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Assessing impact of irrigation water on groundwater recharge and quality in arid environment using CFCs, tritium and stable isotopes, in the Zhangye Basin, Northwest China

Dajun Qin [a,*], Yunping Qian [b], Liangfeng Han [c], Zhimin Wang [a], Chen Li [a], Zhanfeng Zhao [a]

[a] *Key Laboratory of Engineering Geomechanics, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China*
[b] *Hydrology Bureau, Yellow River Conservancy Commission, Zhengzhou, Henan 450004, China*
[c] *Isotope Hydrology Section, Department of Nuclear Sciences and Applications, International Atomic Energy Agency, P.O. Box 100, A-1400 Vienna, Austria*

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SUMMARY

Environmental tracers CFCs, ^{18}O, ^{2}H and tritium were used to determine the natural groundwater recharge and the impact of irrigation activity on the groundwater system in the semi-arid Zhangye Basin of China. Groundwaters in the irrigated areas have been identified as mixtures containing fractions recharged in different periods of time. The CFC and ^{3}H data show that the oldest fraction in the groundwater was recharged before 1950, whereas the younger fractions were recharged in different periods of time since 1950. Stable isotope (^{18}O, ^{2}H), CFC and electrical conductivity data show that most of the samples can be regarded as binary mixtures with the river/irrigation water presents the younger fraction and the regional groundwater presents the older fraction. Binary mixing model is used to estimate the age and fraction of the younger component. Most of the younger fraction was recharged after 1980s, in response to the increasing irrigation activities. Compared to local precipitation surface water plays a major role in recharging the aquifer in the irrigated area. The irrigation activity had more impact on the aquifer under thin unsaturated zone (<10 m), due to short travel times and high amounts of recharge, whereas it had less impact on the aquifer under thick unsaturated zone (tens of meters). CFCs are useful in identifying regions of different impact of irrigation return flow. The positive correlation between nitrate and CFC data show that contaminants are transported to the saturated zone by irrigation water. This study shows that in this semi-arid basin due to strong evaporation of infiltrating surface water and regional groundwater, $\delta^{18}O$ and EC values, in contrast to CFCs, do not show simple relationship with NO_3^- concentration in groundwater. Combined with a proper mixing model, however, they can provide evidences that the CFCs found in groundwater were introduced by infiltrating irrigation return flow and, therefore, reveal that human activities can produce a much localized water circulation and influence groundwater vulnerability.

1. Introduction

In densely populated arid and semi-arid regions, river water and groundwater are essential and scarce resources for life, agriculture and ecology. The assessment of renewability and vulnerability of the groundwater resources as well as the study of interaction of groundwater and river water is an important step to sustainable development in these regions.

In arid and semi-arid regions evaporation typically exceeds precipitation during most seasons, leading to practically negligible continuous recharge from the precipitation. In fact, this is the case in our study area, where precipitation amounts less than 200 mm per year, whereas pan evaporation is of the order of 2500–3500 mm per year. In arid regions, localized recharge is considered to be at least as significant as direct recharge (Stephens, 1994). However, the quantification of localized recharge caused by irrigation is rather complex owing to its heterogeneous character and spatial difference in hydrogeological conditions (e.g. thickness of unsaturated zone and lithology).

The Heihe River, the second largest inland river of Northwest China, flows through the Zhangye Basin, which has a population about 1.8 million. The expansion of agriculture in the middle reaches of the Heihe River in the past 30 years has resulted in a decrease of surface water supply, serious vegetation degradation, and desertification in the lower reaches of the Heihe River. Over 80% of the total river water in the basin is diverted from the main river course to irrigation canals (Gao, 1991; Chen et al., 2006). In

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[*] Corresponding author.
E-mail address: qindj@mail.iggcas.ac.cn (D. Qin).

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order to meet the demands for water in the lower reaches of the Heihe River, particularly in the Ejina Basin, a total of 6–10 × 10^8 m^3 of the river water have been diverted annually from the middle to the lower reaches of the river since 2000 (Hao, 2001). Therefore, groundwater abstraction, which is concentrated in the Zhangye Basin for agricultural and industrial purposes, has been increasing gradually to compensate for the reduced river water supply.

Observations by Cao et al. (2002) show that in this irrigated region irrigation return has been a significant source of recharge. Quantitative estimation of irrigation return flow and residence times are vital for management of the groundwater resources and assessing vulnerability of aquifers to contamination (Böhlke and Denver, 1995; Manning et al., 2005; Moore et al., 2006; Osenbrück et al., 2006; Oster, 2006; Hinkle et al., 2007). However, no systematic age information was available prior to this study.

Chlorofluorocarbons (CFCs) have been used widely to provide information on groundwater residence times and mixing processes for waters up to 50 years old (e.g. Busenberg and Plummer, 1992; Dunkle et al., 1993; Cook and Solomon, 1995; Cook et al., 1995; Oster et al., 1996; Cook and Böhlke, 1999; Solomon and Cook, 2000; Plummer et al., 2001; IAEA, 2006; Kaown et al., 2009; Darling et al., 2010). Some studies have been carried out using CFCs to identify and quantify irrigation water in groundwater mixtures (Plummer et al., 2000; Horst et al., 2008).

At least two processes have to be considered for the CFC dating in agricultural areas: natural recharge and irrigation recharge under various hydrogeological environments (e.g. shallow and deep unsaturated zone). CFCs in water exchange with the atmosphere during irrigation, and if contaminated by other sources, the waters will contain elevated CFCs. Irrigation can be regarded as an anthropogenic recharge process overlapped on natural circulation process, and this may cause elevated CFC concentration relative to natural (or regional) groundwater. Irrigation water can be taken as an end-member of young component in a mixture of irrigation water and natural groundwater. CFCs can be used as indicators for identifying hydrogeological process in the following two environments: modern recharge from irrigation areas of shallow unsaturated zone with high CFC concentrations in groundwater; discharge from shallow unsaturated zone with low CFC concentrations.

In this paper, CFCs, together with tritium, stable isotopes (^{18}O and ^{2}H), as well as electrical conductivity measurements, are used to identify and quantify irrigation water recharge in groundwater mixtures from a shallow sand aquifer in the Zhangye Basin. The objective of the study is to assess the impact of irrigation water on groundwater recharge and quality, in particular, in an arid region where evaporation exceeds precipitation through out the year to provide a better understanding of the aquifer system for improvement of river basin management.

2. Description of study area

The Zhangye Basin is a northwest-trending basin about 180 km long and 35–60 km wide (Fig. 1). The plain slopes generally northwestward from an altitude of about 1700 m above sea level (masl) in the southeast to about 1300 masl in the northwest and is flat relative to the surrounding mountains, where altitudes range from 2000 to 5000 masl in the Qilian Mountains to the west and 1600–3000 masl in the Helishan–Longshoushan Mountains to the east. The entire basin is drained by the Heihe River and its tributaries. The river originates from the upper mountain area and is sourced by rain, melt water from snow and glaciers, which accounts for 80–90% of the surface and ground water of the river-basins in the Heihe Catchment, with only 10–20% from local lateral inflow (Zhang et al., 2004).

Yingluoxia (the Yingluoxia Gorge) and Zhengyixia (the Zhengyixia Gorge) divide the drainage area of the Heihe River into upper, middle and lower reaches, with the Zhangye Basin located in the middle reaches. River water inflow at Yingluoxia was about 1.6 × 10^9 m^3/a, and outflow at Zhengyixia has been less than 1 × 10^9 m^3/a since 1985.

The mean annual air temperature in this basin is about 7.6 °C. The climate is semiarid. The mean annual precipitation ranges from 50 mm to 150 mm and the mean pan evaporation rate is about 2000–2200 mm/year (Gao 1991). Most surface flow and recharge to groundwater originate as precipitation in the Qilian Mountains, the catchment area, with a mean annual temperature of 3–4 °C, mean annual precipitation of 200–500 mm (Wang and Cheng, 1999). Glaciers cover approximately 421 km^2 above 4500 masl (Chen, 2002).

The Zhangye Basin consists of alluvial fans and floodplain downgradient of the distal fan-front. The alluvial fan consists of coarse-grained gravel and sand with a thickness up to 1000 m, and the floodplain consists of silty sand with a thickness of 50–200 m (Fan, 1991; Chen, 1997) (Fig. 2). From the southeast to northwest of the basin, grain size of the sands decreases from coarse to fine, and the aquifer varies from a single-layer to dual- or multiple layers. The water table depth ranges from 50 to 170 m in the southwest, 10–50 m in the middle, and 1–5 m in the northeast near the riverbank and in the lower part of the floodplain. Ground water flow is generally from southwest to northeast, with a hydraulic gradient of about 0.6–0.8% in the southeast, which decreases to 0.3% in the northwest in the Quaternary Porous Aquifer. Hydraulic conductivity values for the porous aquifer range from 5 to 45 m/day.

Regionally, water in the Zhangye Basin moves from the Qilian Mountain front to the river valley (Fig. 1). The Heihe River with its tributaries and extensive canals are the major source of recharge to the Zhangye Basin Aquifer. Given that the mean annual recharge from the river and its tributaries to the basin aquifer remains constant, the amount of recharge to the aquifer will depend on the amount of water used for irrigation.

Irrigation is mainly located between Zhangye–Linze–Gaotai close to the western bank of the river, where the unsaturated zone thickness ranges from several to tens of meters and the river water is relatively abundant. At this particular reach, the system has close interaction between groundwater and surface (irrigation) water. The irrigation water recharge had resulted in a rising groundwater level in the Linze–Gaotai river valley plain since the 1990s (Yang and Wang, 2005).

3. Methods

A total of 59 wells from the Zhangye Basin were sampled in October 2002, June/July 2003, March 2004, July 2004, and September 2004. Sampling locations are shown in Fig. 1. Groundwaters were taken from wells for public supply and water level monitoring wells, and most of the wells are housed in solidly built pumping stations or in chambers with a concrete floor and roof. Water table is in a wide range from a few meters to 170 m, and water depth in wells is in the similar range as the water table (Table 1 and Fig. 3).

