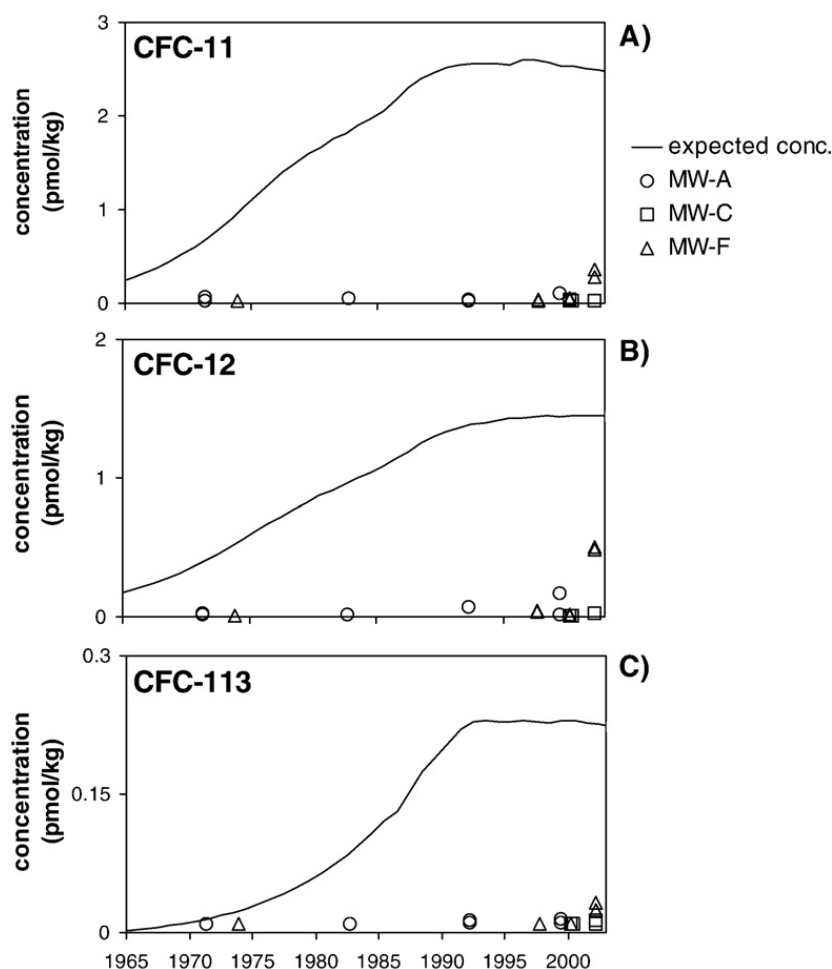

Fig. 4. Measured A) CFC-11, B) CFC-12, and C) CFC-113 concentrations versus $^3H/^3He$ calculated groundwater ages (Stute et al., 2007). Also shown are the expected CFC concentrations for water recharged at 26.3 °C based on $^3H/^3He$ groundwater ages and the atmospheric CFC concentration.

4.2. Dissolved CFCs

The measured CFC concentrations ranged from <0.03 to 0.363 pmol kg^{-1} for CFC-11, <0.01 to 0.509 pmol kg^{-1} for CFC-12, and <0.01 to 0.032 pmol kg^{-1} for CFC-113 (Table 1; Fig. 3). The concentrations measured in the shallowest depth interval at the three multi-level wells were highest for all three CFCs at MW-F (6.9 m, groundwater table at 4.5 m), intermediate at MW-A (7.4 m, groundwater table at 4.3 m), and lowest at MW-C (5.7 m, groundwater table at 3.2 m). The concentrations decrease with depth and are generally at or below the detection limit at depths below 12.4 m at all three sites.

The variability between replicate samples for CFC-11 (Table 1) can in part be explained by multiple peaks interfering with the analysis and in part by the fact that we sampled along a strong concentration gradient. Multiple peaks were not observed on the chromatographs for CFC-12, which also showed better agreement between replicate samples.

