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Using chlorofluorocarbons (CFCs) and tritium to improve conceptual model of groundwater flow in the South Coast Aquifers of Laizhou Bay, China

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Abstract:

The southern coastal plain of Laizhou Bay, which is the area most seriously affected by salt water intrusion in north China, is a large alluvial depression, which represents one of the most important hydrogeological units in the coastal region of northern China. Chlorofluorocarbons (CFCs, including CFC-11, CFC-12 and CFC-113) and tritium were used together for dating groundwater up to 50 years old in the study area. There are two cones of depression, caused by intensive over-exploitation of fresh groundwater in the south and brine water in the north. The assigned CFC apparent ages for shallow groundwater range from 8 a to >50 a. A binary mixing model based on CFC-113 and CFC-12 concentrations in groundwater was used to estimate fractions of young and pre-modern water in shallow aquifers and to identify groundwater mixing processes during saltwater intrusion. Discordance between concentrations of different CFC compounds indicate that shallow groundwater around the Changyi cone of depression is vulnerable to contamination. Pumping activities, CFC contamination, mixing and/or a large unsaturated zone thickness (e.g. >20 m) may be reasons for some groundwater containing CFCs without tritium. Saline intrusion mainly occurs because of large head gradients between fresh groundwater in the south and saline water bodies in the north, forming a wedge of saline water below/within fresh aquifer layers. Both CFC and tritium dates indicate that the majority of the saline water is from >50 a, with little or no modern seawater component. Based on the distribution of CFC apparent ages, tritium contents plus chemical and physical data, a conceptual model of groundwater flow along the investigated Changyi-Xiaying transect has been developed to describe the hydrogeological processes. Three regimes are identified from south to north: (i) fresh groundwater zone, with a mixing fraction of 0.80–0.65 'young' water calculated with the CFC binary mixing model (groundwater ages <34 a) and 1.9–7.8TU of tritium; (ii) mixing zone characterized by a mixing fraction of 0.05–0.65 young groundwater (ages of 23–44 a), accompanied by local vertical recharge and upward leakage of older groundwater; and (iii) salt water zone, mostly comprising waters with ages beyond the dating range of both CFCs and tritium. Some shallow groundwater in the north of the Changyi groundwater depression belongs to the >50a water group (iii), indicating slow velocity of groundwater circulation and possible drawing in of saline or deep groundwater that is tracer-free. Copyright © 2012 John Wiley & Sons, Ltd.

KEY WORDS Laizhou Bay; coastal aquifers; mixing processes; saltwater intrusion; groundwater age dating

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INTRODUCTION

Following improvements in analytical techniques and understanding of hydrological processes, environmental tracer methods have become increasingly useful for extracting information on the hydrological cycle. Evaluation of groundwater age is important in understanding groundwater flow system dynamics and timescales of water circulation. The combination of the information from groundwater tritium and chlorofluorocarbons (CFCs; CFC-11, CFC-12 and CFC-113) concentrations, which have continuous known variations in concentration in the atmosphere over the last 60 years, can provide valuable insight into movement and mixing of recently recharged waters (e.g. since the 1950s). These 'young' groundwater age tracers have been successfully used to determine groundwater recharge ages and flow paths of water in many studies (e.g. Busenberg and Plummer, 1992; Ekwurzel *et al.*, 1994; Cook *et al.*, 1995; Szabo *et al.*, 1996; Oster *et al.*, 1996; Cook *et al.*, 1996; Plummer *et al.*, 1998; Cook *et al.*, 2003; Cook *et al.*, 2006; Hinsby *et al.*, 2007; Newman *et al*, 2010 and references therein), contributing enormously to our understanding of the complex hydraulic dynamics of shallow aquifers, including those affected by anthropogenic influences.

Coastal aquifers often are complex and heterogeneous systems, where multiple sources of water and salinity are present. Hence, the use of multiple age indicators, along with physical and chemical data, has the potential to aid understanding of complex processes occurring in these aquifers. Age/residence-time obtained from ^{3}H and CFCs has been used to aid in the estimation of the timing of

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seawater intrusion and time required for re-equilibration of the saline/fresh groundwater interface (Zakhem and Hafez, 2007). In addition to direct dating methods, the age of saltwater intrusion can be indirectly evaluated by a comparison of the chemical composition of the investigated saline water with that of the host aquifer fluid (Jones *et al*., 1999). However, in general, there have been relatively few studies, which have examined multiple young groundwater age dating indicators in heavily exploited coastal aquifers subject to the combined effects of saline intrusion, inter-aquifer mixing and leakage of irrigation water. Apparently, contradictory age information given by different tracer methods has been observed in many past cases (e.g. Cook and Solomon, 1995; Plummer and Busenberg, 2005) and may indicate complex recharge processes (e.g. incorporation of excess air, diffusion through thick unsaturated zones and local contamination) and/or mixing process of groundwater components of different age.

This research focuses on groundwater and solute movement in the south coastal Quaternary aquifer of Laizhou Bay (Figure 1). This is an important aquifer from a water resources point of view and one where a number of previous hydrochemical-isotope and salinity monitoring studies have helped to understand the salinization and hydrochemical processes. Zhang (1993) and Xue *et al*. (2000) discussed the origin and evolution of underground brines in the coastal plain of Laizhou Bay using stable isotopes (δ^{18}O and δ^{2}H) and tritium, showing that the brine is not simply formed by the evaporation of sea water but that brine also mixed with meteoric water, fresh groundwater and/or river water during formation. Han *et al*. (2011) provided geochemical and isotopic evidence for palaeo-seawater intrusion into the south coast aquifer of Laizhou Bay, based on analysis of groundwater major ion and multi-isotope composition (^{2}H/^{18}O, ^{3}H, ^{14}C and ^{34}S), which determined sources of groundwater salinity and estimated ages of the deep, regional groundwater. However, there is still a great deal of uncertainty in relation to the circulation of shallow groundwater in the system, which has not been previously addressed. This study provides information on the time scales and rates of recharge of this water, and the degree of mixing between modern and pre-modern waters, which is difficult to determine without the multi-tracer approach. Although great care is needed during water sampling, and many parameters such as excess air, recharge temperature and degradation of CFCs, can influence the accuracy of the ages, the CFCs and tritium are considered to be robust age indicators; the presence of existing hydrochemical and isotope data from previous studies in the aquifer allows the findings to be interrogated and checked using multiple lines of evidence (e.g. Kazemi *et al*., 2006).

The objective of this paper is thus to improve the conceptual model for groundwater movement in the south coast aquifers of Laizhou Bay and show how such a model can be developed and improved through the combined use of CFCs, tritium and other groundwater tracers. The controls on the natural baseline water quality and subsequent impacts of the significant water resource development of the past few decades on the groundwater quality are considered against knowledge of the recharge history and the conceptual model. Only by understanding flow processes will it be possible to advance the numerical tools available (e.g. calibrate flow models, cf. Szabo *et al*, 1996) and so improve local groundwater management.

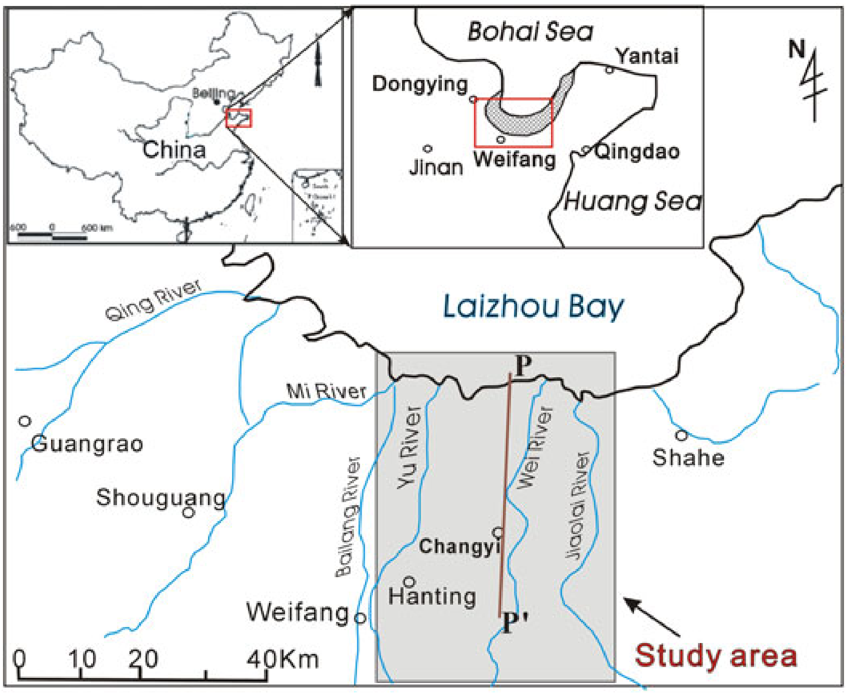

Figure 1. Location map of study area. P-P' line is the location of the cross section in Figure 2

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STUDY SITE

The study area is located in northern Shandong province (Figure 1) in a warm temperate zone with subhumid-monsoon climate. The mean annual temperature and precipitation are 11.9 °C and 660 mm, respectively. Elevation of the coastal plain ranges from 30 m a.s.l. in the south to 1–2 m a.s.l. in the north (Chen *et al*., 1997). The landform changes from proluvial-diluvial plain in the piedmont in the south to proluvial-marine plain in the north. The seafloor of Laizhou Bay is composed of an epicontinental accumulation plain with a gentle gradient of 0.3 ~ 0.8‰ (Yang, 2005). The Weihe River, Yuhe River and Jiaolaihe River flow north through the study area into the Bay.