Fig. 2 indicates that it is almost a single aquifer in the front fan area that consists mainly of middle to coarse-grained sand with pebble. Samples collected from deep wells do not necessarily mean that they consist of mixtures of multilayered water, though certain degree of mixing may occur. During sampling, the information of the well structure and depth of submersible pump was collected, so that it can be used to infer the collected water samples whether it is from a single aquifer or multi-aquifer.

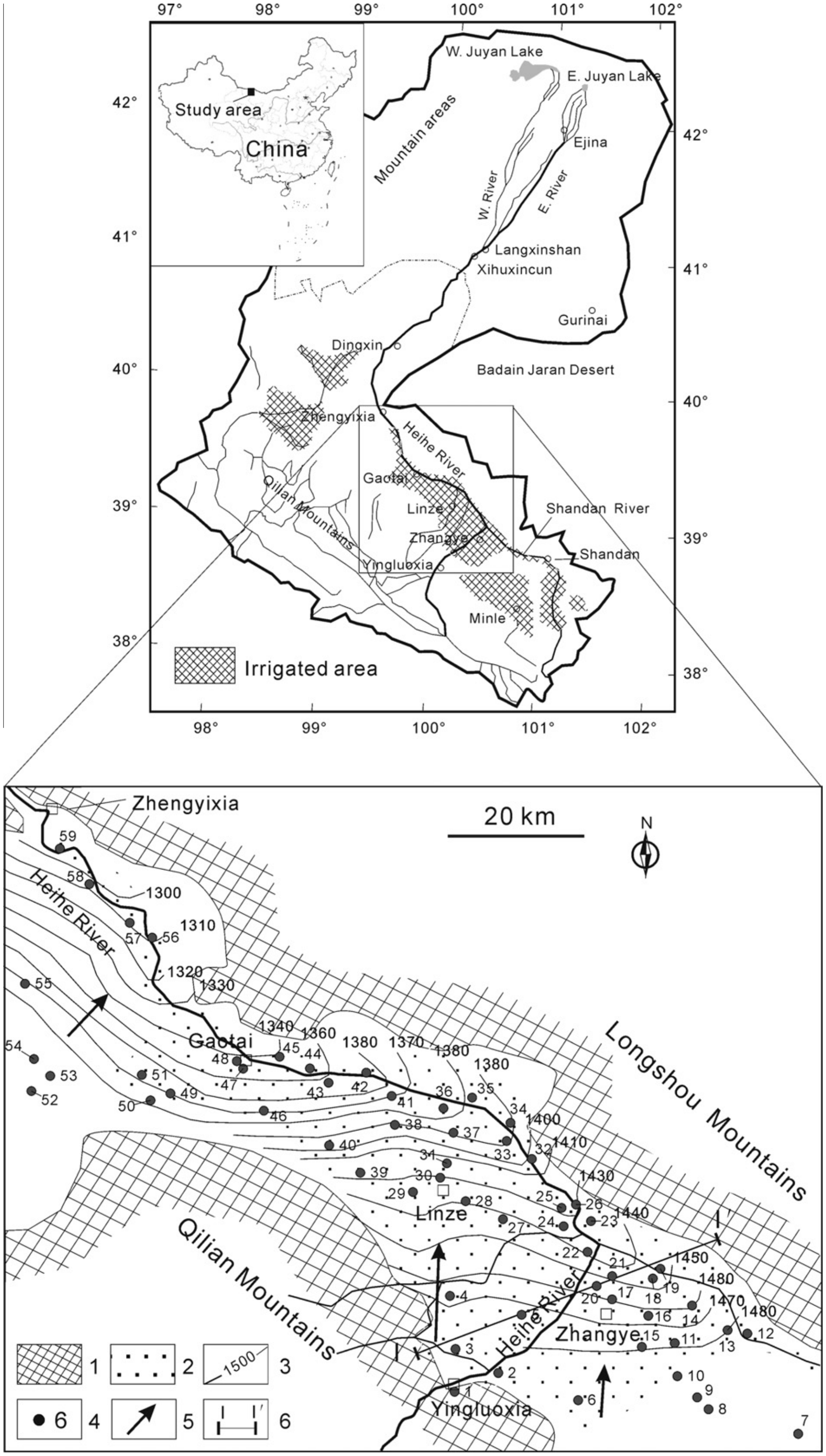

Fig. 1. Water table contours of the unconfined Zhangye Aquifer, irrigated area and location of wells sampled in the Zhangye Basin. 1: Mountain area; 2: Irrigation area; 3: Water table contour (masl); 4: Sampling site; 5: Groundwater flow direction; 6: Location of transect I–I′.

Samples for stable isotope analysis were collected in 50 ml plastic bottles with gas-tight caps. Samples for CFC analysis were collected by filling and capping glass bottles under water, a sampling method later published as IAEA (2006) (also see http://water.usgs.gov/lab/chlorofluorocarbons/sampling/bottles/). This method ensures that the sample is collected without possible atmospheric contamination. For each sample, 3–5 bottles were filled, 2 or 3 of which were analysed. Temperature, pH, electric conductivity (EC), and dissolved oxygen (DO) were measured in the field with a handheld meter.

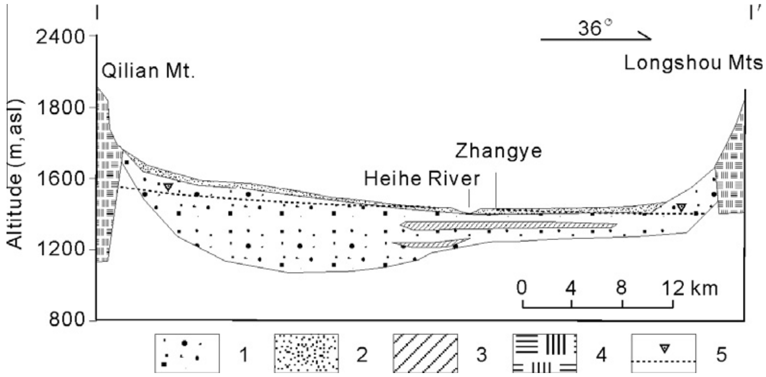

Fig. 2. Hydrogeologic cross-section along transect I–I′in Fig. 1. 1: Sand; 2: Silty; 3: Clay; 4: Mountain area; 5: Water table.

The water samples were analysed at the Groundwater Dating Laboratory of the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGG-CAS). CFC-11, CFC-12, and CFC-113 were measured by a purge-and-trap gas chromatography procedure with an Electron Capture Detector (ECD). The procedures are described in detail by Oster et al (1996). The detection limit for each CFC is about 0.01 pmol/L of water. The analytical error of the CFC measurement is less than ±5%.

Waters for $\delta^{18}O$ were prepared using the CO_2 equilibration method (Epstein and Mayeda, 1953). The Cd-reduction method was used for determination of $^2H/^1H$ ratios. The ratios of $^{18}O/^{16}O$ and $^2H/^1H$ were measured with a Finnigan MAT 252 mass spectrometer. The isotope compositions were reported in standard δ-notation representing per mil deviations from the V-SMOW standard (Vienna Standard Mean Ocean Water). Precisions for δ^2H and $\delta^{18}O$ determination are ±1.0‰ and ±0.2‰, respectively. ^3H measurements were done by direct counting using a liquid scintillation counter (Quantulus-1220). The average measurement precision for tritium is ±3 TU.

4. Results and discussions

4.1. CFC data

The arrangement of the wells in Table 1 is based on geographical locations: from the front mountain area (river mouth), through middle basin to north margin of the Zhangye basin (discharge area).

The results (Table 1) indicate that most of the samples (more than 85%) have CFC concentrations close to or lower than those equilibrated with 2004 air at the recharge temperature of 12.7 °C. The maximum concentrations of CFC-11, CFC-12 and CFC-113 found in the river water are 5.34, 2.62, and 0.45 pmol/kg, respectively.

Seven of the samples (water from wells 5, 11, 18, 24, 25, 27 and 28) had CFC-11 concentrations that were 1.2–1.5 times as high as the saturation value with the 2004 northern hemisphere air. One sample (water from well 10) had CFC-11 concentration that was 2.4 times as high as the saturation value with the 2004 northern hemisphere air. The CFC-11 concentration for water from well 2 was too high to be determined quantitatively. Five of the samples (water from wells 11, 24, 27, 28 and 39) had CFC-12 concentrations that were 1.1–1.3 times higher than the saturation value with the 2004 northern hemisphere air. Only the CFC-113 concentration for water from well 39 was in excess of that of the solubility equilibrium with 2004 northern hemisphere air.

Thirty-five water samples (Table 1) were collected from areas where the water table was in the range of 1–10 m. Except five samples (water from wells 11, 24, 31, 32 and 35) which had CFC concentrations close to that of the solubility equilibrium with modern air (2004), all the other 30 samples had CFC concentrations that were less than those equilibrated with 2004 air.

Four waters (water from wells 1, 2, 3 and 5) collected from depths between 130 and 280 m, where the water level is more than 70 m below ground surface, had high CFC concentrations. The location of these four water samples is close to the Qilian Mountain pluvial front where river water is more abundant than elsewhere. At this location lateral river water recharge is possible.

Water samples collected in the same well, but from different depth show a decrease of CFC concentrations with increasing depth (samples from well 30 and 39). Water samples taken from wells 7, 8, 13, 15, 16 and 19 with depths ranging from 80 to 160 m also show a decreasing trend of CFC concentrations with increasing well depth in comparison with shallower waters nearby. It appears that there exists a vertical distribution of age for deep groundwater in irrigated areas.

The CFC concentrations show that the irrigation activity had more impact on the aquifer under thin unsaturated zone (<10 m) than on the aquifer under thick unsaturated zone (tens of meters) (Fig. 4).

Generally, water recharged by quick infiltration should be relatively young, exhibit little or no separation in CFC-11 and CFC-12 apparent ages. This is commonly observed in waters from the irrigated areas. For shallow unsaturated zones (<10 m), the time lag will be less than 2 years, and for most purposes can be ignored (Cook and Solomon, 1995). In addition, the presence of high concentrations of dissolved oxygen (1.2–8.5 mg/L) and moderate to high concentrations of nitrate (NO_3^-, 3.89–82.85 mg/L) suggest an oxidizing environment. In oxidizing environment CFCs are conservative (Katz et al., 2001; Plummer et al., 1998).