The temperature measured in the shallowest wells (5.7 to 7.4 m below surface) at sites MW-A, MW-C and MW-F, ranged from 26.3 to 26.4 °C (average: 26.33 °C) and was assumed to represent the recharge temperature. Whereas the ^{3}H/^{3}He groundwater ages range from practically 0 (-053 ± 0.47; 1-sigma error) to >40 yr in the three multi-level wells (Table 1), the apparent groundwater ages formally derived from the CFC concentrations are significantly higher ranging from 36 to >48 yr (CFC-11), 29 to >55 yr (CFC-12), and 27 to >33 yr (CFC-113). When comparing the measured CFC concentrations with those expected from the atmospheric time-dependent concentration curve and the ^{3}H/^{3}He derived recharge ages (Stute et al., 2007) it is evident that the measured concentrations for all three CFCs are significantly below the expected values (Fig. 4). For CFC-11, the deficiencies range from $87.1 \pm 2.4\%$ in recently recharged water (MW-F, 6.9 m, ^{3}H/^{3}He$=0.8 \pm 0.4$ yr), to more than 90% in groundwater recharged more than 3 yr ago (MW-A, MW-C, and MW-F). Likewise, for CFC-12, the deficiencies range from $65.8 \pm 1.3\%$ (MW-F, 6.9 m, ^{3}H/^{3}He$=0.8 \pm 0.4$ yr) to more than 90%, whereas the CFC-113 deficiencies range from $87.5 \pm 2.1\%$ (MW-F, 6.9 m, ^{3}H/^{3}He$= 0.8 \pm 0.4$ yr) to more than 95% in all other samples.

Dissolved oxygen was not detected by either a Chemets Oxygen Test Kit or oxygen electrode at any depth in the three multi-level wells. The oxidation–reduction potential (ORP) ranges from 112 mV to -200 mV, with the highest (and only positive) ORP value measured in the shallowest well at site MW-F (6.9 m; Table 2).

Whereas the Fe(II)/Fe(tot) ratios increase with depth at sites MW-C (0.52 to 0.79) and MW-F (0.41 to 0.67), they are variable with depth at site MW-A, but within the same range as the values observed at sites MW-C and MW-F (Table 2, Fig. 3). Significant range and variability with depth is also observed in the dissolved Fe concentrations. The highest dissolved Fe concentrations are found at site MW-C and range from 489 to 1014 µmol L^{-1}. In contrast, the dissolved Fe concentrations are less than 20 µmol L^{-1} down to 20 m at site

Table 2
Measured redox parameters at the 3 multi-level wells

Site	Depth	ORP	Fe(II)/Fe(tot)[a]	Fe[a]	Sulfate[b]	Sulfide peak area at	CH$_4$	H$_2$
	m	mV		µmol L^{-1}	µmol L^{-1}	-0.55 mV	µmol L^{-1}	nmol L^{-1}
MW-A	**7.4**	**−88**	**0.76**	**388.8**	**289.1**	NP	**2.2**	**1.0**
	10.5	**−86**	**0.45**	**120.4**	**179.0**	6E−10±4E−10	**6.6**	**4.4**
	13.4	−159	0.57	316.9	4.3	9E−10±7E−10	316.5	8.4
	16.1	−182	0.67	316.5	5.1	6E−10±5E−11	211.3	19.1
MW-C	**5.7**	**−113**	**0.52**	**684.0**	**28.6**	**3E−10 ± 6E−11**	**ND**	**ND**
	9.3	**−144**	**0.56**	**1014.6**	**22.4**	**1.2E−09 ± 1E−10**	**ND**	**ND**
	12.4	−155	0.67	720.6	4.2	4E−10±4E−11	ND	ND
	15.4	−156	0.79	489.9	5.2	5E−10±1E−11	ND	ND
MW-F	**6.9**	**112**	**0.41**	**0.2**	**65.2**	**9E−11 ± 7E−10**	**2.3**	**3.3**
	12.2	**−20**	**0.48**	**0.3**	**39.1**	**1.2E−09 ± 6E−10**	**ND**	**ND**
	16.2	−71	0.45	9.7	16.7	3E−10±4E−11	2.2	2.1
	20.4	−96	0.52	15.5	43.0	7E−10±8E−11	0.6	2.5
	26.4	−200	0.67	299.6	4.2	1.6E−09±4E−11	79.3	9.7

The depth intervals marked with bold at each site are used for calculating the CFC degradation rates.
NP indicates no peak detected.
Depth intervals in bold are used for calculating the CFC degradation rates.
[a] From Horneman et al. (2004).
[b] From Zheng et al. (2004). ND indicates no data.