The coastal plain is covered by extensive Quaternary deposits composed of gravel, sand, silt and clay, with a thickness of 30 to 50 m in the south, reaching up to 360 m in the north (Peng *et al*., 1992). The bedrock is mainly composed of Archaeozoic and Proterozoic metamorphic rock and Cretaceous basalt, outcropping in the southern mountainous areas. The aquifers in the study area are mainly composed of Quaternary deposits and are characterized by a complex multi-layered framework (Figure 2), often trending from coarse grain size in the lower part to fine grained in the upper part. In the south piedmont plain, mainly distributed south of Zhuli, the aquifer is composed of gravel and sand and contains fresh groundwater. The sand layers with coarse grain size have good permeability with hydraulic conductivity of 35–150 m/d. Because of a lack of stable and continuous aquitards, there is no regional confined aquifer unit. However, local confined and semi-confined layers are found north of Changyi with five layers occurring within 15 km of the coastline, including three local brine aquifers (with depth intervals of 8–20, 20–44 and 35–88 m, respectively, Xue *et al*., 2000) and two deep saline aquifers (with depth intervals of 105–165 and 160–290 m, respectively, Han *et al*., 2011). This paper mainly discusses the aquifers within 85 m of the surface. The thickness of unsaturated zone ranges from 0 to 23 m, gradually rising towards the groundwater depression near Changyi (see below).

Under natural conditions, fresh groundwater likely flowed from south to north through the alluvial and marine sediment plains towards the coastline, mainly recharged by precipitation infiltration, lateral bedrock fissure water flow (from the southern mountains) and vertical leakage from the Wei River. After 1983, intensive over-exploitation of groundwater resulted in changes of the natural flow pattern. Following this, additional recharge occurs because of return flow by agricultural irrigation; saline intrusion and leakage from adjacent aquifer units, whereas groundwater discharge is dominated by groundwater pumping. Pumping has caused development of two depression cones. One cone near Changyi city developed because of intensive exploitation of fresh groundwater since the 1980s, which reduced stream runoff, caused a continuous decline in groundwater tables and induced saline intrusion (TJR, 2006). This depression was initially formed in 1984, with groundwater levels −2.0 m a.s.l. in the center of the depression falling to −22.7 m a.s.l. in 2007. The other cone of depression occurs in the northern Yangzi and Xiaying, mainly because of brine exploitation for salt production (Chen *et al*., 1997). Initially, small sporadic cones formed during the 1990s (Zhang *et al*., 1997); this has now developed into an elongated strip of depressed water levels parallel to the shoreline (Figure 3). The brine originated from paleo-seawater intrusion after three occurrences of marine invasion and regression along the coast of Laizhou Bay since the Upper Pleistocene (Xue

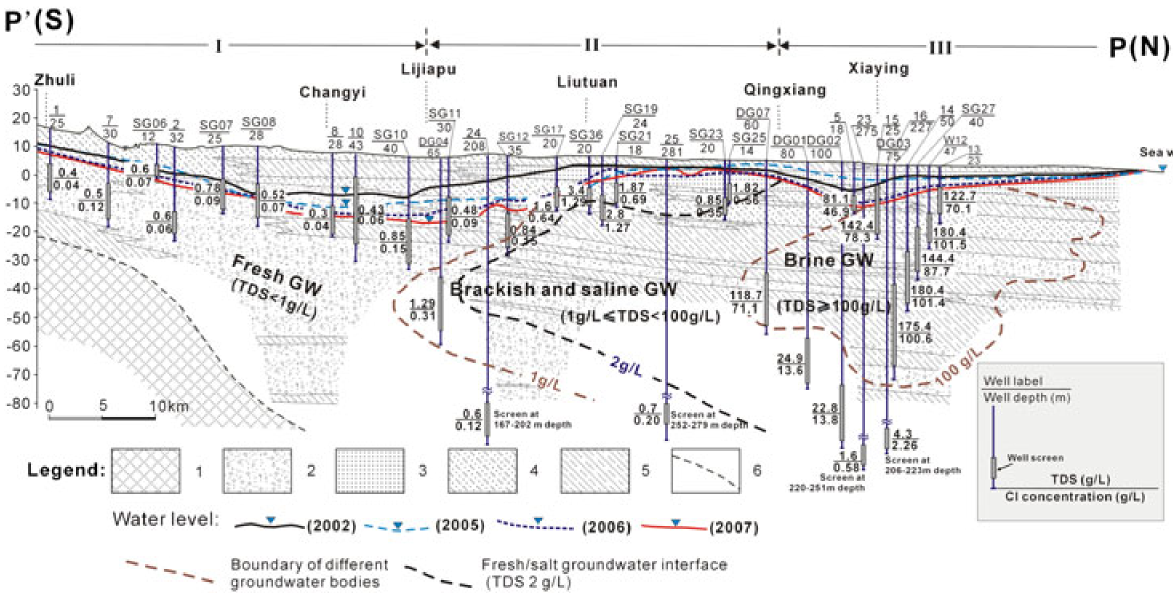

Figure 2. Hydrogeological cross section (P-P' in Figure 1) with groundwater fluctuation and distribution of TDS and Cl⁻ concentration in the study area. The geological cross section has been modified after TJR(2006). Legend: 1, pre-Quaternary bedrock; 2, gravel and sand; 3, medium and fine sand; 4, clayey sand; 5, sandy clay; 6, inferred boundary of bedrock. Fresh/salt groundwater interface refers to the TDS contour of 2 g/l, which is a traditional demarcation in China (Jiang and Li, 1997; Zhang and Peng, 1998; TJR, 2006). I, fresh groundwater zone; II, mixing zone with wedge-shaped saline water in fresh aquifer; III, saline groundwater zone

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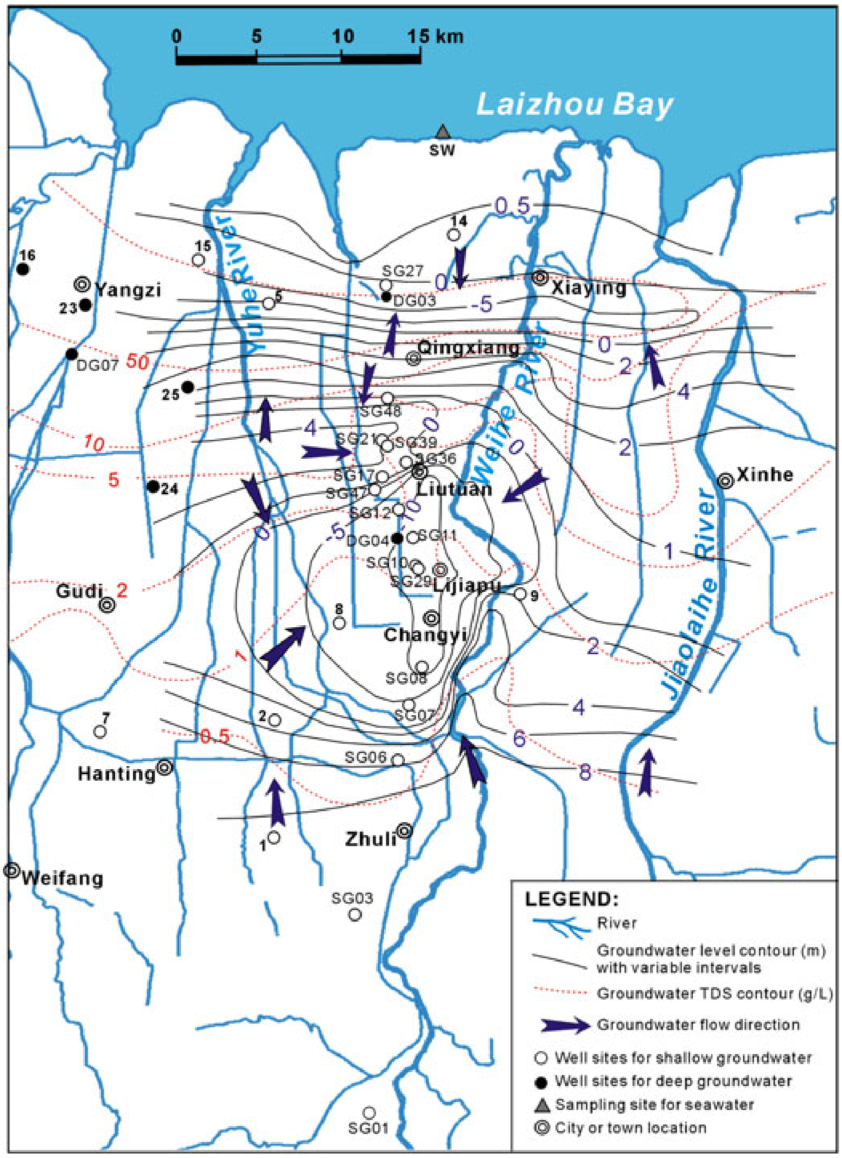

Figure 3. Distribution map for shallow groundwater levels and TDS contours (August 2007), with sampling sites in the study area. Wells of 1, 2, 5, 7, 8, 9, 10, 14, 15, 16, 23, 24 and 25 are referenced from Jiang and Li (1997)

et al., 2000; Han *et al.*, 2011). Besides groundwater over-exploitation, another reason for salt water intrusion may be the decreasing precipitation since the late 1980s, resulting in reduced meteoric recharge. However, the increasing water demand has undoubtedly been the main factor causing modification of the groundwater flow systems (Zhang *et al.*, 1997). The environmental problems caused by saltwater/brine intrusion, such as degeneration of groundwater quality, soil salinization and ecological deterioration, have become the major obstacle to future economic development in this densely populated coastal area.