In groundwater dating using CFCs it is useful to plot CFC data from a regional study of an aquifer in the form of a three-component plot. Fig. 5 shows a three component plot for the fraction of CFC-11, CFC-12 and CFC-113, calculated from their partial pressures in the atmosphere. The solid line (curve) is drawn based on the historical atmospheric concentrations of the three CFCs. The line starts from the year 1970 (lower end) to the year 2004 (upper end). The symbols indicate fractions of the partial pressures of the three CFCs determined from the samples.

In Fig. 5 sample data plotted on or close to the curve are regarded as "well-behaved" in the sense that the fractions of the three CFCs are probably not affected by processes such as contamination, degradation and sorption (presented by full squares). On the other hand, samples, in which the CFC concentration ratios have been modified, would plot away from the curve (ill-behaved).

In Fig. 5, those samples, which have at least one calculated CFC partial pressure exceed the historical maximum value in the air, are presented by empty circles. Some samples have all three calculated CFC partial pressures below the historical maximum values in

Table 1
Summary of sample details, measurement and evaluation results.

No.	Sampling (Date)	Temp. (°C)	Well depth (m)	Water table (m)	DO (mg/L)	EC (μs/cm)	δ^{18}O (‰)	δ^{2}H (‰)	^{3}H (TU)	Concentration in pmol/kg			Model Ages						Binary mixing faction (%)*	
													Apparent recharge year			Ratio-based year				
										CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	CFC-11/CFC-12	CFC-113/CFC-11	CFC-113/CFC-12	CFC-113/CFC-11	CFC-113/CFC-12
1	2002-10-3	18	130	70	7.1	573	−8	−48.9	31	2.71	1.65	0.19	1988	>1992	1988		1988			
2	2002-10-3	13.3	180	90	7.8	1547	−8.2	−49.7		C	2.12	0.27	C	M	1988					
3	2003-6-27	11.9	280	170		753	−7.8	−53	22	3.54	1.45	0.26	1987	1983	1987		1988	1990	95	77
4	2003-6-27	13.7	207	103		872	−7.6	−51.8	20	0.71	0.18	nd	1969	1962						
5	2003-6-27	11	170	100		391	−8	−53.3	28	6.12	1.77	0.32	C	1986	1988			1990		89
6	2002-10-3	16.6	125	67	8.5	914	−8	−48.3	26	1.72	0.99	0.16	1977	1979	1985		1996	1989	52	67
7	2004-7-4	11	210	160		880	−9.2	−62.3		0.09	0.05	nd	1971	1970						
8	2004-7-4	11.8	136	53		360	−9	−60.9		0.28	0.15	nd	1963	1961		1976				
9	2002-10-5	12	40	27		375			30	0.87	0.67	0.08	1970	1972	1978		1996	1985	21	41
10	2002-10-5	11.7	40	14		576	−8.9	−56		9.39	1.25	0.13	C	1980	1981			1983		88
11	2002-10-5	13.6	100	5	3.2	1568	−7.8	−48.6	29	4.64	2.43	0.31	C	C	1990					
12	2004-7-4	12	150	60		1050	−8.9	−61.5		1.25	0.78	0.13	1972	1973	1981			1989		41
13	2002-10-5	9.9	120	26		1117			11	0.33	0.16	nd	1963	1960						
14	2003-6-28	11.2	19	7		2040			28	1.68	0.99	0.14	1974	1975	1982		1990	1986	40	60
	2004-7-3	11.3	80	7		851	−9.3	−63.7		1.29	0.85	0.12	1972	1974	1981		1996	1986	30	52
15	2002-10-5	11.1	120	7		987	−7.9	−48.8	25	0.53	0.72	nd	1966	1972						
16	2002-10-5	11.7	20	4	1.2	1503	−7.9	−46.9		3.15	1.57	nd	1984	1984						
17	2002-10-4	12.6	12	1		563	−8.3	−52.4		0.48	0.27	0.04	1966	1965	1972	1975	1988	1986	13	17
18	2002-10-5	12.3	20	2		2750	−8.3	−51.9	29	4.69	2.27	0.15	C	M	1983					
19	2002-10-5	12	120	80		1405	−9.2	−60.3	10	0.12	nd	nd	1958							
20	2002-10-3	11.6	10	2	3	1547	−7.8	−48.6	29	2.3	1.37	0.21	1977	1981	1985		1991	1988	55	73
21	2002-10-4	10	40	1	2.1	847	−7.8	−49.6	26	1.79	0.17	nd	1974	1961						
22	2004-3-27	9.6	15			930				2.26	1.58	0.19	1976	1982	1983		1989	1984	50	92
23	2003-6-29	14.3	160	80		773	−8.9	−59.4		1.54	0.87	0.16	1975	1976	1984			1992		47
24	2002-10-6	12.1	30	9	7.7	1525	−7.5	−46.6	28	4.72	2.59	0.34	C	C	1989					
25	2002-10-6	11.2	30	12	3	1253	−7.5	−46.6	29	5.2	2.33	0.29	C	>1992	1987					
26	2002-10-4	16.8	14	9	6.9	1279	−9.7	−63.4	17	2.04	1.52	0.18	1980	1988	1986		1992		61	
27	2003-7-29	14.8	40	8		1650				4.01	2.55	0.3	C	C	1990					
28	2003-6-29	12.7	50	11		1250				4.58	2.41	0.35	C	C	1990					
29	2002-10-6	12.8	17	14	7.8	898	−8.1	−48.3		3.47	2.12	0.35	1987	>1992	1990					
	2003-6-30	14.2	20	18		487	−8.5	−58	20	2.67	1.5	0.2	1983	1986	1986		1988	1986	78	
30	2003-6-29	13	80	3		520	−8.1	−53.8	23	0.91	0.77	0.04	1970	1974	1972		1979		41	
	2004-7-2	12.8	100	6		530	−8.5	−57		0.05	nd	nd	1954							
31	2003-6-30	10.9	7	2		1520	−7.7	−52.9		3.67	2.37	0.35	1986	>1992	1989		1996		82	
32	2004-9-23	13	15	6						4.16	2.1	0.36	>1992	>1992	1991					
33	2004-9-22	12	12	4						0.83	0.48	0.08	1969	1969	1977		1992	1989	19	24
34	2002-10-4	14.7	20	17	5.5	1238	−8.2	−51.7	30	3.83	2.12	0.36	>1992	C	M					
35	2004-9-23	13	20	6						4.24	2.08	0.36	>1992	>1992	1991					
36	2004-9-21	11.5	20	10		1330				0.85	0.64	0.07	1969	1971	1976		1988	1983	22	43
37	2003-6-30	12.9	80	10		854	−8.2	−53.8	30	0.48	0.27	nd	1966	1965		1976				
38	2004-3-26	12.8	50			335	−9.1	−58		0.26	0.16	nd	1963	1961		1972				
	2004-3-26	14.6	80			344	−9.4	−57		0.11	0.07	nd	1958	1956		1971				
39	2002-10-6	12.3	16	11	6.7	992	−8.4	−52.8	35	4.2	2.47	0.51	>1992	C	C					
	2003-6-30	14.2	100	13		724	−8.1	−53.4		1.18	0.72	0.05	1973	1974	1976		1981	1978		76
40	2003-6-30	13.5	27	4		586	−9.2	−61.4	15	1.14	0.67	0.04	1972	1973	1972	1974	1975	1975	71	76
41	2004-3-26	8	50	1.77		350	−9.4	−57		0.35	0.31	nd	1963	1964		1963				
	2004-9-21	15.5	20	6		2800				0.14	0.12	nd	1960	1960		1964				
42	2002-10-4	14.7	31	4		549	−8.1	−49.5		3.14	1.8	0.26	1987	1990	1988		1990	1988	89	
43	2003-6-30	13.3	10	3		897	−8	−55.8	28	1.84	2.25	0.19	1976	C	1985					
44	2004-9-23	12.8	14	12		1980				1.09	0.14	0.08	1971	1960	1978		1988		29	
45	2002-10-4	11.8	10	2	1.7	1756				0.92	1.54	0.08	1970	1983	1977		1989		22	

46	2003-6-30	13.2	10.5	2		612	−8.8	−58.9		0.78	0.44	0.08	1969	1969	1978		1996	1990	20	24
47	2004-7-2	11	30	2			−6.3	−47.5		3.67	1.88	0.25	1986	1987	1986		1987	1986	97	
	2004-9-22	13.5	15	10		1590				3.11	1.85	0.21	1985	1989	1986		1986		96	
48	2004-7-2	13.8	10	2		2590				0.02	0.11	nd	1952	1959		1953				
49	2004-7-2	15.2	110	66		497	−9.3	−58.8		0.14	0.08	nd	1960	1957		1975				
50	2004-7-2	15.3	140	60		416	−8.7	−58.1		0.11	0.05	nd	1958	1953						
51	2004-7-2	11	90	40			−7.3	−56.8		0.33	0.21	nd	1963	1962		1971				
52	2004-7-2	11	100	50			−9.2	−62.7		0.09	0.07	nd	1956	1954		1967				
53	2004-7-2	12	110	55			−8.8	−61.6		1.02	0.18	nd	1971	1962						
54	2004-7-2	12	80	40			−9	−63.1		0.08	0.05	nd	1956	1953		1970				
55	2003-7-1	13	22	3		385	−9.5	−65.2	16	0.05	0.1	nd	1955	1958		1956				
	2004-7-2	13	78	42		400	−10.1	−61.9		0.04	nd	nd	1954			1966				
56	2002-10-4	12.4	20	5	4.2	5700	−7	−47.8	32	0.51	nd	nd	1966							
57	2002-10-4	11.9	10	2	3.6	2520	−6.7	−50		1.34	0.71	0.05	1973	1972	1975	1977	1979	1979	57	57
	2004-9-22	13	12	4						0.97	0.57	0.08	1971	1971	1978	1974	1990	1988	25	32
58	2004-7-2	13	7	5		3050	−5.7	−46.2		0.25	0.4	nd	1963	1968		1957				
59	2004-7-2	10.7	6	1		3600	−10.1	−61.9		0.94	0.53	0.09	1970	1969	1978	1975	1992	1989	20	25

nd: Not detected. C: CFC concentration is greater than possible values in equilibrium with modern air (contaminated).