MW-F and intermediate (120–389 µmol L^{-1}) at site MW-A.

The sulfate concentrations generally decrease with depth at all three sites. However, the measured sulfate concentration in the shallowest sample is 5–10 times higher at site MW-A compared to sites MW-F and MW-C. This pattern is also reflected in the increasing reduced sulfur concentrations with depth. The shallowest depth level at site MW-A is practically free of sulfide, whereas sites MW-C and MW-F have low, but detectable sulfide concentrations suggesting active sulfate reduction.

The methane concentrations at site MW-F are constant between 0.6 and 2.3 µmol L^{-1} in the upper 20 m of the shallow aquifer, and increase to 79.3 µmol L^{-1} in the deeper part of the aquifer. At site MW-A the CH_4 concentrations increase below a depth of 10.5 m, and range from 6.6 µmol L^{-1} (10.5 m) to 316.5 µmol L^{-1} (13.4 m). The shallowest depth interval has a dissolved CH_4 concentration of 2.2 µmol L^{-1}, similar to the shallowest depth level at site MW-F. The dissolved hydrogen (H_2) concentrations follow a pattern similar to that of CH_4 at sites MW-F and MW-A. At site MW-F the concentrations range from 2.1 to 3.3 nmol L^{-1} down to a depth of 20.4 m, and increase to 9.7 nmol L^{-1} at the deepest level (26.4 m). At site MW-A the shallowest depth level has an H_2 concentration of 1 nmol L^{-1}. Between 10.5 and 16.1 m depth the concentrations increase from 4.4 nmol L^{-1} to a maximum of 19.1 nmol L^{-1}.

5. Discussion

5.1. Atmospheric CFC concentrations in Bangladesh

Although the time series of atmospheric CFC concentrations is not well established for our sampling site in Bangladesh, the CFC monitoring programs around the world show only modest spatial variation in the atmospheric CFC concentrations away from industrialized regions (Cunnold et al., 1994; NOAA, 2005). Thus, it is reasonable to assume that the time series of average CFC concentrations for the remote Northern Hemisphere should be representative for Bangladesh. This assumption is supported by the atmospheric CFC-11, CFC-12 (1/6/05 sample, but not the 1/5/05 sample; see discussion below), and CFC-113 concentrations in our atmospheric air samples from Araihazar upazila. Daily, as well as hourly, changes in atmospheric CFC-11 and CFC-12 concentrations exceeding the 26% variability observed in this study for CFC-12 have been observed near urban areas (Santella et al., 2003). The variability in the changes in atmospheric concentrations

is related to wind direction, wind speed, and distance from sources (Prather et al., 1987; Ho et al., 1998). The prevalent wind direction during winter in Bangladesh is from northern or north-westerly directions. The Araihazar study area is situated ~25 km east–northeast of Dhaka, pointing to this urban center as a likely source for the elevated CFC-12 atmospheric concentration measured on January 5, 2005. However, it is worth noting that a large part of today's production and use of CFCs is taking place in neighboring India (McCulloch et al., 2001; McCulloch et al., 2003) and that long-range transport might contribute to our observed elevated CFC-12 concentrations.