MATERIALS AND METHODS

Groundwater sampling

Water sampling was conducted between November 2005 and August 2007 in the Changyi-Liutuan area of Laizhou bay (Figure 3). Most of the groundwaters were sampled from irrigation and domestic supply wells, some of which were being continuously pumped. Groundwater samples were collected from <72-m depth in the aquifer and divided into shallow groundwater (<60-m depth, labeled SG) and deep groundwater (>60-m depth, labeled DG). Shallow groundwater refers to pore water in the aquifer with depth 0 ~ 60 m and deep groundwater to water from the aquifer with depth >60 m. Some surface water samples (labeled SU) also were collected. Groundwater samples have been divided into four types, including fresh, brackish, saline and brine water, with total dissolved solids (TDS) of <1, 1–10, 10–100 and >100 g/l, respectively (Fetter, 1994; Nonner, 2006). The *in situ* parameters of groundwater can be seen from Table I.

Analytical techniques

Water samples were analysed for ^{3}H and CFCs, whereas major ions, stable isotopes and ^{14}C data from

Table I. Basic information of groundwater sampling wells

Well	Sampling time	East	North	Altitude	Well depth (m)	Screen interval (m)	Aquifer (deposits)	pH	T (°C)	EC (μs/cm)	TDS (g/L)		Water type
SG01	November 2005	20710405	4051969	30	6		Pleistocene (gravel and sand)	7.64	15.3	1154	0.6	Fresh	HCO_3·Cl-Ca·Na
SG02	November 2005	20710659	4058885	15.3	16		Holocene (coarse sand)	7.57	14.6	2260	1.2	Brackish	HCO_3·Cl-Ca·Na
SG07	November 2005	20713872	4077535	12.5	25	17–23	Pleistocene (middle and fine sand)	7.78	14.5	1401	0.8	Fresh	HCO_3·Cl-Ca
SG08	November 2005	20714613	4079521	13.1	28	16–25	Pleistocene (middle and fine sand)	7.9	14.6	854	0.5	Fresh	HCO_3-Ca·Mg
SG10	November 2005	20713303	4086375	7.1	40	21–38	Pleistocene (gravel and sand)	8.45	14.4	1561	0.9	Fresh	HCO_3·Cl- Na
SG11	November 2005	20714112	4087691	12	30	15–26	Pleistocene (middle and fine sand)	8.06	13.8	1063	0.5	Fresh	HCO_3·Cl-Mg·Na
SG12	November 2005	20713251	4089428	3.6	35	18–31	Pleistocene (middle and fine sand)	8.65	13.9	1242	0.7	Fresh	HCO_3-Na
SG17	November 2005	20712091	4091250	4.5	20	14–19	Holocene (middle and fine sand)	8.49	14.8	3690	1.6	Brackish	Cl·HCO_3-Na
SG21	November 2005	20712229	4093629	3	18	9–14	Holocene (fine and loam sand)	7.78	14.1	3730	1.9	Brackish	Cl·HCO_3-Na
SG23	November 2005	20714016	4096419	3	20	13–18	Holocene (fine and loam sand)	7.7	14	2240	0.9	Fresh	Cl·HCO_3- Ca·Mg·Na
DG03	November 2005	20712653	4103388	4	75	46–72	Pleistocene (middle and fine sand)	7.79	15.6	30 200	17.5	Saline	Cl-Na
SG10	July 2006	20713303	4086375	7.1	40	21–38	Pleistocene (gravel and sand)	7.18	15.4	2870	1.9	Brackish	HCO_3·Cl-Na
SG36	July 2006	20713700	4092277	6.2	20	12–18	Holocene (middle and fine sand)	7.41	15.3	5710	3.8	Brackish	Cl·HCO_3-Na
SG39	August 2007	20712560	4093267	2.5	35	23–32	Pleistocene (middle and fine sand)	7.22	15.3	11 000	7.2	Brackish	Cl-Na
SG29	August 2007	20709980	4080400	7.8	30	22–27	Pleistocene (middle and fine sand)	7.16	15.1	1136	0.6	Fresh	HCO_3·Cl-Ca
SG47	August 2007	20711835	4090595	11.2	35	24–32	Pleistocene (middle and fine sand)	7.74	15.3	5170	4.9	Brackish	Cl-Na
SG10	August 2007	20713303	4086375	7.1	40	21–38	Pleistocene (gravel and sand)	7.41	15.2	2600	1.4	Brackish	Cl·HCO_3-Na
SG12	August 2007	20713251	4089428	3.6	35	18–31	Pleistocene (middle and fine sand)	8.1	14.6	1281	0.7	Fresh	HCO_3-Na
SG48	August 2007	20712611	4096168	4.5	30	16-27	Pleistocene (middle and fine sand)	7.37	15.2	16180	6.7	Brackish	Cl-Na
DG07	August 2007	20693440	4098855	2.3	60	33–48	Pleistocene (middle and fine sand)	6.58	16.1	137 500	118.7	Brine	Cl-Na
DG04	August 2007	20712621	4087869	8.2	65	38–56	Pleistocene (gravel and sand)	7.55	18	3340	1.1	Brackish	Cl·HCO_3-Na

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the area also were measured, as reported in Han *et al.*, (2011). The ^3H contents were measured in the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. After 250 ml of water sample was distilled, the samples were electrolytically enriched at 0.5 °C. Determination was carried out using a 1220 Quantulus ultra low level liquid scintillation spectrometer. The data were normalized and expressed using the method of Rozanski and Gröning (2004). Results are reported in tritium units (TUs), with a typical error of ± 0.5 TU (Table II).

Chlorofluorocarbons are sensitive tools in the study of groundwater age. CFC-11, CFC-12 and CFC-113, which are stable organic compounds entirely of anthropogenic origin, have been released into the atmosphere since the 1940s. A total of 26 groundwater samples were collected for CFCs analysis (14 on November 2005, 2 on July 2006 and 10 on August 2007). The CFC contents were measured in the Laboratory of Groundwater Chronology, Institute of Geology and Geophysics, China Academy of Sciences. After the well was purged, water samples were extracted directly from borehole using a Cu tube sampling line placed in the bottom of a 50-ml borosilicate ampoule, placed in a beaker. After checking, no bubbles appeared in the ampoule; it was filled and sealed underwater to avoid atmospheric contamination, following protocols established during earlier studies, described by Busenberg and Plummer (1992). The CFC concentrations were analysed using a computer-controlled gas chromatograph (GC, Shimadzu, type 8AIE), equipped with an electron capture detector working in constant-current mode. The analytical system is described in detail in Oster *et al.* (1996). CFC analyses are reported in pmole/kg (pg/kg) of water. CFC apparent ages were obtained using the method of Plummer *et al.* (2006). The calculated apparent ages from CFC assumed recharge temperature of 13 °C (the average air temperature of the study area) and elevation of 100 m. The CFC concentrations were measured within 1 month of sample collection. All CFC concentrations are reported on the SIO 1998 absolute calibration scale (Prinn *et al.*, 2000). The analysed results are shown in Table II.