EC: electrical conductivity.

DO: dissolved oxygen.

[*] Means fraction of modern groundwater (based on CFC-113/CFC-11 and CFC-113/CFC-12.

air, however, they plot away from the curve because their CFC ratios have been modified. These samples are presented by empty squares.

It was expected that due to mixing with irrigation water which could have been contaminated by one or more CFCs, many samples collected from the irrigated areas would plot away from the curve. From Fig. 5, however, it can be seen that most of the waters are "well-behaved" implying that the sources of CFC contamination are minimal and can be neglected in most cases.

4.2. Apparent CFC ages

The impact of excess air on CFC concentrations is relatively small (Beyerle, 1999; Busenberg and Plummer, 2000; Zuber et al., 2005), and we did not correct the CFC data for the excess air that is entrained during infiltration of recharge.

The annual mean air temperature in the plain area is 7.6 °C. The measured groundwater temperatures were in the range between 9.6 and 16.8 °C, with an average temperature of 12.7 °C. The water temperature varies significantly, showing no clear correlation with sampling locations and water/well depths, reflecting intensity of local irrigation and infiltration rates. For this reason, the annual mean air temperature may not be a suitable estimation of recharge temperature. The noble gas temperature reflects the ground temperature at the water table depth (Klump et al., 2007), which is approximately equal to the mean annual surface air temperature (Stute and Sonntag, 1992). In this study the measured groundwater temperature from each well as the recharge temperature was used to calculate the water ages, assuming that the measured groundwater temperature is close to the recharge temperature of irrigation water re-equilibrated with air during infiltration.

To evaluate ages of groundwater historical CFC concentrations in North Hemisphere air were used (http://water.usgs.gov/lab/). The excesses of CFC concentrations in Chinese urban air with respect to the global background air (North Hemisphere) were relatively small. Two cities (Lanzhou and Yinchan, both are close to the city of Zhangye) in China had CFC-11 and CFC-12 excesses less than 10% compared to the background of the North Hemisphere atmosphere (Barletta et al., 2006). The averaged excesses of CFC-11 and CFC-12 atmospheric concentrations measured in Beijing during 2005–2007 were slightly higher than that measured in Lanzhou and Yinchuan, about 10–15% above the global background (Qin, 2007). The values measured in Vienna air in 1998 were 12%, 10% and 14% higher than the global background atmosphere for CFC-11, CFC-12 and CFC-113, respectively (Han et al., 2007). The CFC atmospheric partial pressures in Zhangye should be close to the cities of Lanzhou and Yinchuan, but lower than that in Beijing air, because it is located at a rather remote and underdeveloped area. Hence, the CFC input functions derived from the CFC partial pressures in the Northern Hemisphere air were used in the study area without modification.

To evaluate ages of groundwater the CFC partial pressures in solubility equilibrium with the water sample are calculated and compared with historical CFC partial pressures in air. Results of the evaluation are given as "apparent recharge year" and summarized in Table 1. The corresponding apparent CFC ages range from less than 10 to more than 50 years. CFC-based ages could not be assigned to waters with elevated CFC concentrations, although the elevated CFCs indicate the presence of post-1950s recharge.

Most of the CFC-11-based ages agree within several years (generally 1-3 years) with those based on concentrations of CFC-12 and do not show signs of CFC-11 degradation. Many of the CFC-113-based ages are younger than CFC-11 and CFC-12 based ages, indicating that the groundwater samples are mixtures of old and young components.

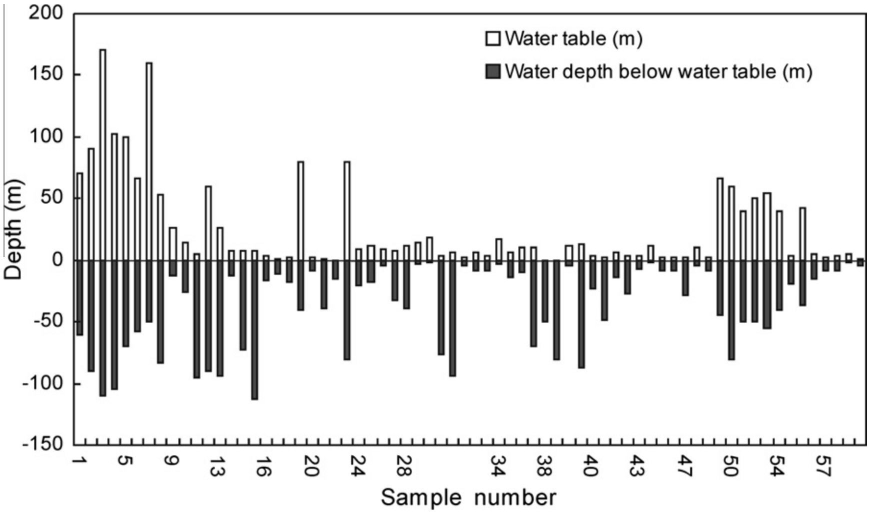

Fig. 3. Water table and water depth below water table in sampling wells.

About 50% of the water samples did not contain detectable CFC-113, but contained detectable CFC-11 and CFC-12, indicating that these groundwaters were recharged after 1950s, but before 1970s.

Waters from wells 48 to 59 (triangles in Fig. 5) were taken from an area between Gaotai and Zhengyixia. Although the unsaturated zone thickness was only 0.3–10 m, these waters did not contain CFC-113, indicating pre-1970s recharge. These wells are located in the regional discharge area where irrigation has little impact on the groundwater.

4.3. CFC ratios and groundwater mixing

CFCs can be used to identify the young fraction in binary mixtures of young and old water, with the younger fraction recharged approximately from 1975 through about 1993 (Plummer et al., 2000). If a sample has CFC-113 age and CFC-113/CFC-12 ratio age younger than its CFC-12 and CFC-11 apparent age, it is considered to be a mixture of old and young waters. Age and fractions of young water component could be calculated from the expected (based on CFC ratio age) and measured CFC-11, CFC-12 and CFC-113 concentrations (Han et al., 2001; IAEA, 2006).

Binary concentration plots based on the ratios of CFC concentrations have been used in a number of studies to identify groundwater mixing (e.g. Talma et al., 2000; Katz et al., 2001; Plummer et al., 2001; Plummer et al., 2003; Cook et al., 2005; Han and Groening, 2006; IAEA, 2006). Fig. 6 shows that most of the samples can be regarded as binary mixtures with the older fraction being free of CFC-113 and the younger fraction being post-1970 recharge (containing CFC-113). Fig. 6 also shows that the younger fractions in some of the binary mixtures were contaminated by CFC-11 and CFC-12 to some extent. However, the water samples are probably not contaminated by CFC-113. In an earlier study of the age of irrigation water in groundwater in irrigated areas Plummer et al. (2000) found that due to land use and irrigation practices some of the water samples were highly contaminated by CFC-11 and CFC-12, but not by CFC-113.

The simple binary mixing model (bmm) was applied to interpret the CFC data, assuming that the water is a mixture of recent (post-1950, age < 54 years) and old (age ⩾ 54 years) recharge water. Four water samples (water from wells 19, 30, 55 and 56) did not contain detectable CFC-12 and CFC-113, but contain minor CFC-11. These samples are regarded as CFC-free water, containing 100% of the older end-member with age ⩾ 54 years in the binary mixing model.

The ages and fractions of young water calculated from the bmm are given in Table 1. Some CFC-11/CFC-12, CFC-113/CFC-11 and/or CFC-113/CFC-12 ratio ages are not listed in Table 1, because the ratio ages are unreasonably greater than the corresponding apparent ages. This could be caused by contamination of the sample with one or two CFCs.

Twelve water samples were contaminated by CFC-11 and/or CFC-12, and it is not possible to make a cross-check of the CFC ages with different CFC compounds. The other 47 samples each has 2– 6 ages that can be used to make a cross-check of the results.

The majority of water samples (water from wells 6 to 47) were collected from the irrigated area. Most of these samples have CFC-113 ages and CFC-113/CFC-12 ratio ages younger than the individual CFC-12 and CFC-11 apparent age. These waters are typical binary mixtures of young and old water. Most of the CFC-113/CFC-11 ratio recharge years range from 1986 to the sampling date.

Many CFC ratio ages of groundwater in irrigated areas were less than 18 years, indicating that the irrigation water has become a predominant factor of controlling recharge to the Zhangye Basin Aquifer since the 1980s. This is consistent with the conclusion that the amount of water used for irrigation has increased in the middle Heihe River Basin since the 1980s (Ren et al., 2002).

4.4. Groundwater mixing indicated by Tritium

^{3}H is the radioactive isotope of hydrogen with a half-life of 12.32 years. Natural ^{3}H background in precipitation is a few TU (Craig and Lal, 1961). Since 1952 the level of ^{3}H in precipitation rose up to a few thousand TU due to nuclear weapons testing primarily in the Northern Hemisphere. The last pre-bomb water (recharged in 1951) would have a maximum concentration of less than 1 TU in 2004 (Fig. 7).

The local ^{3}H input function was constructed with the following method: (1) the tritium values in precipitation during 1953–1959 were approximated by correlating the measured values at Zhangye between 1986 and 1996 with the data of Ottawa, Canada (GNIP, IAEA); (2) the values during the period of 1960 to 1985 were estimated from the Doney model (Doney et al., 1992); (3) the monthly mean values of ^{3}H concentration in precipitation collected at Zhangye for the period of 1986 to 1992, 1995 to 1996 and 2001 to 2002 were from GNIP, IAEA; (4) the values in 1993 and 1994 were interpolated (Chen, 2006, personal communication) and, 2003–2004 because no data are available between these times.