5.2. Redox conditions and CFC degradation

During the dry season (October–April), the unsaturated zone in Bangladesh is typically 2–4 m thick whereas the subsurface is practically fully saturated during the monsoon (May–September). Most of the recharge occurs during the monsoon season. However, because of groundwater irrigation, some artificial recharge might occur during the dry season. Irrigation is most pronounced at site MW-F, which is surrounded by rice fields (van Geen et al., 2006), and less important at sites MW-A and MW-C. The absence of an unsaturated soil zone during the monsoon season limits the age of the soil gas to a maximum of 5–6 months at the time of sampling (January 2005). The observed decrease in soil gas CFC-11, CFC-12 and CFC-13 concentrations (Fig. 2) can therefore not be explained by aging of the soil gas because the atmospheric gradients over such a small time span are practically negligible compared to our measured gradients in the soil gas profiles.

Similarly, comparison of the measured groundwater CFC concentrations with those expected from the $^3H/^3He$ groundwater ages (Fig. 4) excludes groundwater age as cause for the observed low CFC concentrations. A recent study indicated that the loss of CFC by retardation or sorption is insignificant in aquifers (Cook et al., 2006 and references herein). Cook et al. (1995) estimated CFC retardation factors ranging from 1.15 (CFC-12) to 1.70 (CFC-113). Considering the stable or perhaps declining atmospheric CFC concentrations since the mid 1990s, and the CFC deficiencies observed at MW-F (6.9 m) with a $^3H/^3He$ estimated recharge age of less than 1 yr, the CFC retardation factor would have to be more than 8 to explain the CFC loss, which seems to be unrealistic. CFC loss by in situ degassing of methane or carbon dioxide is unlikely, as this process presumably also would affect the $^3H/^3He$ ages through loss of ^3He. The agreement between atmospheric

tritium, $^{3}H/^{3}He$ ages, and $^{3}H+^{3}He$ concentrations (Stute et al., 2007) does not indicate such a loss of ^{3}He. Because of the precautions taken during sampling, the correspondence of the replicate CFC-12 results, and the monotonic profiles for CFC-11, CFC-12 and CFC-113, degassing during sampling cannot account for the observed losses of CFC. The most plausible explanation for the large deficiency of CFC-11, CFC-12 and CFC-113 in soil and groundwater is therefore degradation that affects groundwater and soil gas at our sampling sites.

In a series of laboratory experiments, Sonier et al. (1994) found a higher rate of CFC-11 degradation in sulfate-reducing compared to methanogenic environments. The high CFC-11 degradation rates observed in the Framvaren Fjord study was in a sulfur reducing environment (Shapiro et al., 1997). However, other laboratory experiments link high CFC degradation rates to methanogenic environments (Lesage et al., 1992; Bauer and Yavitt, 1996). A CFC degradation study observed 50–100% degradation in a methanogenic environment at the surface water/groundwater interface in the Everglades, U.S.A. (Happell et al., 2003), whereas recent studies demonstrated CFC degradation under pyrite oxidation conditions (Sebol et al., 2007), as well as in a pyritic sand aquifer, where CFC degradation was attributed to reduction by Fe(II) (Hinsby et al., 2007).

The presence of both sulfate-reducing and methanogenic environments has been documented in shallow Bangladesh aquifers (Ahmed et al., 1998; BGS and DPHE, 2001; Harvey et al., 2002; Zheng et al., 2004). In Araihazar upazila, measurable CFC concentrations are only observed in the shallowest two depth levels in the three multi-level wells (5.7–12.2 m; Table 1). Therefore, the degradation rates can only be estimated in the uppermost part of the shallow aquifer in this study. Although evidence of methanogenesis is observed at depth both at site MW-A and F, the low CH_4 and H_2 concentrations in the shallowest samples at the two sites (Table 2; Fig. 3) indicate that the shallow samples have not reached a methanogenic redox state. In fact, at site MW-F this does not occur at depths above $\sim$20 m. In the shallowest sample at site MW-A (7.4 m), the dissolved Fe concentrations (388.8 μmol L^{-1}), the high sulfate concentrations (289.1 μmol L^{-1}), the absence of dissolved sulfide, and the low dissolved H_2 (1 nmol L^{-1}) concentrations, suggests a redox environment in which iron reduction dominates (Lovley and Goodwin, 1988). At site MW-C (5.7 m) and MW-F (6.9 m), however, the lower dissolved sulfate concentrations (28.6 and 65.2 μmol L^{-1}), measurable reduced sulfur concentrations, and higher dissolved H_2 concentrations compared