CFC age dating

If a binary mixture of young ($\sim< 50$ years) and old water is assumed, ratios of CFC species can be used to estimate the relative volumetric fractions and age of the young fraction in water sample by applying the method of Plummer *et al.* (2006) (Table II). Apparent CFC ages are calculated by converting the measured CFC concentrations (pg/kg) to equivalent atmospheric concentrations (pptv) by using the known Henry's law solubility (Warner and Weiss, 1985; Bu and Warner, 1995) and assigning recharge temperature and elevation. In assigning a piston-flow model age to a CFC concentration measured in a water sample, the measured concentration, in moles per liter, is converted to a dry-air atmospheric mixing ratio in parts per trillion by volume (pptv) (Plummer and Busenberg, 2005). The piston date is the date at which the calculated mixing ratio for the sample is equal to that measured for the atmosphere. Quaternary aquifers contain many different types of pore spaces, within which flow velocities and hydraulic interconnection vary greatly. Wells hydraulically connected to these various types of pore spaces yield distributed ages, and thus, this metric is sometimes referred to as 'apparent age'. In many cases, an exponential or exponential piston flow model are more appropriate (e.g. Cook and Böhlke, 2000); however, in this case, a piston-flow model was adopted as follows: (i) water was generally sampled from shallow bores, with relatively narrow screens (Table I); and (ii) it is the most simple model and was adopted in the absence of more detailed information about flowpaths and mechanisms. CFC 'ages' must hence be viewed with this limitation in mind. An additional limitation with CFC dating is the possibility of contamination of groundwater with particular CFC compounds (Gooddy *et al.*, 2006). Groundwater samples from residential, industrial or disused landfill sites can contain concentrations of CFCs above modern atmospheric concentrations (Busenberg and Plummer, 1992; MacDonald *et al.*, 2003); the possibility of CFC contamination and/or degradation is discussed further below.

RESULTS

Groundwater level and TDS distribution

Groundwater level data show a continuous declining trend in recent years (Figure 2). There are two drawdown cones distributed around Changyi city and Xiaying town with groundwater table depths of 22.7 and 13.2 m below sea level, respectively. The groundwater level contour of -5 m in the Changyi depression in 1990 (Xue *et al.*, 2000) now approximately corresponds to a -10 m contour (Figure 3). Some sporadic drawdown cones with depth to water table of ~3 m near Yangzi and Xiaying in 1990 have now formed an elongated connected depression parallel to the coastline, with groundwater levels lower than -10 m (brine exploitation zone). Between the two depression cones, a groundwater divide occurs between fresh water and brine water to the north of Changyi. North of the divide, groundwater flows towards the depression cone around Xiaying town; south of the divide water flows towards the Changyi depression.

Selected field-measured parameters together with water types are shown in Table I. Groundwater salinity in the study area varies dramatically over several orders of magnitude both in vertical and lateral directions. TDS shows a generally increasing trend towards the coastline, namely, from south to north (Figure 4). TDS increases from 0.4 g/l for fresh groundwater in the south part of study area (around Zhuli) to 180.4 g/l for brine water in the north of the study area (Figure 2). The chemical composition of the groundwater is highly variable but broadly falls within five zones, a Piper plot including these five zones is shown in Figure 5. Fresh groundwater

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Table II. Chlorofluorocarbons and tritium data for the water samples and corresponding tracer ages

Water sample	Sampling date	Well depth (m)	T (TU)	T_error (TU)	Concentration in water (pmole/kg)			Calculated atmospheric mixing ratio (pptv)[a]			Piston date (decimal year)			Assigned CFC age(a)	Recommended year
					CFC-12	CFC-11	CFC-113	CFC-12	CFC-11	CFC-113	CFC-12	CFC-11	CFC-113		
SG01	November 2005	6	7.1	0.6	2.03	4.46	0.38	438.5	254.4	71.3	1987	1988.5	1989	17	1987
SG02	November 2005	16	11.8	0.7	1.73	4.05	0.33	373.7	231.0	61.9	1983.5	1986.5	1988	21	1983.5
SG07	November 2005	25	7.6	0.6	1.93	6.47	0.35	416.9	369.0	65.7	1986	Cont.	1988.5	19	1986
SG11	November 2005	30	6.6	0.6	1.57	3.13	0.28	339.1	178.5	52.5	1981.5	1981	1986.5	23	1981.5
SG12	November 2005	35	9.5	0.6	0.56	1.10	0.08	121.0	62.7	15.0	1969	1970	1977	36	1969
SG17	November 2005	20	5.2	0.5	0.74	1.44	0.13	159.8	82.1	24.4	1971.5	1972	1980.5	33	1971.5
SG21	November 2005	18	10.3	0.9	0.40	0.77	0.07	86.4	43.9	13.1	1966.5	1968	1976	39	1966.5
SG23	November 2005	20	8.1	0.5	0.71	3.44	0.10	153.4	196.2	18.8	1971	1983	1978.5	34	1971
DG03	November 2005	75	ND		1.12	2.04	0.22	241.9	116.3	41.3	1975.5	1975	1984.5	29	1975.5
SG10	July 2006	40	1.8	0.5	0.26	0.68	0.02	56.2	38.8	3.8	1963.5	1967	1966.5	42	1963.5
SG36	July 2006	20	2.6	0.5	0.07	0.08	0.02	15.1	4.6	3.8	1954	1955.5	1966.5	52	1954
SG39	August 2007	35	3.1	0.9	0.23	0.42	0.02	49.7	24.0	3.8	1962.5	1964.5	1966.5	44	1962.5
SG29	August 2007	30			1.5	3.4	0.31	324.0	193.9	58.1	1981	1983	1987.5	27	1981
SG47	Aug.2007	35	2.6	0.8	0.09	0.07	0.01	19.4	4.0	1.9	1955.5	1955	1962	51	1955.5
SG10	August 2007	40	4.4	0.9	0.66	5.88	0.03	142.6	335.3	5.6	1970.5	Cont.	1969.5	36	1970.5
SG12	August 2007	35	15.3	1.3	0.72	6.91	0.07	155.5	394.1	13.1	1971.5	Cont.	1976	36	1971.5
SG48	August 2007	30	6.8	1.0	1.02	1.14	0.12	220.3	65.0	22.5	1974.5	1970.5	1979.5	32	1974.5
SG08	November 2005	28	6.1	0.6	1.38	C	0.22	298.1	0.0	41.3	1978.5	1944.5	1984.5	25	1978.5
SG10	November 2005	40	2	0.5	1.39	C	0.21	300.2	0.0	39.4	1979	1944.5	1984	25	1979
DG07	August 2007	60	3.5	0.9	0.01	0	0	2.2	0.0	0.0	1946	1944.5	1953	>50	Before 1954
DG04	August 2007	65	2.6	0.9	0.05	0.11	0	10.8	6.3	0.0	1952	1957	1953	>50	Before 1954
SU01	November 2005	RiverWater	6	0.5	2.46	5.43	0.46	531.3	309.7	86.3	1994	Cont.	1995.5	8	1994
SW	November 2005	Seawater	7.3	0.6	2.69	6.09	0.62	581.0	347.3	116.3	NA	NA	NA	NA	NA

pptv, parts per trillion by volume; C, groundwater CFC concentrations beyond equilibrium with air; Cont., contaminated sample; ND, not detected; NA, not applicable.
CFC ages in years were calculated for a recharge temperature of 13 °C and 100-m elevation. Recommended apparent age refers to CFC-12 age.
[a] Mixing ratios were calculated from measured concentrations according to Plummer and Busenberg (2005).