^{3}H contents in precipitation in the study area are relatively higher than in other regions in the world (Doney et al., 1992). The weighted mean tritium content in precipitation in 2001 was about 43 TU in the study area. High tritium concentrations in groundwater (up to 163 TU) were reported in a locality near Zhangye (Chen et al., 2006). In the Zhangye Basin groundwater with ^{3}H activities above 50 TU could be an unmixed water recharged in the 1960s ("bomb peak", range *a* in Fig. 7). A groundwater sample with tritium concentration ranges between 15 and 45 TU could be an unmixed water recharged after 1970, or mixed water containing "bomb peak" and ^{3}H-free component (range *b* in Fig. 7). The tritium range 1–15 TU (range *c*) is typical for groundwater mixtures of pre-1950 water with a ^{3}H-bearing contribution. The tritium

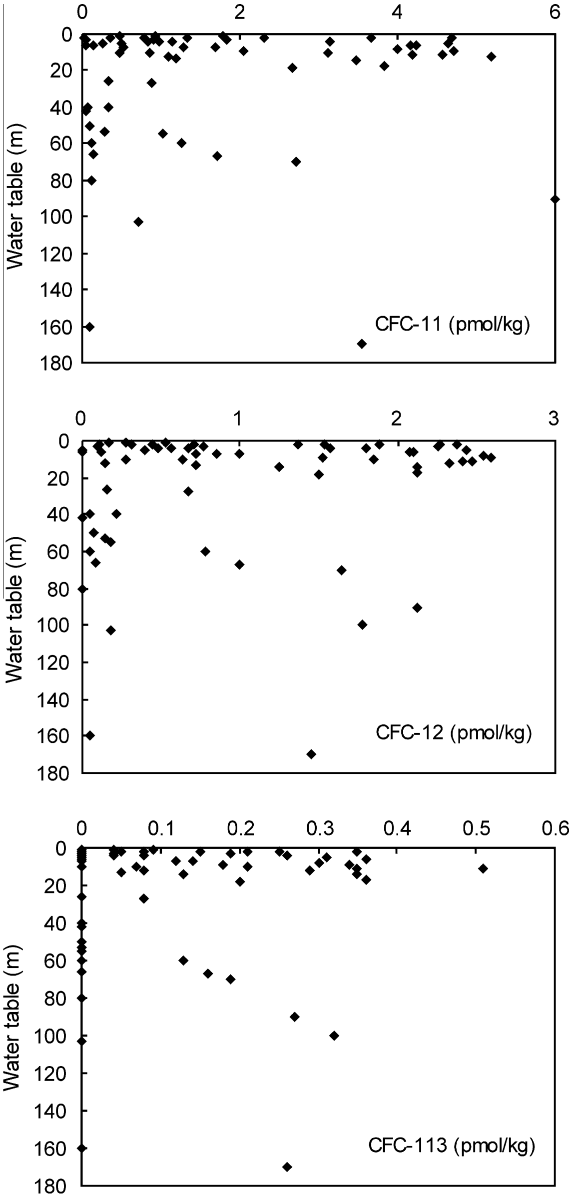

Fig. 4. Plot of CFC-11, CFC-12 and CFC-113 concentrations versus water table.

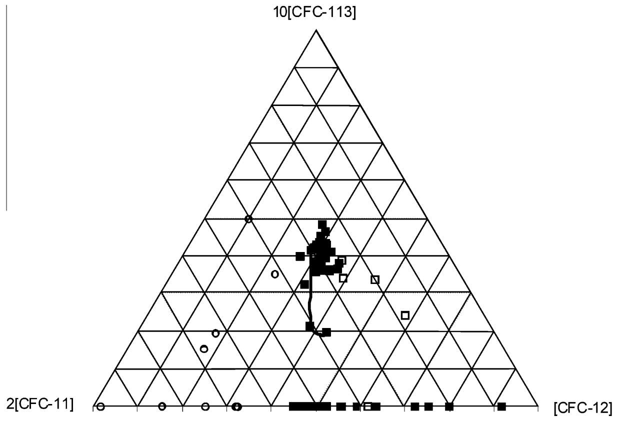

Fig. 5. Three-component diagram for CFC-11, CFC-12 and CFC-113. The curve represents the historical CFC fractions in the atmosphere between 1970 and 2004. For different symbols see text.

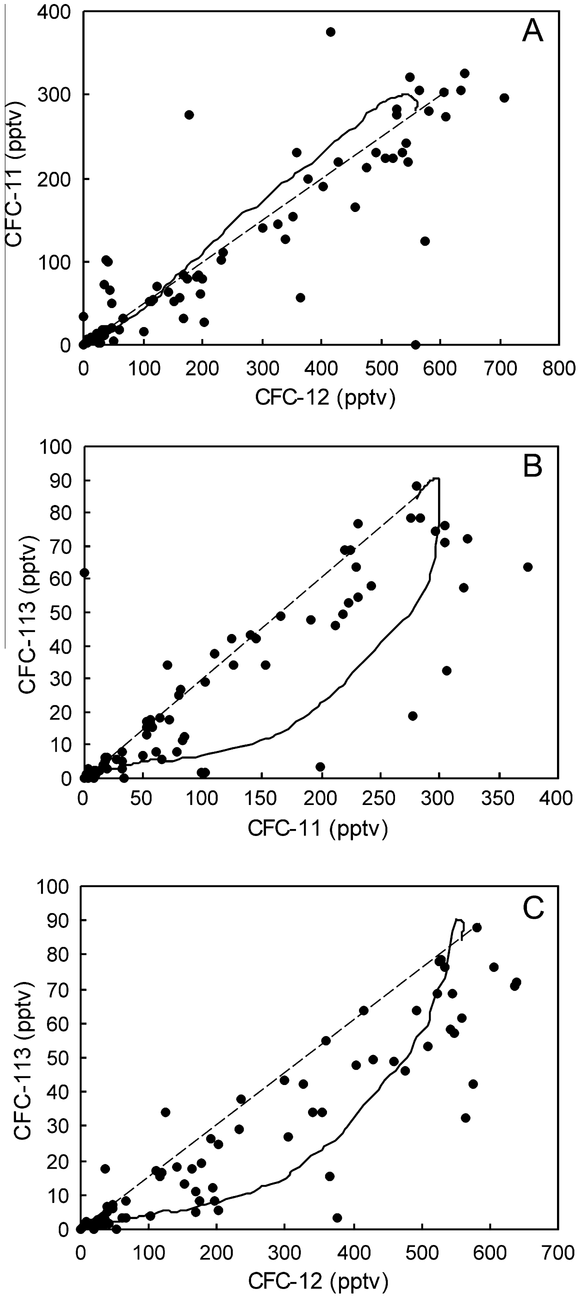

Fig. 6. Plots comparing atmospheric partial pressure of CFC-11 and CFC-12 (A), CFC-113 and CFC-11 (B), CFC-113 and CFC-12 (C). The solid line corresponds to piston flow model. The dashed line corresponds to binary mixing model of older and younger water, assuming that the older end-member is free of CFCs.

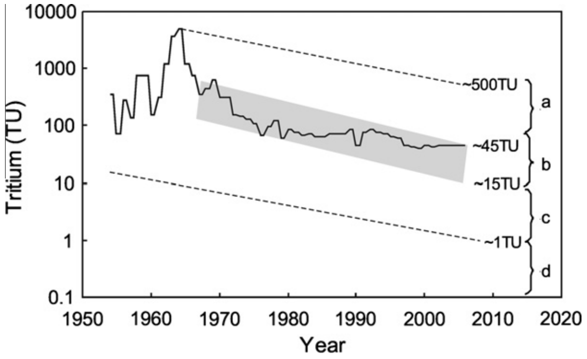

Fig. 7. Semi-log plot of the record of tritium in precipitation in the study region. The two dashed lines show the paths of decay of tritium in groundwater if recharged from precipitation in the early 1950s (lower line) and 1960s (upper line). The grey rectangle represents the tritium decay pattern of most groundwaters recharged since the early 1970s. For tritium ranges *a*, *b*, *c* and *d* see text. (referred to Han and Groening, 2006).

range *d* is regarded as ^{3}H-free water. In this study we have not observed "^{3}H-free water"; and neither have we observed the "bomb peak" directly.

^{3}H values of groundwater from Zhangye were in the range of 10–35 TU (Table 1). As can be seen in Fig. 7, the groundwater samples which have ^{3}H concentration lower than 15 TU must contain some pre-1950 recharge. On the other hand, because the measured ^{3}H data are lower than 45 TU, the fraction of water recharged in the 1960s cannot be identified in the samples by ^{3}H.

The river water was sampled at the same time with groundwater, and tritium value of the river water ranged from 25 to 30 TU. The ^{3}H values in the river water were lower than that in the precipitation (see also Fig. 8). This can be explained by mixing between discharge of low tritium groundwater and river water.

Fig. 8 shows tracer plots comparing ^{3}H with CFC data. Some of the groundwater sampled can be regarded as binary mixtures of older and younger fractions. The older component is essentially free of CFCs. The younger CFC-containing fraction was recharged in different decades.

Some samples (6, 9, 14, 43, and 20) plot close to the piston-flow line. These samples plot in Fig. 6 away from the piston-flow line, on the binary mixing line. An explanation is that these samples are mixtures of younger CFC-113-bearing water with older water which was recharged between 1950 and 1970. Except for sample 6, all these samples were collected from shallow wells with a water depth of less than 13 m. Most probably these samples do not contain pre-1950 (^{3}H-free) recharge.

As can be seen in Fig. 8, in some samples the younger fraction was recharged in the 1960s. The identification of the 1960s recharge can also be achieved by comparing the ^{3}H and CFC data in Table 1. For example sample 4, 9, 13 15, 30, 37 and 40 did not contain detectable CFC-113 and their CFC-11 and CFC-12 concentrations were very low. However, these samples contain ^{3}H well above the detection limit (>10 TU). It is likely that these samples were recharged in the 1960s and contain "^{3}H bomb peak". Due to mixing with a fraction of water recharged before 1950s the ^{3}H concentration was so diluted that it cannot be recognized as "bomb peak" by ^{3}H data alone.

4.5. Sources of groundwater recharge

Local precipitation and river/irrigation water are two potential sources of recharge. Due to limited amount of local precipitation (annual rainfall < 200 mm), river/irrigation water is expected to be a significant source of recharge in the irrigated areas.