to MW-A (MW-F: 3.3 nmol L^{-1}), suggest a well-established sulfate-reducing environment. MW-C (5.7 m) is perhaps the more reducing well due to lower dissolved sulfate and higher reduced sulfur concentrations. Therefore, although site MW-A becomes more reducing with depth than site MW-F (and possibly site MW-C), the shallowest depth intervals at site MW-A appear to be less reducing.

It has been demonstrated that the reducing conditions at the root zone of rice paddies, the most prevalent crop in Araihazar upazila, can promote methane formation (Khalil et al., 1990), as well as sulfate reduction (Kimura et al., 1991). The consistent CH_4 concentrations of $\sim$1 ppm in the soil gas do not provide evidence of variations in the redox conditions of the unsaturated zone.

5.3. CFC decrease in the unsaturated soil zone

The decrease of CFC in the unsaturated soil zone appears to be linear for all CFCs at the three sites (Fig. 2). When normalizing the soil gas CFC concentrations to the Northern Hemisphere mixing ratios, the highest decrease with depth is observed for CFC-11 (0.16–0.29 per meter depth), intermediate for CFC-113 (0.11–0.23 m^{-1}), and lowest for CFC-12 (0.08–0.15 m^{-1}). The decrease per meter depth seems consistent at all three sites for CFC-11, CFC-12 and CFC-113. The linear soil gas profiles can be explained by diffusion of CFCs from the atmosphere through the unsaturated soil zone to a sink at the groundwater table. To test this hypothesis, a 1-D box model was constructed assuming mixing only by diffusion as described by Santella et al. (2003). We added an atmospheric source and a groundwater sink to this box model, assuming an effective diffusivity in the soil of $\sim$0.2 m^2 d^{-1}. The box size was 25 cm and the calculations were performed in 10^{-3} day (d) intervals (1.44 min). The model results indicate that the unsaturated zone needs less than 30 days to reach a linear steady-state CFC profile if the only source is the atmosphere and the only sink is flux into the groundwater across the water table. Therefore, it is unlikely that the observed decrease of CFCs is driven by degradation in the unsaturated zone.

Using the fluxes of CFCs from the atmosphere to the groundwater table calculated with the simple diffusion and mixing model suggests similar groundwater degradation rates for the three CFCs ranging from $\sim$1.8 yr^{-1} for CFC-12 to 3.9 yr^{-1} for CFC-11. These values are within the range estimated from groundwater concentration profiles in the following sections.