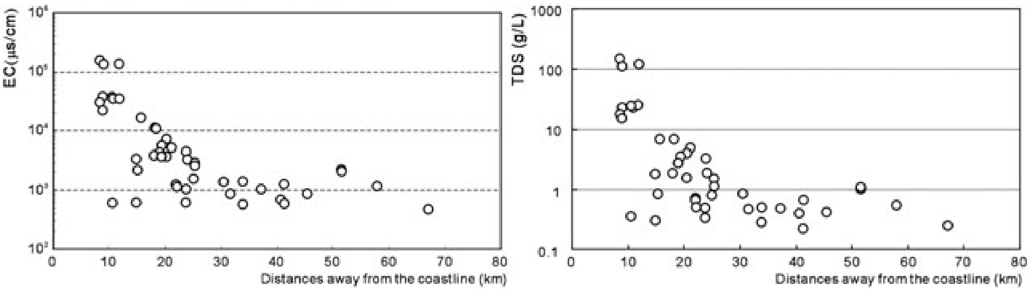

Figure 4. Variations of EC and TDS with distances away from the coastline

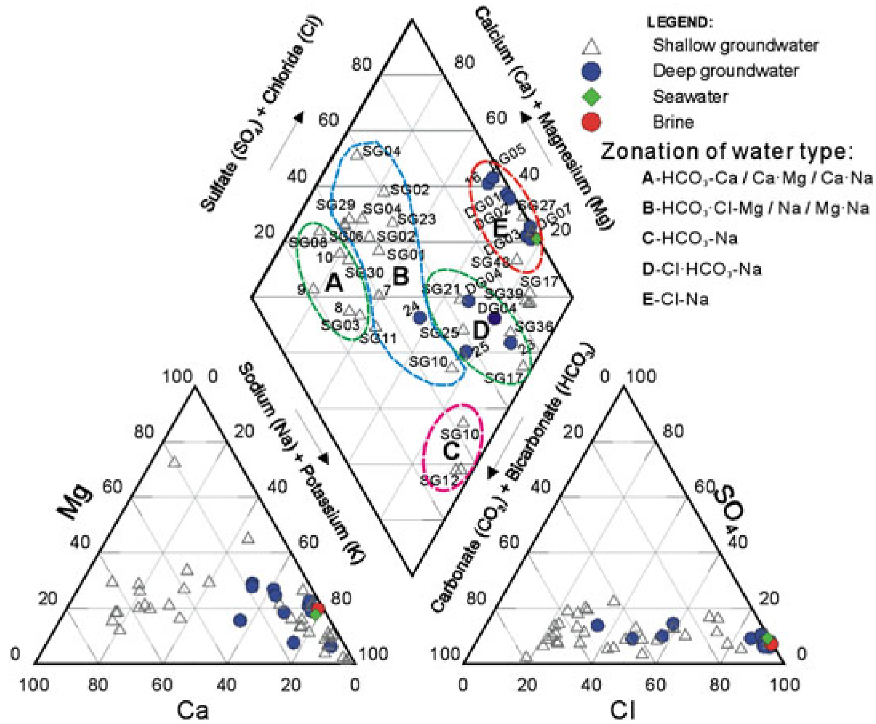

Figure 5. Piper plot of water samples in south coastal aquifers of Laizhou Bay

in the upstream aquifer (south of the area) is characterized by HCO_3-Ca or HCO_3-Ca·Mg type (zone A). Towards the coastline, in the transition zone, groundwater exhibits a range of types, including HCO_3·Cl-Mg/Na/Mg·Na type (zone B); Cl·HCO_3-Na type (zone D); and locally, HCO_3-Na type water (SG10 and SG12, in the center of the Changyi depression). Cl-Na type water (zone E) dominates the groundwater in the northern part of the study area (with TDS > 2 g/l).

Total dissolved solid contents show a typical zonation, increasing towards the coastline (Figure 2). Compared with 1980 (Zhang *et al*., 1997), the contour of TDS = 2 g/l (traditionally designated as the saltwater–freshwater interface in China) has moved approximately 5 km south. Three salinity zones are demarcated on Figure 2, a freshwater zone with TDS <1 g/l (I); a transition zone between Lijiapu and Qingxiang, where salt water forms a wedge-shaped intrusion into the fresh water aquifer (II), resulting in a fresh-saline-fresh pattern with depth; a salt/brine water zone north of Qingxiang (III).Additionally, the distribution of groundwater TDS deviates from a simple landward decrease, forming a downstream tongue shape in the vicinity of the Weihe River, indicating significant surface water recharge into the shallow aquifer.

Chlorofluorocarbons and tritium concentration

Most groundwater samples from wells in the south coastal aquifer of Laizhou Bay contain CFC-11, CFC-12 and CFC-113 concentrations (4.0–394.1 pptv, 2.2–438.5 pptv and 1.9–71.3 pptv, respectively) within the range possible for air–water equilibrium at the determined recharge temperatures. The variations of CFC concentrations with the change of well depths and distances from the coastline can be seen from Figure 6 a-b. CFC concentrations generally increase with increasing distances from the coastline, especially CFC-12 and CFC-113, and decrease with increasing depth (Figure 6). However, the concentrations have a wide range in groundwater between 20- and 40-m well depth. CFC-12 and CFC-113 concentrations have maximum values of 438.5 pptv and 71.3 pptv at about

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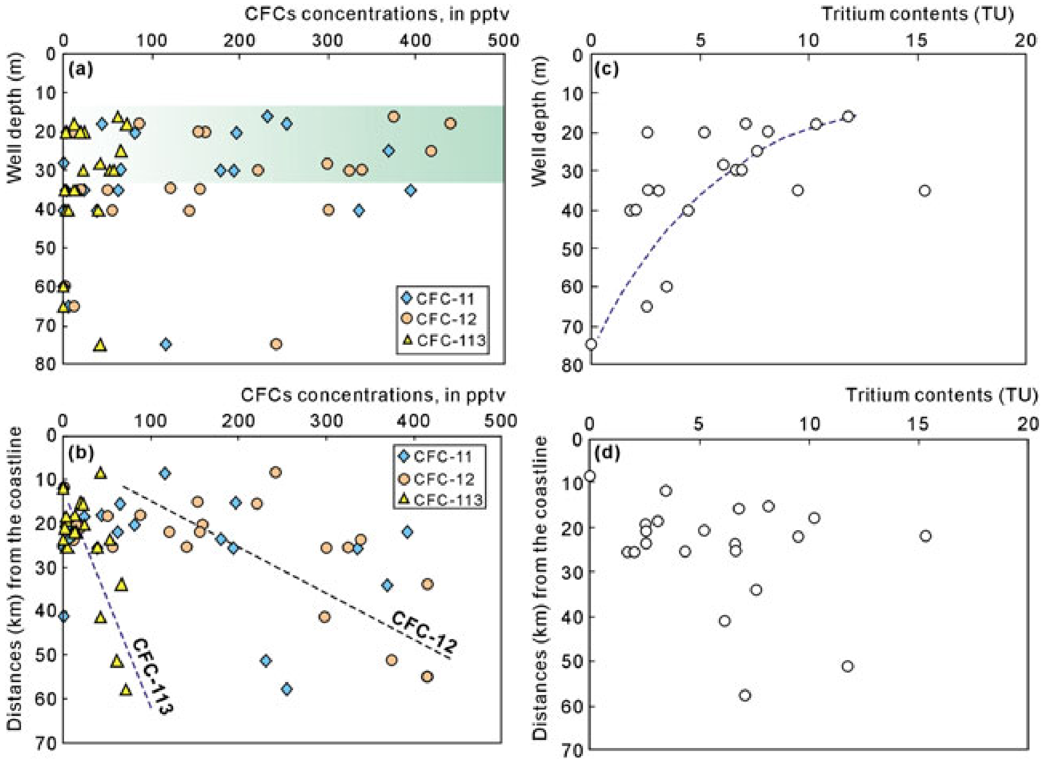

Figure 6. Variation of measured CFCs and tritium concentrations in groundwater samples, with well depth and distances from the coastline

20-m well depth. The lower CFC contents in deep groundwater indicate that the fraction of modern water is lower, whereas the decrease from inland areas to the coast broadly agrees with the inferred natural horizontal flowpath. With greater distance from the coastline, modern water is more likely to participate in groundwater circulation because of local recharge by stream and rain water (in the more permeable sediments). Concentrations of CFC-11, CFC-12 and CFC-113 from the 20 water samples also are depicted in Figure 7, showing the concentrations (as curves) expected in groundwater recharged between 1940 and 2000.

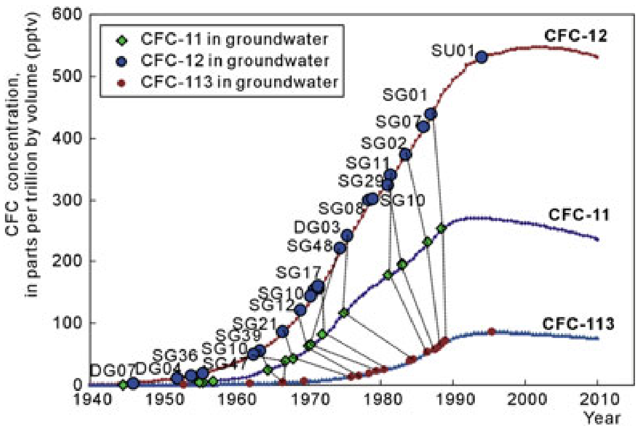

Figure 7. Northern hemisphere atmospheric CFC concentrations from 1940 to 2010 and concentrations of CFC-11, CFC-12 and CFC-113 in water at 13 °C based on atmospheric mixing ratio data from spreadsheet of Busenberg and Plummer (2005), available at http://water.usgs.gov/lab/software/USGS_CFC/

Tritium contents in groundwater also exhibit a decreasing trend with increasing well depth (Figure 6-c) and an increase with distance away from the coastline, in broad agreement with the CFC ages (Figure 6-d). The scatter in the data (Figure 6-d) again suggests complex/disturbed flow paths, which are affected by the presence of groundwater depressions, mixing between units and local recharge. The tritium content of modern seawater (7.3 TU) is lower than that of present precipitation (16 TU at Yantai station in 2002, IAEA/WMO, 2006). Sample tritium concentrations are basically consistent with CFC apparent ages. Samples having very low concentrations of tritium had CFC-12 apparent ages >50 years, and sample concentrations ranging from 1.8 to 15.3 TUs correspond to younger apparent ages (Table II). There is no detected tritium in some deep groundwater samples, such as DG02 and DG03.