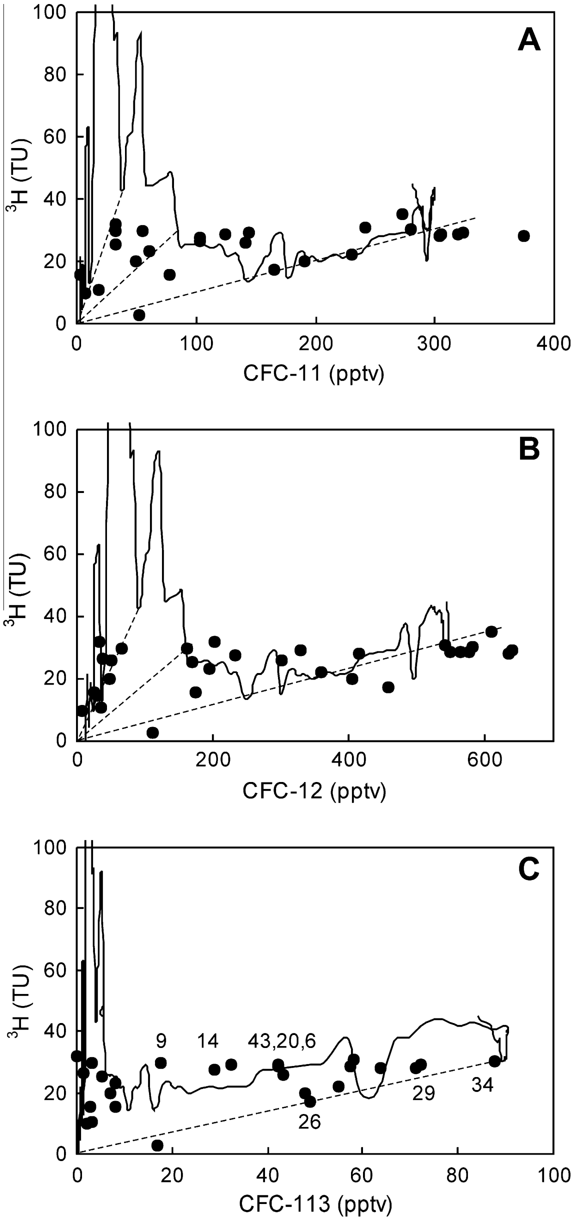

Fig. 8. Plots showing relationship of ^{3}H activity and CFC-11 (A), CFC-12 (B) and CFC-113 (C) atmospheric partial pressures for waters sampled between 2002 and 2004. The data are compared to models of piston flow (solid line), and binary mixing model (dashed line). The input function for ^{3}H is same as in Fig. 7, corrected for decay to 2004.

4.5.1. Local precipitation

The isotope data of rainfall in Zhangye during 1986–1996 are from GNIP (IAEA), averaged to monthly mean values (Fig. 9A). The monthly variations of stable isotope ratios of rainfall between 1986 and 1996 measured at Zhangye were similar to those measured in 2003 at Yingluoxia (Fig. 9B). Precipitation at Yingluoxia varies seasonally with heavier isotopes enriched in summer and depleted in winter (Fig. 9B). This is comparable to the nearest station of the IAEA-WMO GNIP network (Zhangye Station) (http://isohis.iaea.org) (Fig. 9A).

River water samples monthly sampled in 2003 at Yingluoxia show depletion in heavier isotopes from January to June (−8.5‰ to −9.7‰ for δ^{18}O; −58.9‰ to −64.4‰ for δ^2H), in response to snowmelt (8–12%), and enrichment of heavier isotopes (−7.4‰ to −8.3 ‰ for δ^{18}O; −51‰ to −47‰ for δ^2H) from July to December in response to the rainfall season (Fig. 9C and D).

The weighted mean values of $\delta^{18}O$ and $\delta^{2}H$ in the precipitation are less negative (enriched in heavier isotopes) compared to the river water. This rules out the possibility that the local precipitation contributes to the groundwater in the area significantly (recharge is usually isotopically close to bulk rainfall – Clark and Fritz, 1997).

4.5.2. River/irrigation water

The isotopic compositions of river water from the section along Zhangye–Linze–Gaotai (River water I in Fig. 10) are in the range of −7.7‰ to −8.2‰ for $\delta^{18}O$ and −44.7‰ to −48.7‰ for $\delta^{2}H$, relatively enriched in heavier isotopes compared with those from the catchement in the upper reach of Yingluoxia (River water II).

Snow-melt in the Qilian Mountain area (at the elevation above 2500 m) has lower values of $\delta^{2}H$ and $\delta^{18}O$ (more negative) compared to the river water downstream of Yingluoxia and the groundwater. Groundwater samples with more negative values of $\delta^{2}H$ and $\delta^{18}O$ distributed mainly in the piedmont front and deeper wells in the basin. They may originate from the modern snow-melt from the mountains, or recharged under cooler climatic conditions in the past.

In non-irrigated areas between Gaotai and Zhengyixia where the water table is very shallow some groundwater samples collected from dug wells of about 0.3 m deep are essentially CFC-113 free. This implies that gas exchange between surface zone air and groundwater can be neglected and the observed CFCs in groundwater are introduced by irrigation return water.

4.6. Spatial distribution of irrigation water

4.6.1. CFCs and stable isotopes

From CFC concentrations in groundwater, three regions can be identified in the Zhangye Basin (Fig. 11A): Region I is located in the upper reaches of the river, between Yingluoxia and Linze. Groundwater in this region has CFC-12 concentration of >1.5 pmol/kg, CFC apparent age of <32 years, and contains young fraction of 60–80%. Region II is located mainly in the lower reaches of the river. Groundwater in this region has CFC-12 concentration of 0.5–1.5 pmol/kg, CFC apparent age of 25–40 years, and contains young fraction of 40–60%. Region III is mainly located beyond the river-irrigated area between Gaotai and Zhengyixia in the northwest part of the Zhangye Basin. Groundwater in this region has CFC-12 concentration of <0.5 pmol/kg, CFC apparent age of >32 years, and contains young fraction of <20%.

These three regions can also be delineated based on concentrations of the other two CFCs. For example, as can be seen in Fig. 11B, in Region I, where irrigation water predominates, groundwater has CFC-113 concentrations of >0.2 pmol/kg. In Region II, where fractions of irrigation water are lower in groundwater compared to that in Region I, groundwater has CFC-113 concentration between 0.1 and 0.2 pmol/kg. In Region III, groundwater has CFC-113 concentrations of <0.1 pmol/kg, and water age is relatively old (apparent recharge date before 1970s).

In Fig. 11C the distribution of $\delta^{18}O$ value is shown. As can be seen in the figure, waters in the basin have characteristic ranges of $\delta^{18}O$ value. In the irrigation area between Zhangye and Linze (Region I) where the unsaturated zone varies in the range from several to >50 m depth, the groundwater is isotopically similar to the surface water with $\delta^{18}O$ values between −7‰ and −8‰. In the areas where the groundwater contains very low concentrations of CFCs the $\delta^{18}O$ values have two ranges. One range is higher than the river water (between −5.5‰ and −6.5‰), the other range is lower than the river water (between −8.7‰ and −10.1‰). Water samples with higher $\delta^{18}O$ values were collected from the northwest of the Zhangye Basin along the river. Water samples with lower $\delta^{18}O$ values were collected from wells concentrated in two zones. One of the zones extends from the northwestern alluvial fan aquifer (wells 49, 50, 52, 53, 54, and 55) in the northwest of the Zhangye Basin and the other is located in the southeast of the basin (wells 7, 8 and 10). Some water samples collected along the river course (water from wells 12, 14, 19, 23, 26 and 41) also have lower $\delta^{18}O$ values. It is likely that waters having lower $\delta^{18}O$ values contain large fractions of recharge originated from precipitation under colder conditions. Irrigation water and river water seem to be insignificant in these waters.

4.6.2. EC and Nitrate

It is expected that the groundwater in the irrigated areas in the Zhangye Basin should contain higher concentrations of dissolved solutes if the groundwater contains a fraction of irrigation water. Correspondingly, the electrical conductivity of the groundwater may reflect the recharge of irrigation water to the aquifer. Similar to the $\delta^{18}O$ values water samples in the basin have different characteristic specific conductivity. For waters with high CFC concentrations the electrical conductivity values are typically in the range of <800 μS/cm, comparable with the Heihe River water which has electrical conductivity values ranging from 500 to 800 μS/cm.

For waters with very low CFC concentrations the electrical conductivity values have two ranges. Waters in the northwestern alluvial fan aquifer has EC values in the range of 1500–5700 μS/cm, higher than river water, whereas waters concentrated in the southeastern part of the basin as well as some waters collected along the river course has EC values lower than river water (<800 μS/cm) (Table 1 and Fig. 11D).

Zhang et al. (2004) have investigated NO_3^- concentration in the basin. The NO_3^- concentration in river water was found to be in the range of 1.6–9.6 mg/L. NO_3^- concentration in groundwater was found less than 10 mg/L in the areas without irrigation, between Gaotai and Zhengyixia. In irrigated area (Zhangye–Linze–Gaotai) NO_3^- concentrations in groundwater ranging from 45 to 150 mg/L were found. High NO_3^- concentration up to 497 mg/L in soil from a depth of 20 cm below ground surface in the irrigated area was observed. It was concluded that nutrients leaching through the vadose zone had resulted in the increase of NO_3^- in groundwater, and caused deterioration of groundwater.

Groundwater with high concentration of nitrate ($NO_3^- > 45$ mg/L) is mainly located in the centre of the irrigated area (Zhangye–Linze). Groundwater collected from this area has higher EC and CFC concentration, enriched in ^{18}O and ^{2}H as well. In another area (Gaotai–Zhengyixia), though the groundwater contains also higher EC values and enriched in ^{18}O and ^{2}H, however, the concentration of NO_3^- and CFCs are low. NO_3^- concentration has positive correlation with CFC concentration not only in the irrigated area but also in the non-irrigated area. On the other hand, positive correlations between NO_3^- concentration and $\delta^{18}O$ or EC values were observed only in irrigated area. Beyond the irrigated area, NO_3^- does not show positive correlation with EC and $\delta^{18}O$ values (see discussion in Section 4.7).

In the areas between Gaotai and Zhengyixia, where the intensity of irrigation is much lower than in the centre of the irrigated area, low CFC and nitrate concentration in groundwater were found. The low CFC and nitrate concentration in groundwater indicates that irrigation return flow is negligible in these areas. It appears that groundwater used for irrigation in these areas is lost due to evaporation.