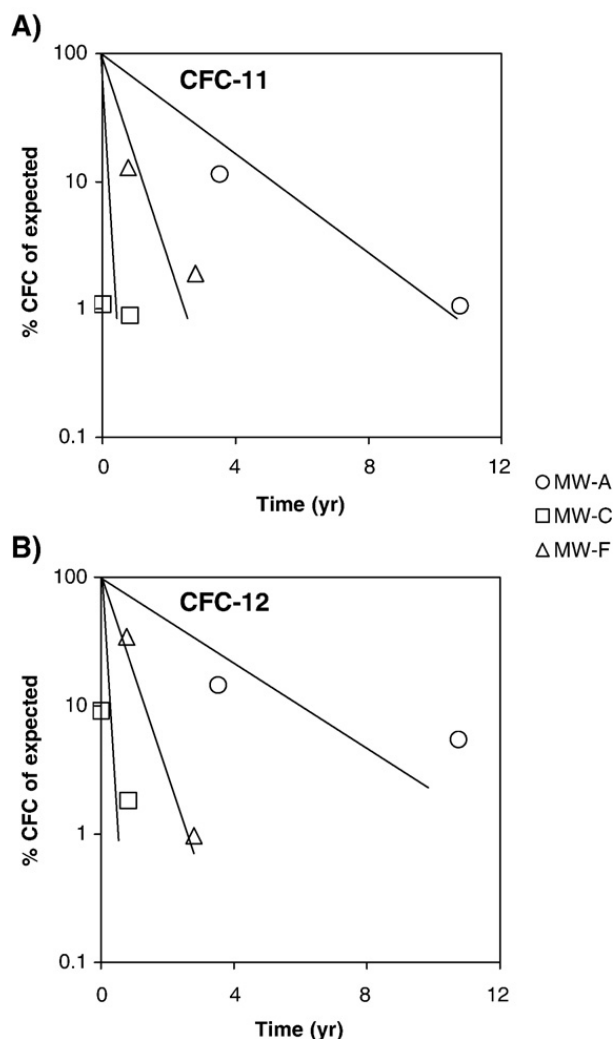rates of CFC-11 and CFC-12 in the shallow aquifers can be constrained by either assuming that the CFC concentrations in the shallowest water samples are in equilibrium with the soil gas at the groundwater table or, more likely, due to the absence of an unsaturated soil zone during the Monsoon season, in equilibrium with the atmosphere at the time of recharge. As expected, the CFC-11 and CFC-12 profiles appear to be exponential pointing to a first-order degradation reaction (Fig. 5). Using both equilibrium with the deepest soil gas samples (the lower degradation rates stated below) and atmospheric CFC concentrations (the higher degradation rates stated below) as boundaries for the CFC concentrations in the most recently recharged water, the degradation rates can be calculated for CFC-11 and CFC-12 using the measured CFC concentrations in the two shallowest wells at each of the three sites. At site MW-C the degradation rates of CFC-11 and CFC-12 range from ~5.1 yr^{-1} to ~6.0 yr^{-1}, and ~4.8 yr^{-1} to ~5 yr^{-1}, respectively. The degradation rates range from ~1.3 yr^{-1} to 1.5 yr^{-1} (CFC-11) and ~1.6 yr^{-1} (CFC-12) at site MW-F, and ~0.4 yr^{-1} to 0.5 yr^{-1} (CFC-11) and ~0.25 yr^{-1} to ~0.3 yr^{-1} (CFC-12) at site MW-A (Table 3). A minimum CFC-113 degradation rate of 0.5 yr^{-1} and 1.6 yr^{-1} can be estimated based on the shallowest sample at site MW-A (7.4 m) and MW-F (6.9 m), respectively. Both these rates, however, are based on only one low concentration measurement (Table 1).

The observed degradation rates of CFC-11 and CFC-12 are consistent with the redox conditions in the top 12.2 m of the shallow aquifer at the three sites. They are highest at site MW-C, intermediate at site MW-F, and lowest at site

Fig. 5. Semi-log of percent measured A) CFC-11 and B) CFC-12 of expected CFC concentrations. Expected CFC concentrations for water recharged at 26.3 °C are inferred from the $^3H/^3He$ derived groundwater ages and avg. NH CFC concentrations. The initial groundwater concentration at time=0 is assumed to be in equilibrium with the atmosphere.

5.4. CFC degradation in the saturated zone

The rate of CFC degradation occurring within the shallow aquifers is difficult to determine due to the low concentrations measured in the youngest waters caused by the high rate at which the degradation occurs, the related relatively few data points per profile, and an unknown CFC concentration in the most recently recharged water. Whereas the CFC-113 concentrations in all cases except MW-F (6.9 m) are at or below the detection limit, up to 1/5 and 1/3 of the expected concentrations of CFC-11 and CFC-12, respectively, are found in waters with $^3H/^3He$ ages of less than 1 yr.