DISCUSSION

CFCs age dating in shallow groundwater

Chlorofluorocarbon-11, CFC-12 and CFC-113 modeled recharged dates are given in Table II; the ages of young fractions range from 17 to >50 years (Figure 7). As noted above, the CFC apparent ages generally increase with depth/distance from the natural recharge area in the south, although the pattern is complicated (Figure 8). Additionally, a positive correlation exists between groundwater specific electrical conductivity (EC) and CFC ages in fresh and brackish water (EC < 5000 μS/cm) (Figure 9). Brackish groundwater (mean 39 years) has longer residence time than fresh groundwater (mean 25 years),

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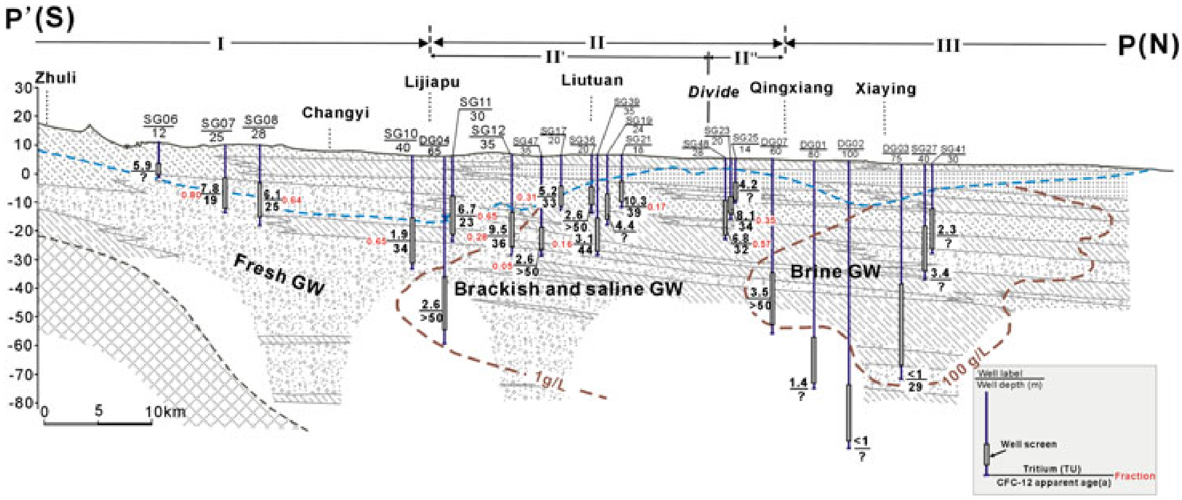

Figure 8. Distribution of tritium contents and CFC-12 apparent ages with fraction of young groundwater along the hydrogeological cross section (P-P' in Figure 1)

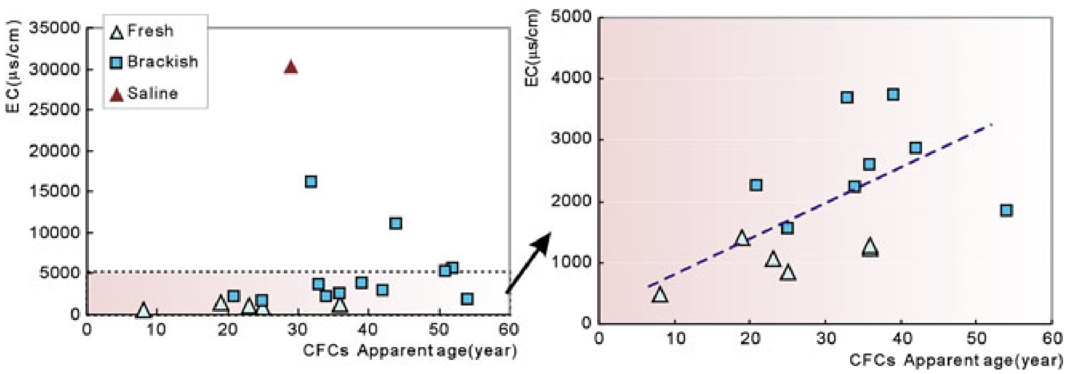

Figure 9. Relationship of CFC apparent ages *versus* EC

indicating recent recharge and/or fast circulation of fresh groundwater in the aquifers in the south of the area. This also concurs with the conclusion that the salinity source is not simply modern seawater intrusion (which would have high CFC concentrations) but rather is a result of palaeo-seawater intrusion and/or mixing with brines formed in pre-modern times (e.g. Han *et al*., 2011).

The three apparent ages for each sample are depicted in Figure 7, showing the level of agreement/disagreement between ages calculated on the basis of three different gases. For several samples, such as SG07, SG08 and SG12, there is poor agreement between CFC ages estimated by CFC-11 and CFC-12 (these samples are marked as 'contaminated' in the table). A number of processes may have altered CFC concentrations, for example, contamination with particular CFC compounds during sampling or CFC degradation and sorption processes. For this study, dissolved oxygen values range from 0.14 to 6.41 mg/l, with Eh ranging from 8 mV to 341 mV, indicating a largely aerobic environment, making CFC degradation under anoxic conditions unlikely (Plummer and Busenberg, 2005). Point-source contamination or deviations in CFC mixing ratios because of the proximity to urban areas (e.g. the major city of Tianjing) are thus more likely explanations for the discordance. In a number of cases, CFC-11 has showed a greater propensity for degradation and/or contamination than CFC-12 (Plummer and Busenberg, 2005; Long *et al*., 2008); because of this, and for ease of data display, CFC-12 age is selected as the 'assigned age' in most of the figures.

Groundwater from the shallow aquifer in Changyi depression center, such as SG10 and SG12, typically show poor agreements, indicating the water is particularly vulnerable to contamination. Around the Changyi depression, the CFC apparent ages are generally high. A basic assumption of the CFC method is that the concentration of CFCs in soil air at the water table is equal to the concentration of CFCs in the atmosphere at the time of recharge (Rademacher *et al*., 2001). For a thick unsaturated zone, CFC ages are overestimated because the CFC concentration in soil air at the water table lags the CFCs concentration of the atmosphere (Cook and Solomon, 1995; Cook *et al*., 1998; Plummer *et al*., 2000). Therefore, the higher CFC apparent age around the Changyi depression may be overestimated and result from the thick unsaturated zone with thickness of over 20 m. This is complicated by the fact that water levels in this region have dropped significantly in the last 10–20 years; hence, the unsaturated zone thickness has

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changed and was historically higher than that at present. The high level of drawdown/disturbance because of pumping also may cause discrepancies in the ages because of high water table fluctuations (which may entrain excess air), and/or induced mixing of water from a range of different flow-lines/ages (e.g. Plummer and Busenberg, 2005). Note that SG12 (in the depression) also contains the highest tritium concentration observed (15.3 TU).

Comparison of CFC-modeled ages and tritium data

Because of ambiguities in distinguishing age distribution models and the possibility of degradation or contamination of various constituents, it is important to consider simultaneously as many different tracer measurements as possible in a single sample to determine its history. Generally, higher tritium values are observed in the fresh groundwater in the south of the area, indicating a large component of recent precipitation. High tritium signals were produced in northern China during the 1957–1963 period of high thermonuclear input (Lin and Wei, 2006); hence, 'recent' could essentially mean any time since this peak. However, the CFC recharge dates in these waters are indicative of recharge predominantly during the 1980s in the fresh water zone. In contrast to fresh water, salt and brine water have low tritium values, indicating little component of modern precipitation and a relatively closed environment. Deep saline groundwater (DG01, DG02, DG03, DG05 and DG06) from the saline intrusion zone in the coastal aquifer of Laizhou Bay has ~ zero tritium content, which indicates long residence time (>50 years) and low flow rates, with limited or no contribution of modern seawater.

A number of samples have low tritium contents (<2 TU) but significant CFC concentrations. For example, SG10 (40 m depth) has only 2 TU of tritium but significant concentrations of CFC-12 and CFC-113 (300.2 and 39.4 pptv, respectively), indicating equilibrium with air ~21–26 years ago. This sample has a thick unsaturated zone (18.2 m) because of drawdown/pumping. DG03 (screen interval of 45–72 m) also has significant CFC concentrations but an absence of tritium. There are three possible explanations for this situation: (i) groundwater pumping has caused the entrainment of excess air (e.g. during large water table fluctuations) (Qin and Wang, 2001) (ii) CFC contamination, or recharge from local precipitation or surface water with high CFC concentrations but minimal tritium (iii) mixing, with the fraction of young groundwater being low, such that tritium concentration is below the detection limit, but CFCs are still detected. Mixing is further discussed in the following section. Considering the first alternative, water pumping could introduce advective gas flow through porous media into groundwaters, which may incorporate CFCs but minimal tritium. Contamination was discussed previously – as noted earlier, the greater occurrence of discordant ages in the samples near the Changyi depression indicates that this may be an issue in these samples.

The ^{3}H values for nearly all of the post-1964 waters are from wells located in fresh water zone (regime I in Figure 8) (such as SG02 and SG01), and the ^{3}H input for 'pre-1960s' waters is derived almost exclusively from wells located near the Changyi depression center (such as SG10 and SG29), semi-confined zones or areas of low hydraulic gradient in mixing zone (regime II in Figure 8) (such as SG36 and SG47) (Figure 10) where older waters occur. The interpretation of tritium data is somewhat complicated as tritium derived from the peak atmospheric fallout of the early 1960s (peaking in 1963, cf. Lin and Wei, 2006) is likely yet to decay below background cosmogenic levels. Hence, water recharged around the peak fallout period will likely have values that are hard to distinguish from recent rainfall (e.g. the last ~10–20 years). Thus, in this study, the presence of more than ~5TU of tritium is broadly interpreted as indicating the presence of 'post-1960s' water, with no more precision regarding recharge dates possible on the basis of tritium contents.