Assuming that the porosity of the aquifer is 0.25, the CFC tracers need 16 years to reach the water table at a depth of 10 m, it is estimated that the aquifer in the irrigated areas, such as in Zhangye and Linze, would receive about 156 mm recharge from irrigation water at the most. In areas without or with negligible irrigation activities, such as areas between Linze and Gaotai, the amount of irrigation return should be much lower (<100 mm).

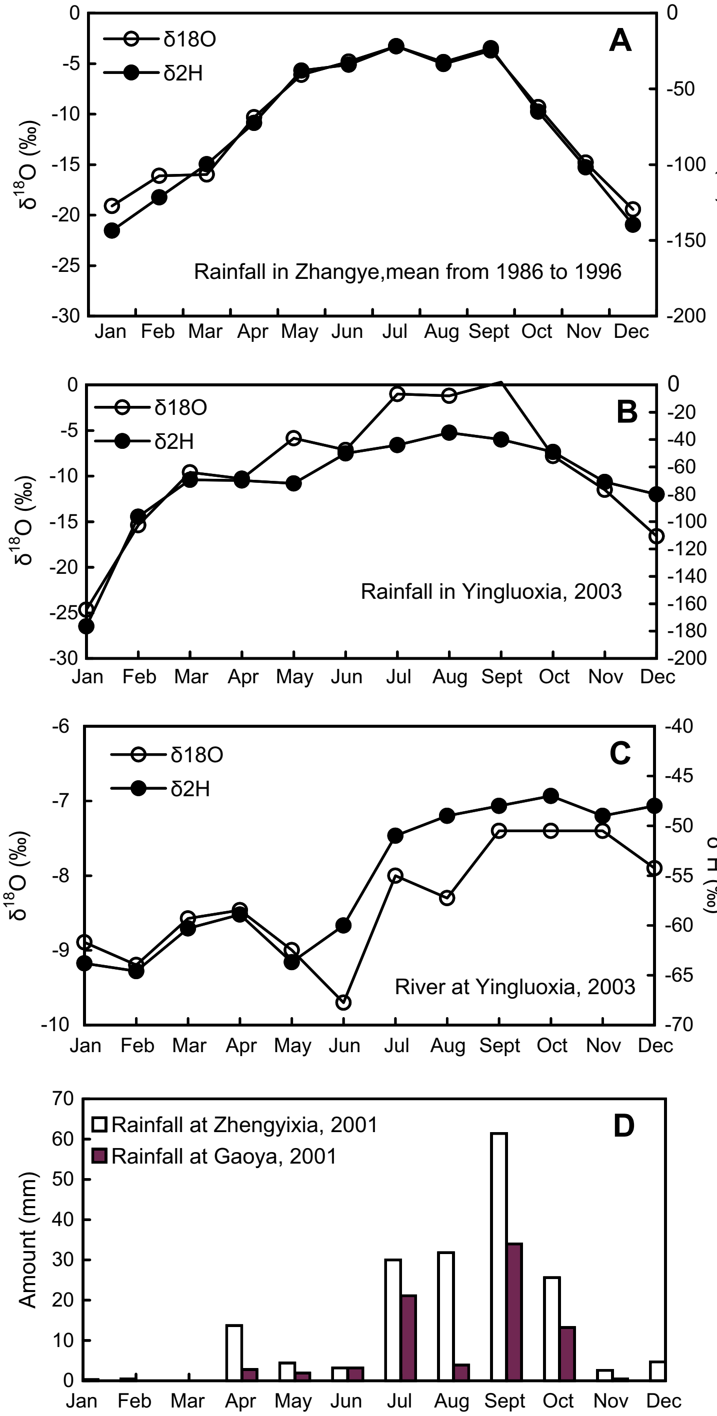

Fig. 9. $\delta^{18}O$ and $\delta^{2}H$ distribution in precipitation in Zhangye, monthly mean values between 1986 and 1996 (A). $\delta^{18}O$ and $\delta^{2}H$ distribution in precipitation and river water, sampled at Yingluoxia in 2003 (B and C). Amounts of precipitation recorded at Gaoya and Zhengyixia in 2001 (D).

4.7. Infiltration process of irrigation water

The complex relations among NO_3^-, CFCs, EC and $\delta^{18}O$ in groundwater collected from irrigated and non-irrigated areas imply complex mixing scenarios between surface and ground water.

Fig. 12A–C shows the relationship between CFC-11, $\delta^{18}O$ and EC. From Fig. 12 a mixing model can be used to account for the data: End-member (IW) has CFC-11, $\delta^{18}O$ and EC values of about 5 pmol/kg, $-7‰ \sim -8‰$ and $\sim$1000 μS/cm, respectively. This end-member represents the river/irrigation water. End-member (UW) has low CFC concentrations and low EC. Its $\delta^{18}O$ values are more negative than river water. This end-member represents the regional groundwater. End-member (LW) has CFC concentrations lower than river water, but its $\delta^{18}O$ values are less negative than river water, and its EC values are higher than river water.

In Fig. 12, Line E1 represents a collection of waters originated from river water and evaporated to different extent. For example, assuming that e1 and e2 are two samples originated from river water, with e2 has evaporated to a greater extent compared to e1. Due to evaporation, sample e2 would be more enriched in

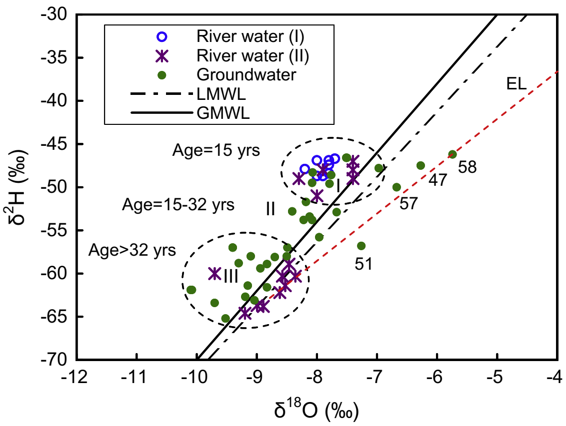

Fig. 10. Comparison of isotopic compositions of groundwaters with that of the river water. The ranges of the CFC age are given for reference. GMWL: Global meteoric water line; LMWL: Local meteoric water line. River water (I) presents samples of river water taken from downstream of Shingle, where the river water was mainly composed of summer rainfall; River water (II) presents samples of river water taken from Yingluoxia, where the river water was composed of base flow of groundwater (depleted in heavier isotopes) and summer rainfall (enriched in heavier isotopes). I, II and III indicate regions from where the water samples were collected (see discussion below). Dashed line indicates evaporation line (Also see Fig. 12C).

heavier isotopes and have a higher EC value compared to e1. The mixing model in Fig. 12 also indicates that water sample e2 would have longer residence time than e1 during infiltration in the unsaturated zone. Correspondingly, this water would contain less CFCs compared to e1.

M1 in Fig. 12 indicates mixing of river/irrigation water with regional groundwater. M2 also indicates mixing of irrigation water with regional groundwater, but with the irrigation water has evaporated to the greatest extent among all the samples. Sample points between these two lines are mixtures containing regional groundwater and river/irrigation water, with the river/irrigation water has evaporated to different extent during infiltration. It appears that the points close to M1 represent samples which contain surface water as the younger fraction that has not undergone evaporation during infiltration. In contrast to these samples, the points away from M1 represent samples which contain surface water that has undergone evaporation during infiltration. The parallel two dashed lines in Fig. 12C, arrow E1 and E2, represent evaporation of river/irrigation water (E1) and regional groundwater (E2).

Samples 18 and 26 are plot on the evaporation line (E2), away from the mixing lines (M1 and M2) (Fig. 12C). These waters could originate from unmixed regional groundwater. Fig. 12A and B show, however, that these two waters contained significant amount of CFCs. An explanation for this inconsistence is that these waters could probably contain recharge that originated from regional groundwater but was abstracted from the aquifer for irrigation. Their CFC concentrations were increased by the higher CFC content in the air and they had undergone evaporation during re-infiltration.

Samples from wells 56, 19, 57, 58 and 59 have undergone evaporation and they have very low CFC concentration. Except for sample 19, which was collected from a well with a water table depth of