Whereas the measured CFC-113 concentrations are too low to estimate degradation rates, the degradation

Table 3
Estimated degradation rates for CFC-11, CFC-12 and CFC-113, and corresponding redox conditions

Site	CFC-11 [a] yr^{-1}	CFC-12 [a] yr^{-1}	CFC-113 [b] yr^{-1}	Redox conditions [c]
MW-A	~0.4 to ~0.5	~0.25 to ~0.3	~0.5	Iron reducing
MW-C	~5 to ~6	~4.8 to ~5	ND [d]	Sulfate reducing
MW-F	~1.3 to ~1.5	~1.6	~1.6	Sulfate reducing

[a] The degradation rates at each location are based on the measured CFC-11 and CFC-12 concentrations in the shallowest two depth intervals and assumption of equilibrium with the atmosphere or soil vapor at the time of recharge.

[b] The CFC-113 degradation rates represent minimum rates based on the shallowest depth interval at site MW-A and MW-F.

[c] The estimates of the redox states are based on the discussion in Section 5.2.

[d] ND: The CFC-113 concentrations were below the detection limit at the shallowest depth interval.

MW-A. It cannot be ruled out that the variations of the degradation rates estimated at site MW-A (screens of 0.9 m), MW-C (screens of 1.5 m), and MW-F (screens of 1.5 m) are affected by sampling in a strong concentration gradient. The degradation rates, however, in the more sulfate-reducing environments (site MW-C and MW-F) appear to be between 3.3 and 15, and 5.4 and 20 times higher for CFC-11 and CFC-12, respectively, if compared to the less reducing site MW-A. Generally, the degradation rate of CFC-11 appears to be higher or equal to CFC-12. Therefore, as also found in the literature, rather than CFC degradation being restricted to a certain redox regime such as sulfate reduction or methanogenesis, it occurs over a range of redox conditions. In this study the CFC-11 and CFC-12 degradation rates increase with reduced sulfur concentrations in the shallow and intermediate depth levels at the three sites (Fig. 6). The rate of CFC-11 and CFC-12

degradation is an order of magnitude higher in the sulfate-reducing environments of the shallow and intermediate depth levels at sites MW-F and MW-C than in the mixed iron and sulfate-reducing environments of the shallow and intermediate depth levels at site MW-A.