Fractions of young groundwater and binary mixing model

The identification of water mixing processes can give useful information in hydrological investigations. The binary groundwater mixing approach is widely used for the interpretation of variations of physical and chemical parameters (e.g. conductivity, water chemistry and stable isotopes) and also can be applied when multiple CFCs are analysed (Plummer *et al.*, 2006). In this study, the simplest binary mixing model is assumed, based on CFC-113 and CFC-12 concentrations, with a mixture of two end-members with atmospheric CFC concentrations (for a given recharge date derived from piston-flow model) and CFC-free water (Figure 11). Simple binary mixtures of water recharged in the years 2005, 1995, 1990, 1985, 1980 and 1975 with old, CFC-free water are shown as dashed lines. The fraction of young water is estimated according to the position on the two end-member mixing lines (Plummer *et al.*, 2006). For example, SG10

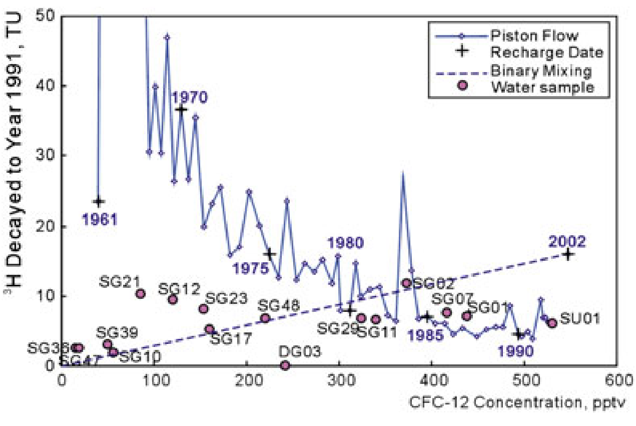

Figure 10. Tracer plots comparing ^{3}H in precipitation from Hong Kong, decayed to the year 2002 with CFC-12 concentration in pptv for Hong Kong air. The solid lines represent unmixed (piston) flow with selected apparent ages ('+'). The dashed lines show one example of binary mixing, for the case of water recharged in 2002 diluted with old, CFC-free water

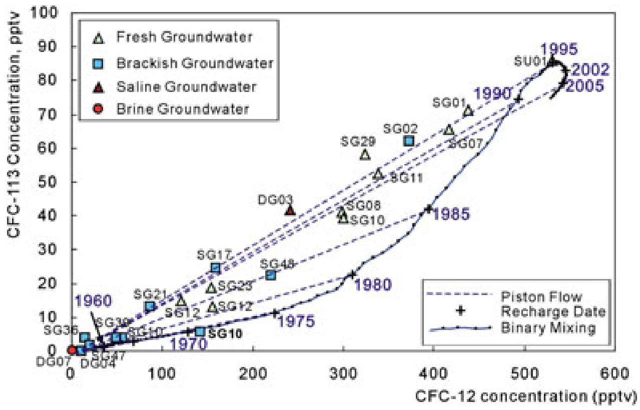

Figure 11. Binary mixing model ideal curves based on CFC-113 and CFC-12 concentrations in groundwater. The '+' denotes selected apparent ages. Selected apparent recharge dates of 1960–2005 are noted at '+'. The points outside the area enclosed by the piston flow curve and the straight line with the greatest slope indicate the influence of other concentration-modifying effects such as CFC contamination or CFC degradation

(sampled in August 2007) shows the location of an unmixed sample approximately recharged in the year 1971. SG48 shows the location of a 50:50 mixture of water recharged in 1985 with old, CFC-free water. The region bounded by the CFC input function (solid line) and upper-most mixing line (1995 to pre-CFC line) represents the range of CFC-113 and CFC-12 concentrations that can be expected in waters if air–water equilibrium and mixing with old, CFC-free water account for the observed variations in CFC concentrations. Samples that plot outside the region bounded by piston flow and binary mixing have probably been affected by other processes besides those of air–water equilibrium and dilution. For example, sample SG29 could contain an excess of CFC-113 relative to CFC-12 from contamination, or (less likely) degradation of CFC-12 relative to CFC-113.

According to these calculations, the fraction of young water has been estimated and shown in Table III. The apparent age is primarily influenced by the fraction of young water in the sample, which decreases as apparent age increases (Figure 12). Generally, the fraction of young water in the shallow aquifer decreases towards the north. The fraction of young water in the south of Changyi depression ranges from 0.80 to 0.65, in the salinity regime I (Figure 8). In salinity regime II (north of the Changyi depression), the fractions range from 0.05 to 0.31 in regime II′ and from 0.35 to 0.57 in the regime II″. This indicates that there are different ranges of young water fraction on the two sides of the groundwater divide (Figure 8). Intensive groundwater abstraction can result in the upcoming of old groundwater and mixing behavior in this zone. There are no 'young' fraction data for regime III; these samples are considered to have little modern input. The tritium concentrations range from 1.9 to 7.8 TU, 2.6 to 10.3 TU, 4.2 to 8.1 TU and <3.5 TU, in regimes I, II′, II″ and III, respectively. Generally, the fractions of young groundwater decrease towards the coastline (Figure 13 a-b) and with depth, although the depth/young fraction relationship is less clear and

Table III. Fraction of young groundwater based on the binary mixing model

ID	Sampling time	Distance(km) from the coastline	Well depth (m)	Screen interval (m)	CFC-12	CFC-113	Mixing water	Fraction of young groundwater	Mean fraction of young groundwater
SG07	November 2005	33.80	25	17–23	416.86	65.65	1991.5	0.82	0.80
							1997.5	0.77	
SG11	November 2005	23.66	30	15–26	339.11	52.52	1990.5	0.68	0.65
							1999	0.62	
SG12	November 2005	21.97	35	18–31	120.96	15.01	1987	0.28	0.28
SG23	November 2005	15.21	20	13–18	153.35	18.76	1987	0.35	0.35
SG12	August 2007	21.97	35	18–31	155.51	13.13	1982	0.45	0.45
SG08	November 2005	41.20	28	16–25	298.07	41.27	1988.5	0.64	0.64
SG10	November 2005	25.35	40	21–38	300.23	39.39	1988	0.65	0.65
SG17	November 2005	20.28	20	14–19	159.83	24.38	1990.5	0.32	0.31
							2000.5	0.29	
SG21	November 2005	17.96	18	9–14	86.40	13.13	1990.5	0.17	0.17
							2000.5	0.16	
SG10	July 2006	25.35	40	21–38	56.16	3.75	1979.5	0.19	0.19
SG39	August 2007	18.38	35	23–32	49.68	3.75	1980.5	0.16	0.16
SG47	August 2007	21.13	35	24–32	19.44	1.88	1984	0.05	0.05
SG48	August 2007	41.20	28	16–25	220.31	22.51	1984.5	0.57	0.57

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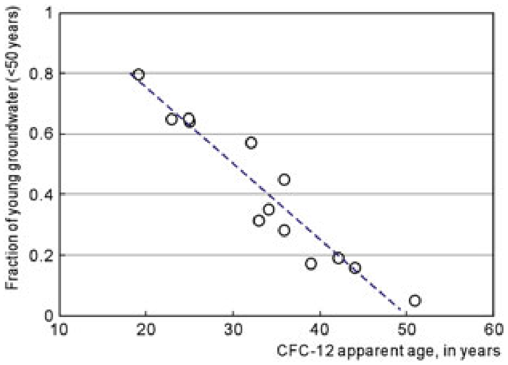

Figure 12. Relation of CFC-12 apparent age to the fraction of young water based on CFC-113/CFC-12 ratios

may be complicated by the high degree of mixing/upconing in the depression zone.

Conceptual groundwater flow system

Chlorofluorocarbons age and tritium content, together with stable isotopes and chemical compositions, can be used to assist delineation of the groundwater flow paths in Laizhou Bay. The different patterns of tracer distributions and mixing fractions imply the following regarding hydrodynamics and flow paths:

(1) In the fresh groundwater zone (regime I in Figure 8), the fraction of young groundwater is relatively high, changing from 0.80 to 0.65 towards the north, with young groundwater ages less than 34 a, and increasing age along the horizontal flow path. In this regime, tritium contents in shallow groundwater range from 1.9 to 7.8 TU, showing a decrease along the flow path. TDS of most groundwater is less than 0.8 g/l with Cl concentration of less than 0.15 g/l. The young water fraction close to 0.65 suggests that the exploitation of the southern fresh component is the main part in present exploitation.