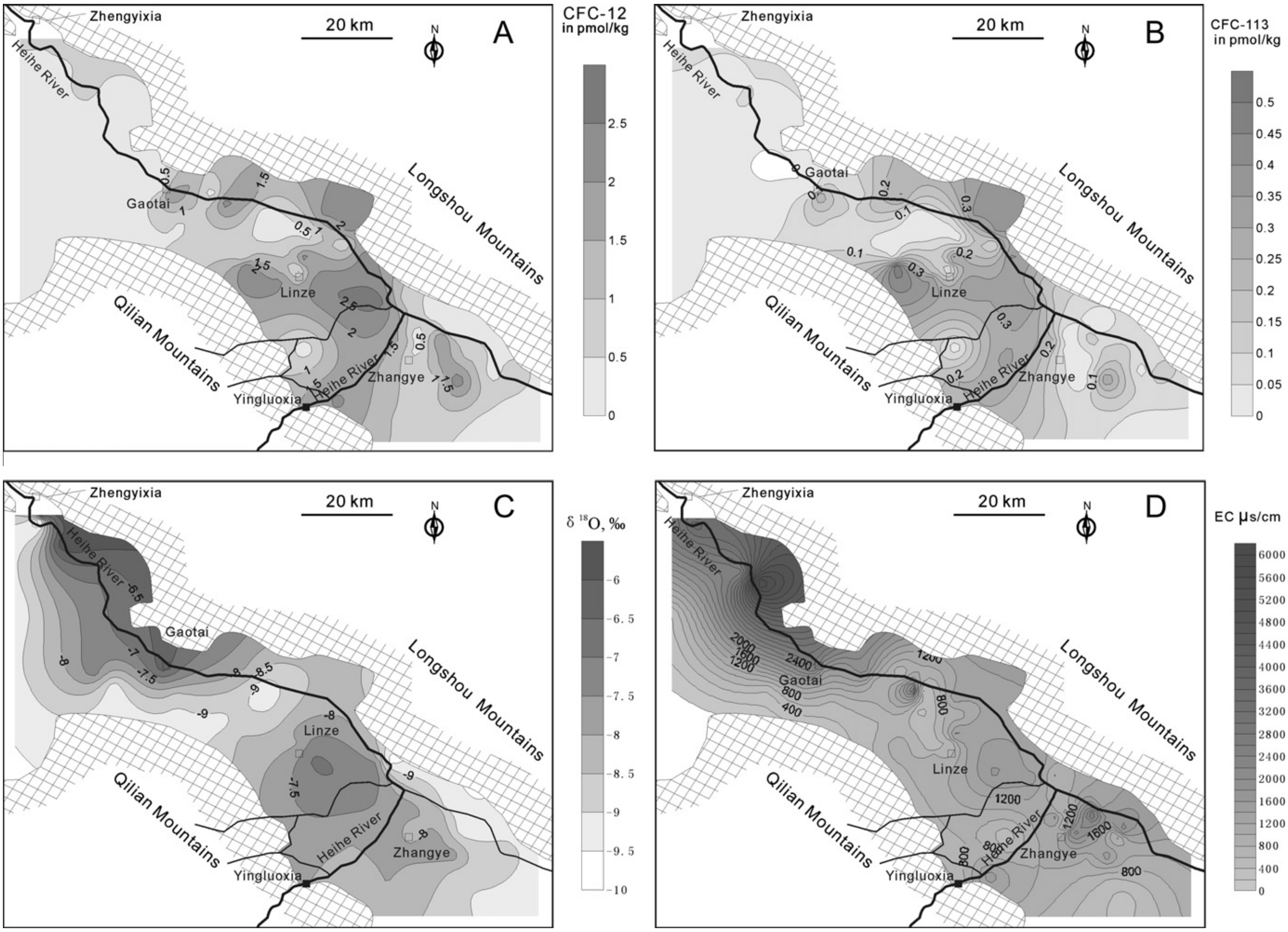

Fig. 11. Plot showing distribution of CFC-12 (A), CFC-113 (B) concentrations (pmol/kg), δ¹⁸O (‰) (C) and EC (μs/cm) (D) in groundwater from the Zhangye Basin. The contour maps for the east parts of the Heihe River are partly extrapolated due to lack of data.

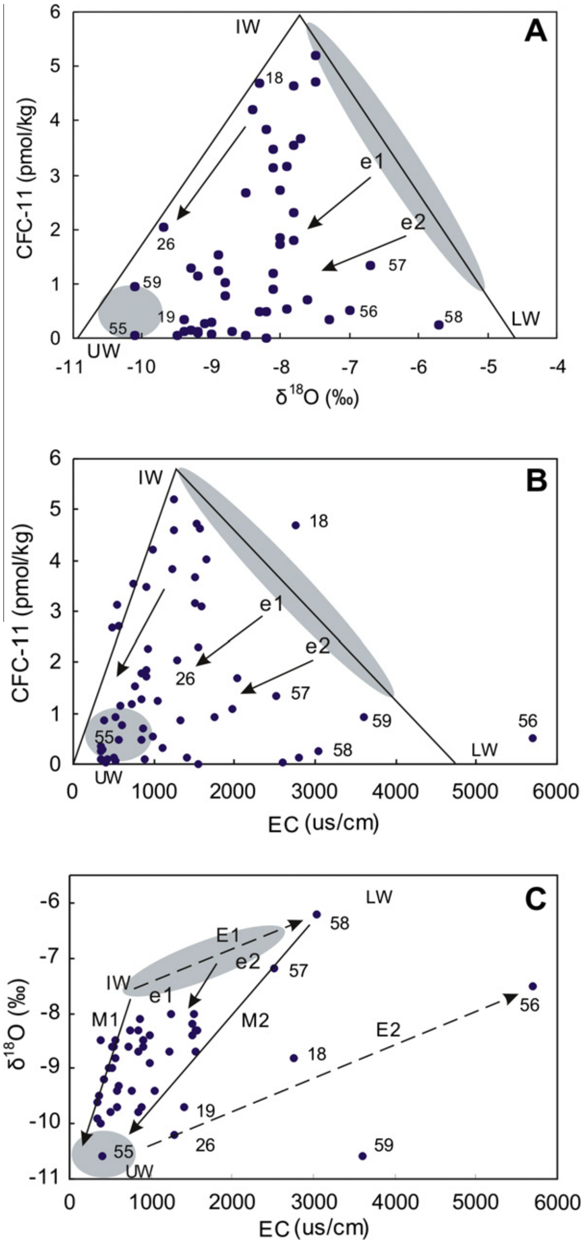

Fig. 12. Relationship of $\delta^{18}O$, CFC-11 and EC in groundwater and river water. The full arrow lines denote mixing of surface water with regional groundwater. Shadow areas indicate mixing end-members.

80 m, the other wells are only a few meters deep. This implies that without younger recharge the groundwater would evaporate through capillary effect. It should be pointed out, that, as can be seen in Fig. 12C, sample 57 and 58 have different origin as sample 56 and 59, although all the four samples were collected from wells located close to each other along the river (Fig. 1). It is likely that sample 57 and 58 originated from river water, recharged in the past, whereas sample 56 and 59 originated from unmixed regional groundwater.

Fig. 12 shows that in this semi-arid basin due to strong evaporation of infiltrating surface water and regional groundwater, $\delta^{18}O$ and EC values, in contrast to CFCs, are not proper indicators for NO_3^- contamination in groundwater. Combined with a proper mixing model, however, they can provide evidences that the CFCs found in groundwater were introduced by infiltrating irrigation return flow.

All samples between M1 and M2 lie on the local and global meteoric water line. These data indicate that evapotranspiration is not a main controlling factor to the variation of isotopes and EC values in groundwater from irrigated areas, and it is because that the presence of modern recharge from irrigation in the arid and semi-arid environment likely lowers the potential of groundwater evaporation through vapour and capillary upward water movement.

4.8. Impact of irrigation on groundwater quality

As discussed in Section 4.6, because irrigation-induced recharge would increase $\delta^{18}O$ and EC in groundwater, $\delta^{18}O$ and EC in groundwater should reflect the impact of irrigation water return. It should be pointed out, however, that evaporation can also increase $\delta^{18}O$ and EC in groundwater. Whereas positive correlations between CFCs and nitrate in groundwater through out the entire basin is observed, positive correlations between nitrate and $\delta^{18}O$ or EC are found only in regions with significant irrigation return flow. Therefore, CFCs are more indicative of NO_3^- transport and infiltration of water than $\delta^{18}O$ and EC.

CFC, ^3H, stable isotopes (^{18}O and ^2H) and electrical conductivity data can provide information about sources, residence times, and mixing scenarios of the groundwater for assessing the impact of irrigation on groundwater quality.

As discussed in Section 4.6, based on CFC apparent ages the study area can be divided into three regions. Groundwater samples collected from Region I had the youngest CFC apparent ages and the highest NO_3^- contents, whereas those collected from Region III had the oldest CFC apparent ages and the lowest NO_3^- contents. The founding that irrigation had less impact on the aquifer under thick unsaturated zone may imply that the impact of anthropogenic activities on the natural environment depends not only on the intensity of the activities, but also on the hydrogeological settings.

Irrigation using both the river and groundwater would accelerate localized circulation of water, and result in a faster downward movement of solutes. This could cause higher NO_3^- content in groundwater. Therefore, using river and groundwater for irrigation can, on the one hand, make better use of the local water resources, avoid salinization of the soil, but, on the other hand, it can only be achieved at the cost of the water quality because it would cause deterioration of the quality of the groundwater.

In Fig. 12C it can be seen that compared to the number of samples which contained recharge originated from river water, only two samples (samples 18 and 26) contained recharge originated from regional groundwater. Most probably water abstracted for irrigation from the aquifer has been completely lost due to evaporation. This may have implications for water resources management: in arid regions irrigation using river water may save more water compared with using groundwater.

Groundwater flow is a key factor in controlling the natural water chemistry in the aquifer. In the specific hydrogeological settings of the Zhangye basin, groundwater flow is relatively gentle due to the flat gradient and less local recharge. The recharge of the aquifer highly depends on river water and irrigation water. The process of infiltration of river water and irrigated water plays important roles in changing the natural water chemistry, particularly the mixing process.

5. Conclusions

The CFC dating and tracing method in combination with ^3H, ^{18}O, ^2H and EC data have provided useful information on sources and timing of recharge and vulnerability to contamination of the aquifer in the Zhangye Basin. Groundwater from irrigated areas contains significant amount of CFCs, with the highest being close to that equilibrated with North Hemisphere air. The CFC concentrations decrease with (1) increasing depth of unsaturated zone; (2) increasing distance from the centre of irrigated areas. The apparent groundwater ages determined by CFCs range from less than 10 to more than 50 years, and are younger in the irrigated areas than in the non-irrigated areas. CFC and ^{3}H data show that the groundwater contains fractions recharged in different periods of time and most of the groundwaters can be regarded as binary mixtures of older (pre-1950) and younger (post-1950) waters. CFC, ^{3}H, δ^{18}O, ^{2}H and EC data show that mixing of surface water with groundwater has occurred in irrigated areas. The recharge consists of a natural and an anthropogenic component. The natural recharge consists of water from precipitation that was formed under colder conditions, and however, natural recharge through local precipitation is negligible as indicated by δ^{18}O and ^{2}H data. The anthropogenic component consists of irrigation return flow. Using CFCs as tracers three regions with different impact of irrigation return flow can be identified. The positive correlation between nitrate and CFC data show that contaminants are transported to the saturated zone by irrigation water. In contrast to CFCs, due to evaporation of infiltrating surface water and regional groundwater, δ^{18}O and EC values are not appropriate to correlate NO_3^- contamination with irrigation return flow. However, combined with a proper mixing model, δ^{18}O and EC data confirm that CFCs found in groundwater indicate irrigation return in the study area.

The temporal relation of isotopes and water chemistry is in particular important for waters which were recharged within the last decades, during which time significant changes of the natural recharge conditions occurred. CFC dating, in combination with water chemistry, has allowed separating the variations of hydrochemical changes due to natural inflow and due to local anthropogenic effects.

The results of this study imply that in arid regions irrigation using river (surface) water would save more water compared with using groundwater. The information gained can be used to formulate appropriate sustainable water management strategies.

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