Previous studies of CFC degradation, typically carried out under temperate climate conditions, have found the degradation to affect either solely CFC-11 (e.g. Cook et al., 1995) or all three CFCs (e.g. Hinsby et al., 2007; Sebol et al., 2007). The comparable CFC-11 and CFC-12 degradation rates found in this study are in contrast with previous results from the literature where the CFC-11 degradation rates typically have been orders of magnitude higher than those of CFC-12. The similar degradation rates of CFC-11 and CFC-12 observed in this study are, however, consistent with theoretical dechlorination rates calculated by thermodynamic data and Marcus equation
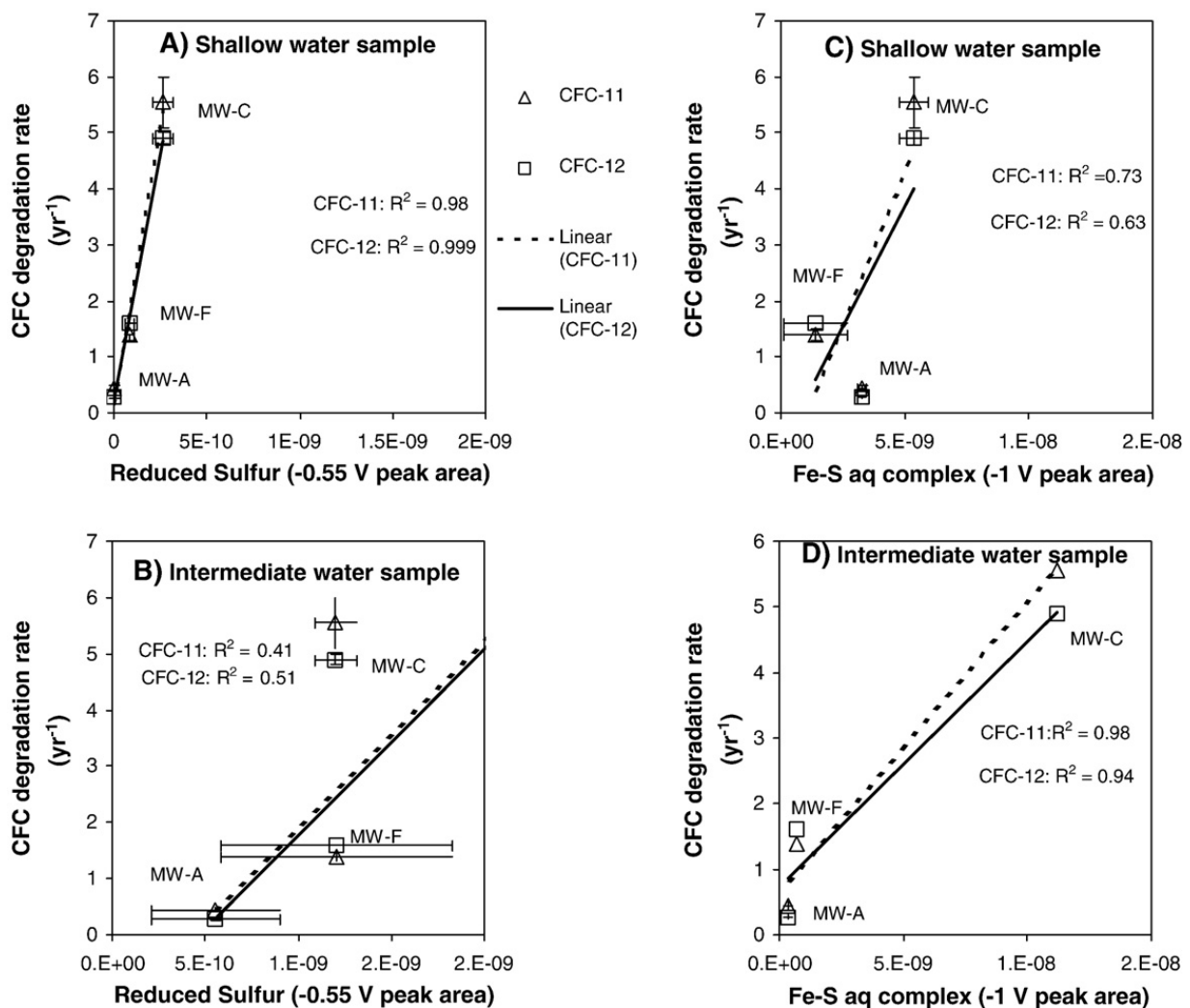

Fig. 6. Comparison of CFC degradation rates and the reduced sulfur and aqueous Fe–S complex in A) and C) shallowest water samples and B) and D) intermediate depth water samples. The CFC degradation rates are the mean value obtained when assuming either initial equilibrium with CFC concentration in deepest soil gas sample or equilibrium with the atmosphere at the time of recharge.

(Eberson, 1982; Balsiger et al., 2005). The redox conditions found in the Araihazar upazila study area are typical for the shallow aquifers in Bangladesh (BGS and DPHE, 2001; McArthur et al., 2001; Harvey et al., 2002; Horneman et al., 2004; Zheng et al., 2004), as well as other tropical deltas found in Southeast Asia. It is therefore reasonable to expect that similar CFC degradation rates will be found throughout the region and in other tropical floodplain environments of the world.

6. Conclusion

This study shows that CFCs do not behave conservatively in reducing shallow aquifers of Araihazar, Bangladesh. Rather, CFC-11, CFC-12, and CFC-113 in groundwater undergo degradation which results in a >95% removal of CFCs in groundwater with $^3H/^3He$ ages above 10 yr. The rate of CFC degradation is related to the type of prevalent reducing environment, with higher degradation rates in sulfate-reducing environments compared to a mixed iron reducing and sulfate-reducing environment. The study found that CFC-12 appears to degrade at a rate similar to CFC-11 in these aquifers, with rates ranging from ~0.25 yr^{-1} to ~6 yr^{-1}.

It is likely that similar CFC degradation takes place in other aquifers in humid tropic deltaic systems. Thus, CFCs have to be applied to groundwater studies in these regions with great caution.

Acknowledgments

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