(2) In the mixing zone (regime II in Figure 8), located between two drawdown cones, the fraction of young groundwater varies between 0.05 and 0.65. Compared with variation along flow path, there are relatively obvious decreasing trend with the increasing sampling depth, especially in regime II'. Groundwater ages change between 23 and 44 a, with tritium contents of 2.6–10.3 TU. TDS of groundwater is characterized by wide range of 0.48–3.4 g/l with Cl concentration of 0.9–1.29 g/l, showing obvious stratification. Based on the measured CFC data in November 2005 and August 2007, the fraction of young water in the well SG12 show increased trend from 0.28 to 0.45, indicating that the vertical infiltration has locally increased in recent years. However, for the well SG10 located near the Changyi depression center, the young water fraction reduced from 0.65 in November 2005 to 0.19 in July 2006, indicating that there is upconing older groundwater into shallow aquifer because of the intensive exploitation, which caused mixing in this regime. This observation indicates that the mixing fractions/age distributions are highly variable within the zone of groundwater exploitation, depending on the level of pumping. At the divide between fresh and brine water bodies, precipitation infiltration is very limited, possibly because of the thin unsaturated zone with poor permeable layers (such as clay and sandy clay). This has resulted in

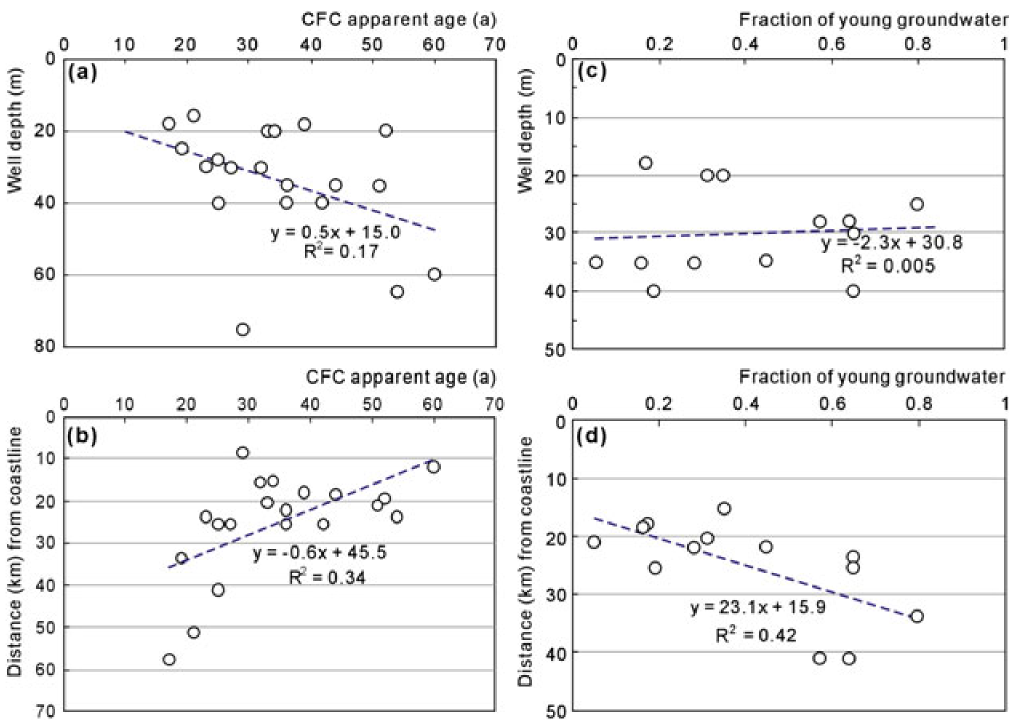

Figure 13. Variation of CFC apparent age (a, b) and fraction of young groundwater (c, d) with well depth and distance from the coastline

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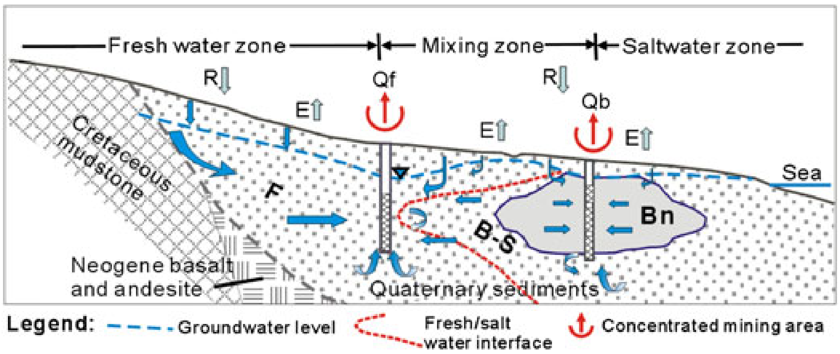

Figure 14. Conceptual model showing groundwater flow system through the investigated coastal plain. Explanation: R, precipitation and surface water recharge; E, evaporation; Qf, fresh groundwater exploitation; Qb, brine water exploitation; F, fresh groundwater; B-S, brackish and saline groundwater; Bn, brine. Arrows in aquifer indicate groundwater flow directions

lesser young water fractions, indicating slow velocity of groundwater circulation and less mixing here.

(3) The salt water zone (regime III in Figure 8), located south of Qingxiang, has tritium contents of less than 3.5 TU, indicating old groundwater is distributed in this area with less young water recharge. Strong evaporation, which has been revealed by variation of Cl/Br molar ratio and $\delta^{18}O$-$\delta^{2}H$ isotope compositions in groundwater (Han *et al*., 2011), may be one of the main discharge mechanisms in the modern/pre-modern water of this region. TDS of most groundwater in this area is higher than 100 g/l within 85-m depth. Compared with the other groundwater samples, the deep groundwater is generally depleted in isotopes, which may be related to cooler temperatures during recharge and concurs with ^{14}C ages about >10 ka (last glacial maximum) as discussed by Han *et al.* (2011).

Despite uncertainties in the interpretation of the age results, it may be concluded that the fresh and most brackish groundwaters were recharged mainly within the last 50 years. The deeper groundwaters have relatively old recharge dates and distant recharge areas. The present groundwater flow field is clearly derived from the depression cones. A conceptual model to describe groundwater flow in the south coastal Quaternary aquifer of Laizhou Bay has been devised and is presented in Figure 14. Around the center of Changyi depression and on the upper reach area of Weihe River, where the unsaturated zone is very deep and horizontal flow predominates; between Liutuan and Qingxiang, where the unsaturated zone is much thinner and there is mixing between the old groundwater from up gradient and modern water from recent recharge; along the Weihe River channel, there is interaction between groundwater and river water. According to the hydrochemical monitoring data (Han *et al*., 2011), the surface water is freshwater and recharges the local shallow aquifers.

CONCLUSIONS

Investigation of multiple environmental tracers in groundwater systems can help refine the interpretation of ages, hydrological concepts, identify mixing behavior and vulnerability to contamination. Because of the limits of individual tracers, the combination of different tracing tools is essential. CFCs and ^{3}H tracer approaches have been applied to resolve the extent to which groundwater mixing occurs and, therefore, provide indicators of the likely groundwater flow mechanisms in the southern coastal aquifer of Laizhou Bay. This is particularly important in interpreting the patterns and processes involved in saline intrusion and groundwater exploitation, which occur extensively in the aquifer system. Groundwater recharge dates were interpreted from the CFC data and evaluated in relation to the known hydrogeology, water chemistry and ^{3}H data. The following is a summary of the findings:

Use of CFCs and ^{3}H can help eliminate some conceptual mixing models and refine estimates of mean tracer age. To a first approximation, the ages and mixing fractions of many samples from Quaternary aquifer can be interpreted using a simple binary mixing model. CFC-modeled recharge years for groundwater in this study range from older than 1940 to modern. Groundwater ages of young fractions in mixed samples, calculated from CFCs range from 17 to nearly 50 years. Some processes that can affect CFC dating, such as entrainment of excess of air and sorption onto soils, are likely unimportant for the shallow groundwater in the study area. However, local point source contamination of samples and/or degradation of particular compounds is indicated by discordant CFC ages, particularly in the zone of intensive groundwater extraction near Changyi. Contamination and/or pumping activities may explain the presence of CFCs in groundwaters without detected tritium.

Along the investigated Changyi-Xiaying transect, based on the distribution of CFC apparent age and tritium contents in groundwater, in conjunction with chemical composition, a conceptual model of groundwater movement has been devised to describe the hydrogeological processes. Three regimes have been identified from south to north, including the following: (i) fresh groundwater zone dominated by horizontal flow, with fraction 0.80–0.65 of young water and young groundwater age of less than 34 a; (ii) mixing zone characterized by fraction of 0.05–0.65 and young groundwater age of 23–44 a, accompanied by local vertical recharge and upconing of older groundwater; and (iii) salt water zone, with little or no tritium or CFCs ('pre-1960s' water). Some shallow groundwater in a groundwater divide north of the Changyi depression also belongs to the pre-1960s group, indicating the slow velocity of groundwater circulation in this area, between two groundwater depressions.

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